The Thermal Decomposition of Ozone.

Evidence for the Existence of Activated Molecules in a Chemical Reaction.

Possible Limits for the Heat of Dissociation of Oxygen.

Thesis

by

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CONTENTS

THE THERMAL DECOMPOSITION OF OZONE.

Introduction

This research is being carried out to investigate as completely as possible the thermal rate of a simple chemical change in the gas phase, in order to make the reaction available as a tool for the general study of the mechanism of chemical reaction. This purpose can indeed be realized only when the complete mechanism of the reaction is understood.

A survey of the known gas reactions which possess an appreciable rate at convenient temperatures showed very few that offered possibilities. The decomposition of ozone, however, seemed to be an exception, possessing unusual opportunities, and it was therefore chosen. The reaction possesses the relative simplicity which is usually characteristic of decompositions. Whatever the mechanism might prove to be, in effect the change could apparently be only the reversion of two molecules of ozone into three of oxygen. The normal thermal rate of this change is convenient for measurement at 100°C, while at room temperature it is negligibly small. The walls of the containing vessel in general promote catalytic decomposition, but by suitable cleaning of the walls this can so far be eliminated that at 100° and above it can be neglected in comparison with the homogeneous change.

Although a large number of experimental measurements have been made, and their results collected in this thesis, it is necessary to state here that the purpose of this work has not yet been accomplished. However, two further important results have been obtained. First, a critical survey of the work done up to this time on the reaction can now be made in a way impossible heretofore.

Considering the remarkable apparent discordancy that existed among the previous investigations of this gas reaction, such a survey alone is felt to be of value. Secondly, observations made during the present research have indeed increased the importance of ultimately reaching a complete explanation of the mechanism of the reaction, because it has been found that the reaction will then lend itself in an effective way to several closely related studies.

In Part I there is given a critical survey of the work done up to the present time on this reaction. Part II contains the results of the present investigations using the "static method", and Part III gives the results of a series of experiments performed to determine in particular the effect of the total gas pressure and of the partial pressure of oxygen upon the decomposition. Part IV contains the results of a series of experiments carried out at a higher temperature by the "dynamic method", which are believed to be leading to an explanation of the mechanism of the decomposition.

These researches have been carried out under the direction of Professor Richard C. Tolman, to whom the author is indebted for constant help and advice. The author is also indebted to Beatrice Wulf with whom a considerable amount of the work was done. The researches have been aided on the financial side by the Carnegie Institution of Washington through a grant made to Professor A. A. Noyes.

PART I

Critical Survey of Previous Investigations.

There are seven outstanding researches in recent times that have contributed to our knowledge of the kinetics of the decomposition of ozone. The following paragraphs summarize these in a brief way from the standpoint of our present knowledge.

The careful work of Warburg[1] showed that the decomposition of ozone at 100 and 127°C follows a second-order course over at least two thirds of the total decomposition. The measurements were made by the so-called static method in an apparatus especially devised for the purpose. In it the rate of change of the concentration of ozone contained in a reaction chamber is followed by differential pressure measurements against a second chamber containing pure oxygen immersed in the same temperature bath. The temperature coefficient was found to be 2.47 fold for 10° between 100 and 127°. Water vapor was shown to have a real but small accelerative effect on the decomposition between the conditions of strong drying and 0.154 mm. water vapor. The difference in the influence of various drying agents was investigated and shown to be practically negligible. Different apparata were shown to have different accelerative effects on the rate. But also at 100° many good values of the second-order specific rate were obtained with the most inert apparata. In these experiments the reaction followed the second order. There were found, even here, deviations that were not due to the apparatus and that could not be explained. The maximum deviation of the results from the mean value was 14%. The average value of the second-order specific reaction rate at 100° and approximately 100 cm. Hg pressure was 1.25×10^2 cc/mol. sec., and at 126.9° and the same pressure it was 1.42×10^3 cc/mol. sec.

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[1] Warburg, Ann. d. Phys.(4) 9, 1286 (1902).

Clement[2] investigated the decomposition by the so-called dynamic method, in which the gas passes at a known rate of flow through a reaction vessel of known volume. From these two facts and an important assumption as to the conditions of flow through the reaction chamber, the time during which the gas is in the chamber is calculated. Analysis of the gas is made before entering and after leaving the reaction chamber. Moreover, by varying the rate of flow different lengths of time in the reaction chamber may be employed. Clement confirmed the fact that the reaction was second-order, but the test in this case was much less sure. The value of the specific rate at 127° and 73.5 cm. Hg pressure was 3.70×10^3 cc/mol. sec. - considerably greater than that found by Warburg at the same temperature but at 100 cm. Hg pressure. Apparently this was due in a large measure to an incorrect assumption made in regard to the conditions of gas flow through the chamber, although, as will be seen later, the total pressure is also a factor. The rate of decomposition was determined from 100 to 243°. The temperature coefficient was approximately the same as that found by Warburg. The chief importance of the work lies in the fact that the rate was followed to much higher temperatures than it had been hitherto, and in the great speed of decomposition an explanation found for the failure to obtain ozone in the attempts in which oxygen was heated to high temperatures, since the cooling of the gases, in order to isolate the ozone there formed, would have to be almost impossibly fast.

Jahn[3], in a painstaking research, studied the decomposition of ozone at 127° with the purpose of investigating any influence of oxygen on the rate. The work was done by two different methods. First, a series of experiments were made using the dynamic method of Clement, but with an apparatus that appears free from the difficulty which caused Clement's results to be high. Two pressures

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[2]Clement, Ann. d. Phys. (4), 14, 341 (1904).

[3]Jahn, Z. f. anorg. Chem., 48, 260 (1906).

were used, namely 76 cm. and 30 cm. Hg. Thus in the latter case the oxygen concentration was less than half the value in the former. These experiments showed the specific second-order rate to be inversely as the first power of the total pressure. The numerical value of the second-order rate at atmospheric pressure was practically the same as the value found by Warburg, when compared at the same pressure.

By the static method of Warburg, using the same type of apparatus, Jahn performed a series of experiments working at 95 cm., 71 cm., 47 cm., and 35 cm. respectively. These results confirmed in a satisfactory manner the linear dependence of the specific rate on the reciprocal of the total pressure. Jahn, however, working to study the effect of the oxygen pressure on the reaction, interpreted the apparent dependence on the total pressure as dependence on the oxygen pressure. Such dependence was a possibility, but not a necessary consequence, of these experimental results. On the basis of his interpretation Jahn suggested as the probable mechanism of the decomposition the following reactions:

$$O_3 \rightleftharpoons O_2 + O \quad \text{(equilibrium, far to left)}$$

$$O_3 + O \longrightarrow 2O_2 \quad \text{(slow, and to completion).}$$

Thus it must be said that Jahn's research established the linear dependence of the specific second-order rate on the reciprocal of the total pressure of the gas. While it is true that there is the possibility that this might have been characteristic of the particular gas used, this is not probable, since the character of the ozone, if susceptible to variations, would probably have been different in the two methods; in each, however, the gas behaved the same.

Jahn investigated the effect of moisture on the decomposition with about the same result as Warburg, finding a real but small acceleration.

He also investigated the effect of dilution with air. This procedure was important, as it differentiated between the effect of the total pressure and the true partial pressure of oxygen. Seven satisfactory experiments gave specific rates which agreed better with the inverse proportionality with the oxygen pressure than with that of the total partial pressure of the ozone mixture. We will in the following consider this as strong evidence in favor of the decomposition mechanism suggested by Jahn.

Perman and Greaves[4] studied the homogeneity of the decomposition and the order of the reaction using the static method. Their observations approximate nearest the second-order, but at temperatures above 80° the calculated second-order constant increased through each run. This indicates probably the presence of a positive catalyst. They did not, however, so interpret their results; and in their experiments in which the surface-to-volume ratio was considerably increased, they found a marked increase in the rate. They conclude that the decomposition takes place mainly at the surfaces with which the gas is in contact. The temperature coefficient of 3.2 fold for 10° degrees which they found is much higher than the values found in the researches already described. Perman and Greaves found that water vapor moderately accelerates the decomposition. In general the description of the experimental procedure is not given sufficiently for a complete interpretation of the results. The most important experiments which they call "varying the pressure of oxygen" and "effect of diluting with air" appear to be in the first case varying the total pressure, while for the second case too few words are given to understand the procedure. They conclude as follows. "The rate of decomposition is a linear function of the oxygen pressure.

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

A greater effect is produced by diluting with nitrogen than by simply reducing the pressure of the oxygen". Since it is not possible from their article to determine definitely the experimental procedure, the possible important inferences that might be drawn must be regarded as uncertain.

The work of Clarke and Chapman[5] was carried out with the purpose of determining whether or not the decomposition of ozone is a homogeneous gas reaction. Their research appears to have answered this question satisfactorily. With vessels of different surface-to-volume ratios the decomposition proceeded at the same rate. The static method was used. It must be remarked that in the six experiments which Clarke and Chapman reproduced, the second-order character of the decomposition is only fairly well exhibited, and the second-order constant shows considerable fluctuation from run to run.*

Chapman and Jones[6] tested in a particularly helpful manner the mechanism which Jahn considered as established for the decomposition. Their method consisted in filling two bulbs with the same ozone† at one-half atmosphere pressure, and then forcing into one of these bulbs one-half atmosphere additional pure oxygen. The decomposition in the two bulbs at the same temperature was observed side by side. Chapman and Jones conclude from these experiments that oxygen is without influence on the decomposition. Actually the four sets of curves which they present show in every case a small retardation in the bulb containing the higher oxygen concentration; but it is indeed small. The results appear to be strong evidence against the mechanism proposed by Jahn. There are, however, peculiarities in the decompositions observed by Chapman and Jones which make such conclusions uncertain. These should therefore be discussed.

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[5] Clarke and Chapman, Jour. Chem. Soc., 93, 1638 (1908).

*These conclusions result from calculations made by the present author on their graphs of the pressure change.

[6] Chapman and Jones, Jour. Chem. Soc., 97, 2463 (1910); 99, 1811 (1911).

†(See following page).

†It must be noted that the word ozone is often used in this thesis to designate the mixture of oxygen and ozone, which the common methods of preparing ozone all yield. Only mixtures containing a few percent of ozone have been used in the studies of the thermal decomposition. The words ozonized oxygen will be employed to designate such mixtures, wherever this fact must be recalled to mind.

Using a similar procedure in four more experiments, the effect of water vapor on the decomposition was studied. The two bulbs were filled with one atmosphere of ozonized oxygen, but the gas which entered one was first saturated by passing through distilled water. The results showed, as was found by both Warburg and Jahn, that the effect of moisture was small, although slightly accelerating.

An important check which the authors do not mention is possible from these combined data. If we compare the rates found in the four bulbs at one-half atmosphere in the oxygen experiments with those at one atmosphere in the water vapor experiments, we find* that, except for small variations, these are the same. This would indicate that these experimenters did not observe even the effect of the total pressure, which from Jahn's research would be expected to yield half the rate in the one atmosphere bulbs than was observed in those at one-half atmosphere. The only way of accounting for this discrepancy is that Chapman and Jones may have made an error in designating in their paper the units used in the first experiments; that is, in the oxygen experiments. The following facts seem to render this probable.

Chapman and Jones tested the influence of nitrogen on the decomposition in three experiments, of carbon dioxide in one experiment, and of carbon monoxide in one experiment, by a method similar to the above. Both bulbs were filled with one-half atmosphere of ozonized oxygen. The control was filled to one atmosphere with oxygen, while the other was filled to one atmosphere with the gas whose effect was to be investigated. The particular result of these experiments was to show a slight accelerative effect due to nitrogen with an increasingly larger one for carbon dioxide and carbon monoxide respectively.

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*Calculations made by the present author on the curves given by Chapman and Jones.

But the important data from these experiments is that the control bulbs should, in all five cases, be strictly comparable with four oxygen bulbs in the experiments on the effect of oxygen. As a matter of fact these last five yield constants which are indeed of the order of twice the value given by the four in the oxygen experiments. While this may have been actually a variation in the ozone, since an error of a factor of two in designating the units in the first four experiments would bring these into agreement with the rest, it seems probable that such an error may have been made. If such is the case, the experiments on the effect of oxygen definitely disagree with Jahn's hypothesis, and with his dilution experiments, unless the oxygen introduced by Chapman and Jones into the ozone bulb in the first four experiments happened to contain an amount of positive catalyst which nearly compensated for the negative acceleration of the oxygen. However, because of the conjecturing necessary to straighten out these difficulties, it is felt that little weight should be given to the conclusion drawn by Chapman and Jones on the effect of oxygen.

In the second research Chapman and Jones tested rigorously the effect of moisture on the decomposition. By careful, long drying they showed that, over a wide range, the presence of water vapor is not attended by any large effect upon the rate.

Since the researches of Chapman and Jones no important work has been published on the thermal decomposition of ozone until the recent paper by Griffith and McKeown[7]. These experimenters have examined the decomposition by the static method at four different total pressures, namely: 33.5 cm., 54 cm., 76 cm., and 102 cm. Hg. Their results agree qualitatively but not quantitatively with those of Jahn. The apparent rate increased more slowly

[7] Griffith and McKeown, Jour. Chem. Soc., 127, 2086 (1925).

than inversely as the total pressure. However, in all experiments these authors found not a second-order decomposition, but rather the second-order constant as calculated increased with the time. This points to the presence of a positive catalyst, acting to give a first-order portion to the decomposition. The presence of such a catalyst would explain why no quantitative check with Jahn was obtained. It also would explain the fact which these investigators record: that the increase in the second-order constant throughout a run is accentuated as the total pressure is reduced. It therefore appears probable that the presence of a positive catalyst explains the disagreement of these results with those of Jahn and Warburg. It should be noted, moreover, that from these tatal pressure experiments in the absence of any dilution or oxygen addition experiments no conclusion as to the effect of oxygen is justifiable.

Griffith and McKeown tested further the effect of addition of helium, carbon dioxide, nitrogen, and argon upon the decomposition, and observed that all of these accblerated the reaction by amounts increasing in the order given.

Griffith and McKeown suggested a rather intricate mechanism to account for their observations. In view of the results of earlier researches and the fact that their data appear to indicate the presence of a positive catalyst in their ozone, this does not seem to be a probable one.

PART II.

Experiments Using the Static Method.

Experiments were first carried out to determine independently the specific rate of the thermal decomposition. Since the value of the specific rate at 100° had been found to be different by several investigators, and furthermore since in certain cases the order of the decomposition had been markedly different from a second order, it was apparent that the source of oxygen and the method of ozonization were probably important factors. A method not greatly different from the static methods used in the earlier researches was therefore employed to measure the specific rate of decomposition of ozone from two different sources. Conditions were varied considerably to try to determine the factors influencing the rate. Measurements were made upon thirty seven decompositions, and they are described in this section of the thesis.

Apparatus

The apparatus with which the decomposition was observed is illustrated in Figure 1. The reaction chamber R is of pyrex glass. It is connected by capillary tubing to a capillary U-shaped manometer I containing sulfuric acid, and to the two stopcocks (or constrictions) at A and B. The reaction chamber is contained in a brass cylinder, the exit tubes going out through stuffing boxes in its ends. The brass cylinder is covered in asbestos insulation. Saturated steam from a boiler enters at C and leaves at D, thence to a condenser at some distance. An electric heater insures a constant steam supply from the boiler. At E a thermometer enters the jacket.

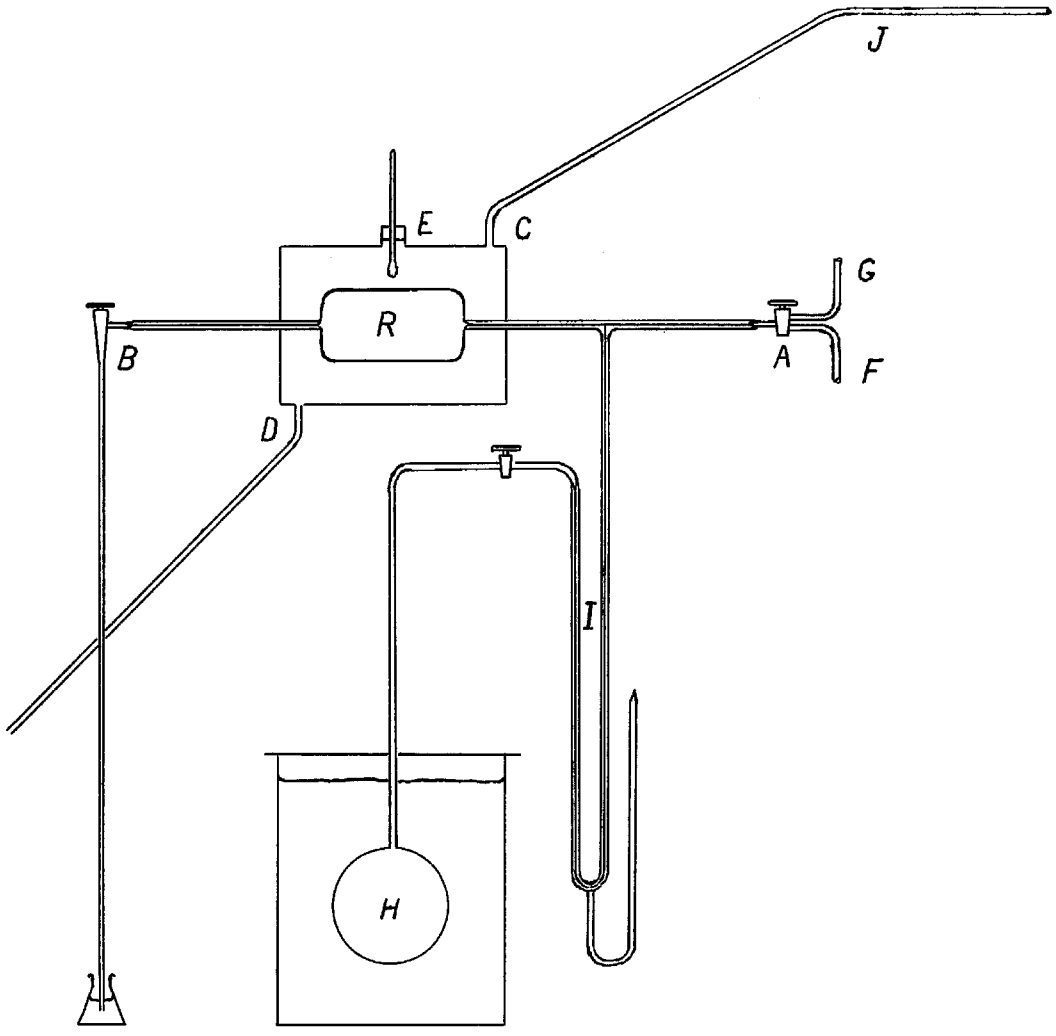


Figure 1.

The manometer liquid is concentrated sulfuric acid whose density has been determined. The side arm is not capillary. By warming the air trapped at the top of the side arm, the liquid can be raised in the manometer arms. This is employed when the meniscus on the right-hand side shows a tendency to become moist, for by raising and lowering the acid in the tube arms this is overcome.

The manometer works against the constant pressure of a volume of dried air enclosed in the bulb H. This bulb is immersed in a water bath whose temperature is controlled by a mercury thermal regulator and a small immersed electric heating coil, operated from a storage cell by a relay connected with the regulator. The bath is stirred by a slowly rising current of air bubbles. The vessel is loosely covered on top by a card-board piece. A thermometer, read with a magnifying eye piece, allows the temperature of the bath to be read to $\pm$ 0.005°.

In the early runs at A and B there were no stopcocks but constrictions in the tubing, which were sealed before the blast lamp. Later, at a point that will be mentioned, stopcocks lubricated with concentrated sulfuric acid were substituted; and still later on, these were cleaned and lubricated with vaseline..

From C to J the steam line is of brass tubing, beneath which fan burners are arranged so that it is possible to superheat the incoming steam to such an extent that the chamber is raised from 100 to 150° in the course of thirty minutes, and can be held at 150° $\pm$ 1° with ease.

Preparation of the Ozone

Two distinct methods were employed for making the ozone. In one case it was made by the electrolysis of a dilute sulfuric acid solution with a very high current density at an artificially cooled platinum anode. Under these conditions at room temperature the gas coming off at the anode is oxygen containing an appreciable amount of ozone, a concentration of several percent being not difficult to obtain.

Figure 2 represents the apparatus. The electrolysis was carried on in a dilute solution of C.P. sulfuric acid, of specific gravity 1.075. The acid is contained in a pyrex beaker E. The cathode D is large, and is a collar of lead. The anode consists of a small platinum tube sealed into the glass tube B at the point C. It is sealed in so that a few small patches of the metal surface remain exposed and only on the upper side. The rest is entirely covered with glass. Cooling water enters at H and passes directly through the platinum anode and out at G. The exposed platinum surface has an area of about 2 sq. cm. The current density at this surface is from 80 to 100 amperes per sq. cm. The evolved oxygen-ozone mixture is collected in the bell A and led from here through capillary tubing to a small glass trap designed to catch condensed water, and thence to a small tower filled with beads newly wet with concentrated sulfuric acid. From here the gas passes into the reaction apparatus at point F in Figure 1.

In the second method ozone was prepared by subjecting oxygen to the action of the silent electric discharge, in an ozonizer of standard design, constructed of pyrex glass. It was operated by means of a transformer, whose maximum secondary voltage was 25,000 volts using 110 volts on the primary circuit. The voltage across the secondary terminals was controlled by a rheostat in the primary circuit. The oxygen was obtained in all cases except one from a Linde tank, either bubbling through concentrated sulfuric acid or passing over fused calcium chloride, before entering the ozonizer. In one experiment oxygen from an electrolytic generator was employed. In this the electrolyte was saturated barium hydrate solution and the electrodes were of nichrome.

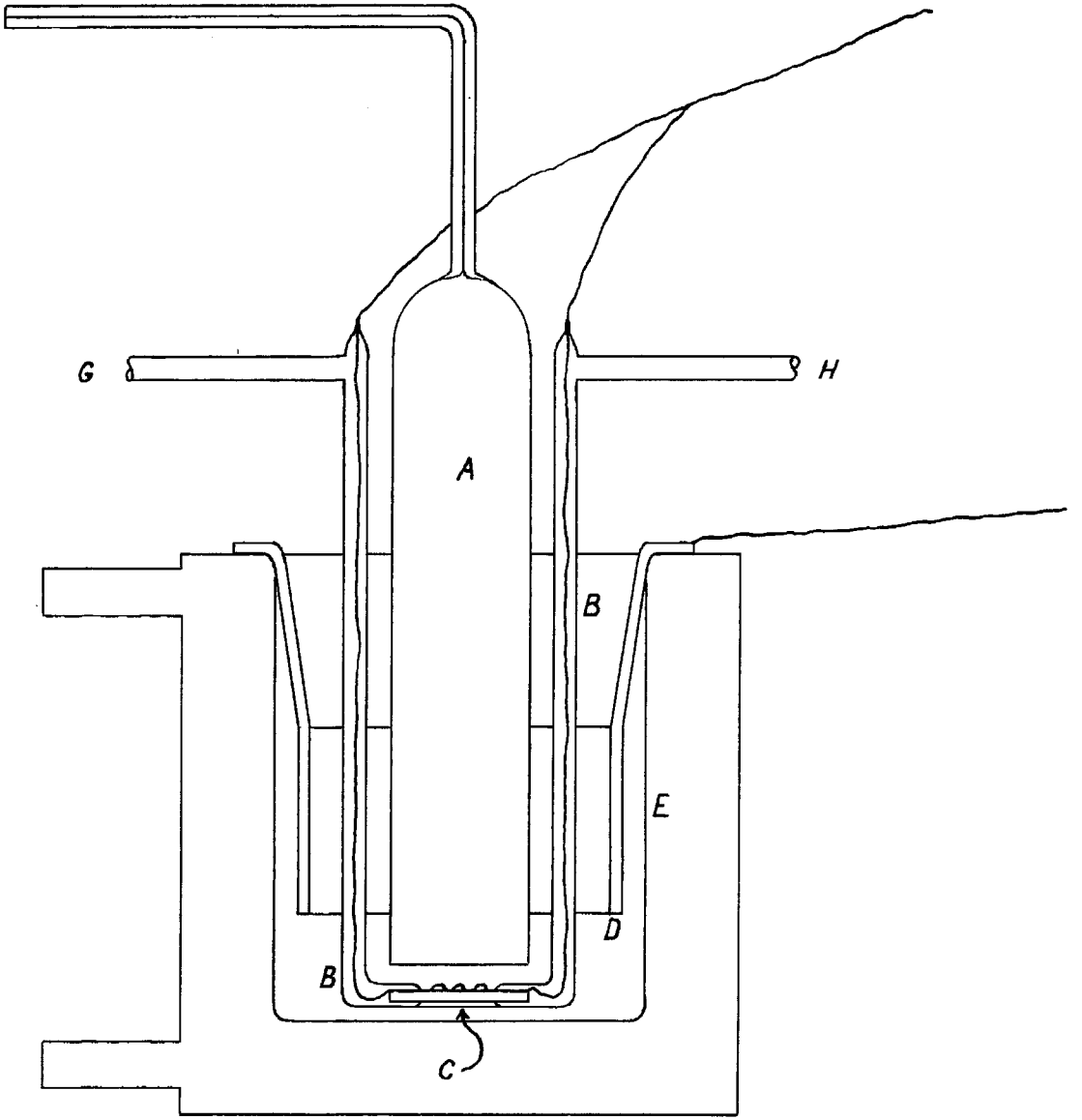


Figure 2.

The oxygen after passing through the annular chamber of the ozonizer passed to a drying tube filled with granular calcium chloride or with beads wet with concentrated sulfuric acid. From this tube it was led to the reaction apparatus at G in Figure 1.

Experimental Method

The reaction chamber was first swept out with ozonized oxygen for a period of one to four hours to clear the apparatus. Referring to Figure 1, the ozone entered at G or F, passed through the reaction chamber, through a long exit tube of small bore, and finally out at B, bubbling through concentrated sulfuric acid. Without altering the gas flow, saturated steam was admitted to the jacket and the chamber brought to 100° in about twelve minutes, this time varying somewhat with room temperature. After the chamber had been at 100° for five minutes, the gas flow having been unaltered up to this point, the chamber was closed, either before the blast lamp or by turning the stopcocks. The constriction or stopcock nearest the ozone supply was closed first, and the total pressure of the oxygen-ozone mixture in the chamber was therefore practically that of the atmosphere at the start of the measurements. The pressure change in the reaction chamber was observed from this time, usually for a period covering about one half of the decomposition. In some of the runs it was, however, considerably greater than this. The temperature of the constant-pressure bulb against which the manometer operated was held by the regulating device at 29° $\pm$ 0.02°.

After the desired portion of the run had been followed, the pressure corresponding to complete dissociation was measured by raising the temperature of the reaction mixture, completing quickly the decomposition, and cooling again to 100°. To do this the constant-pressure bulb was closed and the incoming

steam superheated until the jacket was at 150° (except in a few exceptional cases). This required about 25 minutes. The chamber was held at this temperature for fifteen minutes, the decomposition of ozone of concentrations between one and four percent being practically complete in this time. This was determined roughly by calculation and checked by experiment. The slowness with which the superheating occurred made the time at which ozone was at a temperature near to 150° considerably greater than fifteen minutes. Upon cooling to 100° the final pressure was read; this, with the initial pressure being sufficient data to calculate the initial ozone concentration. Thus the "start" of the reaction could be taken wherever desired, the corresponding pressure giving with the final pressure the "initial" ozone concentration.

At the beginning and end of each run the pressure of the atmosphere was read, either by means of a barometer or by means of the apparatus manometer itself, in order that no marked change in the atmospheric pressure should cause unnoticed a change in temperature of the steam.

To illustrate this procedure the data obtained in Run 15 are here tabulated.

Table I (Run 15)

Ozone made by corona discharge using Linde tank oxygen.

Time (min.)	Manometer (cm. H_2SO_4)	$\frac{p_{O_3}}{2}$ (cm. H_2SO_4)
0	2.44	4.72
1	2.46	4.70
2	2.47	4.69
3	2.49	4.67
4	2.53	4.63
5	2.54	4.62
6	2.58	4.58
7	2.60	4.56
8	2.63	4.53
9	2.65	4.51
10	2.68	4.48
12	2.74	4.42
14	2.79	4.37
16	2.85	4.31
18	2.88	4.28
20	2.94	4.22
23	2.98	4.18
26	3.04	4.12
29	3.11	4.05
32	3.18	3.98
36	3.25	3.91
40	3.33	3.83
44	3.38	3.78
49	3.47	3.69
54	3.57	3.59
59	3.64	3.57
64	3.72	3.44
69	3.81	3.35
74	3.87	3.29
79	3.93	3.23
84	3.99	3.17
94	4.14	3.02
104	4.24	2.92
106	4.26	2.90
108	4.28	2.88
110	4.30	2.86
112	4.32	2.84
Reaction chamber superheated.		
153	Chamber first at 150°	
168	Cooling of chamber to 100° begun	
Final pressure	7.16	0

The second column indicates the difference in pressure between the reaction chamber and the constant-pressure bulb. The third column contains the differences between the values in the second column and the final value in the same column. These represent the values of half the ozone pressure at the respective times, expressed in centimeters of sulfuric acid. Thus the initial ozone pressure is seen to be 2 x 4.72 or 9.44 cms. H_2SO_4. A column of sulfucia acid (sp. gr. 1.832) of 564 cms. in height corresponds to a pressure of one atmosphere. Hence 9.44 cms.(H_2SO_4) pressure of ozone corresponds to a concentration of

$$C = \frac{P}{RT} = \frac{9.44}{564 \times 82.07 \times 373} = 5.465 \times 10^{-7} \text{ mols/cc.}$$

This corresponds to a percentage by volume of ozone in the oxygen-ozone mixture at 1 atmosphere of

$$\frac{5.465 \times 10^{-7}}{1/82.07 \times 373} = \frac{5.465 \times 10^{-7}}{3.266 \times 10^{-5}} = 1.68\% \text{ ozone (vol.)}$$

It may be remarked here that the concentrations used in this work extend from about 4.5% to 0.37%.

The final pressure is obtained from a series of observations of the pressure when the chamber, after the cooling from the superheat, has reached thermal equilibrium; that is, after the pressure has reached a constant value not changing with time at 100°. The final pressure of the second column, 7.16 cms. for Run 15 given above, is the mean of such a series of readings taken after the cooling.

Method of Analysis of the Data.

A simple graphical method for the determination of the order of the reaction and the numerical value of the constant was devised. From the equation

$$2O_3 \longrightarrow 3O_2$$

it is evident that the pressure increase after complete decomposition of the ozone is a measure of the initial ozone pressure, it being equal to one half this value, i.e. $2(p_\infty - p_0) = p_{O_3\ (initial)}$, where $(p_\infty - p_0)$ indicates the observed pressure increase after an infinite time has elapsed. Similarly, at any time t the pressure increase then observed is related to the ozone pressure then existing in the mixture by the relation

$$2(p_\infty - p) = p_{O_3} \tag{1}$$

And if the decomposition is purely second-order, then the equation

$$2\frac{dp}{dt} = -\frac{dp_{O_3}}{dt} = 4 \cdot k \cdot (p_\infty - p)^2 \tag{2}$$

should represent the facts. Rearranging

$$\int \frac{dp}{(p_\infty - p)^2} = \int 2k\,dt$$

and integrating

$$\frac{1}{p_\infty - p} = 2kt + C \tag{3}$$

Taking as a starting point in time any convenient place in the observations, setting this pressure at t = 0 equal to p_0, since we may start the measurements from any point, we have

$$\frac{1}{p_\infty - p} = 2kt + \frac{1}{p_\infty - p} \tag{4}$$

Plotting against the time the reciprocals of the differences of the final pressure and the pressure at the various times at which observations were made, a straight line should be obtained, if the decomposition follows strictly the second-order expression. And the slope of the line is just twice the specific

reaction rate, so that k may be read very simply from the curve. The intercept on the pressure axis is the reciprocal of the total pressure change over the decomposition. The data given in Table I for Run 15 are plotted, in accord with this method, in Figure 3 and the specific rate is calculated from the slope of the line. Thus a rapid graphical method of good accuracy for the interpretation of a run and the evaluation of the constant is so obtained. This has another important advantage. The graphs become pictures with real meaning, for when the curve is not a straight line, one can with experience often say what kind of effect is superimposed upon the normal second-order, as will be shown later.

In several cases the data have been treated in the usual way by calculating the specific rate for intervals of time spread over the course of the run. Writing the integrated form for two different observations and subtracting, there results

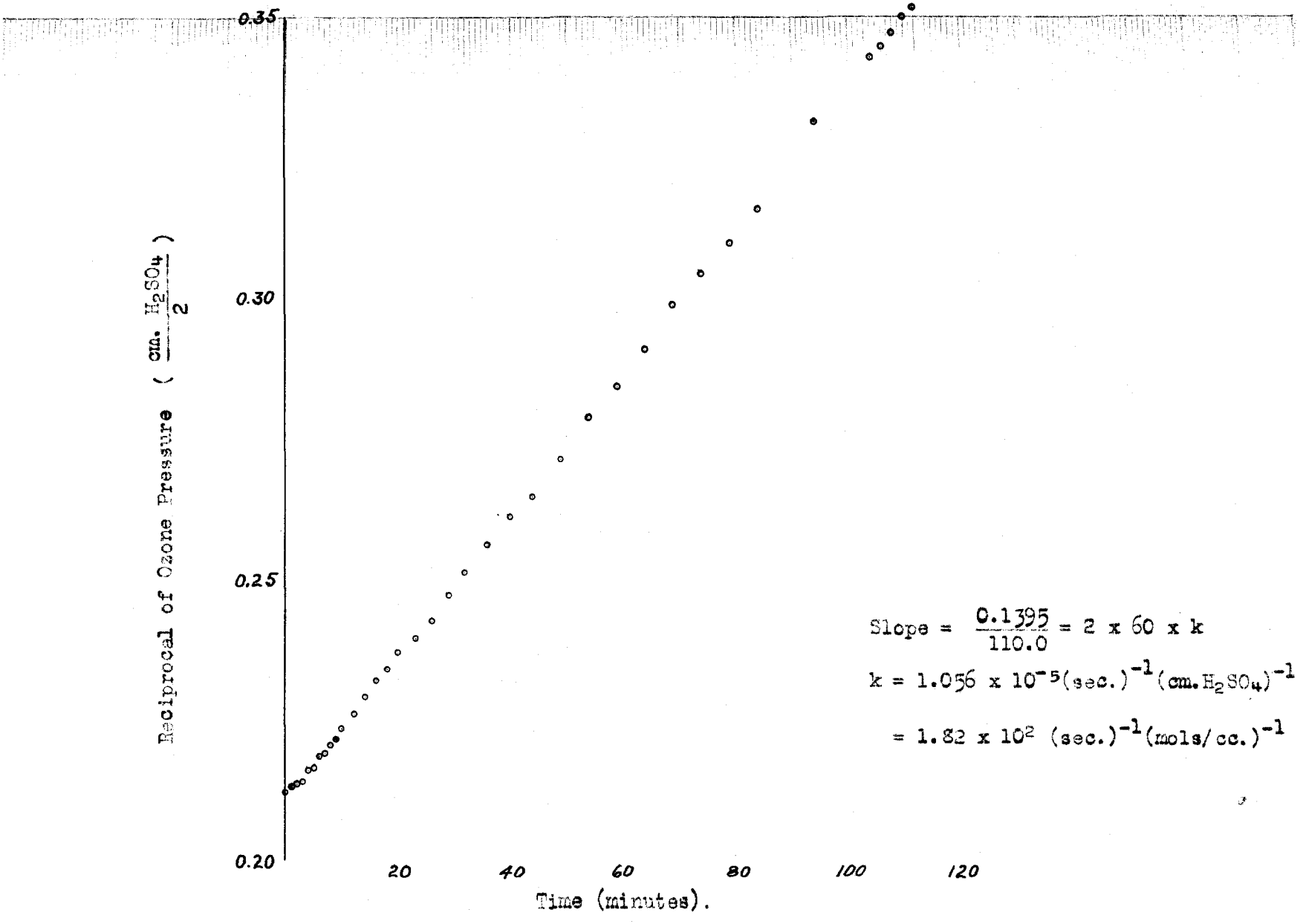
$$2k_2 = \frac{1}{t_2 - t_1}\left(\frac{1}{p_\infty - p_2} - \frac{1}{p_\infty - p_1}\right) \qquad (5)$$

A third method was used to some extent, and because it possesses a certain use by itself, it is given here, partly as an illustration of a convenient way of following such a change. Just as before, after sufficient time has elapsed in the reaction course near the start, such that conditions have become uniform, a particular pressure is chosen as a starting point, but this pressure, p_o, is set equal to zero, thus measuring the pressure p thereafter from this point. Then

$$\frac{1}{p_\infty - p} - \frac{1}{p_\infty} = 2kt \qquad \text{See (4)}$$

Rearranging, and solving for $\frac{1}{p}$ there results

$$\frac{1}{p} = \left(\frac{1}{2kp_\infty^2}\right)\frac{1}{t} + \frac{1}{p_\infty} \qquad (6)$$



$$\text{Slope} = \frac{0.1395}{110.0} = 2 \times 60 \times k$$

$$k = 1.056 \times 10^{-5} (\text{sec.})^{-1} (\text{cm.} H_2SO_4)^{-1}$$

$$= 1.82 \times 10^{2} \ (\text{sec.})^{-1} (\text{mols/cc.})^{-1}$$

Figure 3.

Therefore, if the reciprocal of the pressure is plotted against the reciprocal of the time, a straight line is given if the reaction is of the second-order. Moreover, this graph can be made while the reaction is in progress, and it may be of assistance in planning the run in a reasonable way. The intercept on the axis of ordinates is $1/p_\infty$. While this is not an accurate method of determining p_∞, it permits an estimate of its value to be made early in the run, and continually indicates the behavior of the reaction.

It is essential to point out that each of these methods must give the same results when applied to a change which is of the second-order. For such changes as are not purely second-order, all three methods are of limited application.

Discussion of Results

A total of thirty seven runs have been completed, and Table II gives in outline the results. The experiments are arranged in chronological order, the first column giving the number of the run in the order performed. The second column gives the specific reaction rate calculated for a change of the second-order with respect to the ozone concentration in mols per cc. at unit concentration multiplied by 10^{-2}. The third column gives the final value of the pressure change in centimeters of sulfuric acid after complete decomposition, corresponding to a time equal to infinity, and designated here simply p_∞. This is an observed value in all cases, except in the first six runs where it is calculated*, later results justifying the method of calculation save that the possible error in these first six values is greater than the rest. This applies to the values of the constants as well for these runs, but the error is not sufficient to account for their differences. The fourth column

*This value for Run 20 is also calculated.

describes the ozone, whether made by electrolysis (Elec.) or by subjecting oxygen to the corona discharge (Cor.). The fifth column describes the material used in drying the gas, whether concentrated c.p. sulfuric acid or fused "commercial" calcium chloride. The sixth and seventh columns are self-explanatory.

Table II

Run	$k \times 10^{-2}$ $\frac{cc.}{mol.\ sec.}$	p_∞ cms. H_2SO_4	Gas	Drying agent	Changes between runs	Remarks
1	3.10	12.0	Elec.	H_2SO_4		In first 5 runs apparatus corrections are large. The final pressures are calculated. The latter is true of Run 6 also.
2	6.38	9.5	"	"		
3	5.00	11.5	"	"		
4	3.45	12.0	"	"		
5	5.69	10.7	"	"		
6	20.3	3.9	"	"	Fresh H_2SO_4 in generator	Constant shows no increase with time; final pres. is calculated.
7	14.3-17.2	5.5	"	"	First superheat	Constant shows real increase with time. Final pressure is observed.
8	12.9-17.2	5.6	"	"	Double superheat.	Constant shows real increase with time.
9	1.86	12.5	"	"	Anode cooled with ice-cooled water	Constant shows no increase with time.
10	1.79	9.61	"	"		
11	1.88	11.41	"	"		
12	1.69	12.64	Cor.	"	New drying agents	Flow unknown
13	1.60	13.33	"	"		Volt. same, flow approx. same as in 12.
14	1.90	8.04	"	"		Same as 12 and 13, except flow increased.

Table II (Cont.)

Run	$k \times 10^{-2}$ $\frac{cc.}{mol.\ sec.}$	p_∞ cms. H_2SO_4	Gas	Drying agent	Changes between runs	Remarks
14	1.83	4.72	Cor.	H_2SO_4		Flow same as 14; volt. decreased
16	2.28	1.05	"	"		Flow same as 15; volt. further decreased.
17	2.09	6.37	Elec.	"		Tap-water cooling.
18	2.54	3.97	"	"		Tap-water flow reduced from 17.
19	1.60	8.90	"	"	Apparatus not in use for a month.	Tap water at 23.7°.
20	2.62	5.48	"	"	Capillaries replaced by stopcocks; H_2SO_4 lubricant.	Tap water at 24.7°. Stopcocks leaked on superheating. Final pressure calculated.
21	2.16	8.78	"	"		Tap water 22.6°, Triple superheat.
22	10.3-17.2	5.22	"	"	Fresh H_2SO_4 in generator.	Tap water 23°. Double superheat.
23	11.4-24.1	5.17	"	"		Tap water 23°.
24	2.95	10.41	Cor.	$CaCl_2$		Flow 39 cc/min. Volt. = 60
25	2.67	3.71	"	"		Flow 39 cc/min. Volt. = 32
26	2.57	7.98	"	"	Manometer repaired and refilled before run.	Apparatus swept out several mins. before ozonization. Flow 39 cc/min. Volt. = 40
27	2.52	8.48	"	"		Made to duplicate 26. Flow 39 cc/min. Volt. = 40
28	2.41-2.07	3.88	"	"		Flow 178 cc/min. Volt. = 40 Note increased flow.
29	2.40	7.87	"	"		Flow 39 cc/min. Volt. = 40 Made to duplicate 27

Table II (Concl.)

Run	$k \times 10^{-2}$ $\frac{cc.}{mol.\ sec.}$	P_∞ cms. H_2SO_4	Gas	Drying agent	Changes between runs	Remarks
30	3.62-2.76	7.32	Cor.	$CaCl_2$	Vaseline lubricated stopcocks	Thorough rinsing with dist. water before this change. Flow 39 cc/min. Volt. = 40
31	3.53	5.39	"	H_2SO_4	New drying agent substituted in both drying tubes.	Flow 39 cc/min. Volt. = 40
32	3.15	5.85	"	"		Made to duplicate 31. Flow 39 cc/min. Volt. = 40
33	3.36	6.38	"	"	Performed to see if long sweeping with oxygen before runs has effect.	Flow 39 cc/min. V.=40
34	7.75-5.69	2.54	"	"	Performed to duplicate 33, except volt. lowered to lessen conversion of N_2 to NO.	Flow 39 cc/min. Volt. = 34
35	2.41-3.97	11.49	"	"	Performed to accentuate effect of volt. found in 33 and 34, and to test for heat piling-up.	Flow 39 cc/min. Volt. = 60
36	4.14	6.68	"	"	Electrolytic oxygen New transformer.	Performed to test effect of purer oxygen. Flow 13 cc/min. Volt. = 40
37	4.65-3.10	4.25	"	"	Drying tubes rinsed and refilled.	Performed to test effect of new drying agent. Flow 39 cc/min. Volt. = 40.

In order to make more clear the discussion of these results a conclusion that has been reached in this work will be first stated here.

It is a matter not proven, though strongly probable, that large variations in the rate of decomposition among different runs are due to some characteristic of the gas mixture itself, and not to external causes such as the conditions of the walls of the reaction vessel, or the kind of drying agent used. Two kinds of runs are to be distinguished: those in which within the run k is constant, and those in which k varies within the run. The larger number are in the first group. Where k varies in the run the first and last values are given and a dash placed between them. It is remarkable that in the majority of runs k is extraordinarily constant, and thus the change adheres almost strictly to that of the second-order. Thus Runs 13 and 24 followed rigidly a second-order change over the region investigated (one half to two thirds of the total change), while the value of the specific rate in 24 is almost twice that in 13. Again it should be emphasized that runs, such as 13 and 24 in which k does remain constant throughout, are the rule rather than the exception. Were it not for the fact that all possibilities of some physical second-order change have been investigated and excluded, it might be suspected that the change is of this character. It should be noticed that in all runs made in this investigation the concentration of oxygen has been practically constant, not varying at any rate by more than 4%.

The following brief discussion of each run consecutively is given to point out relations that seem important.

The first five runs were made with the apparatus described above, except that certain improvements had not yet been made. The temperature of the constant-pressure bulb varied, and was observed and corrected for. The manometer was of such bore that the volume change occurring with the movements of the liquid could not be neglected and this was corrected for also. Moreover, the pressure change corresponding to complete decomposition, p_∞, was not observed but calculated from the data and the second-order character of the reaction (the latter being proved independently of p_∞). Thus the corrections were large and the errors in the values of $\underline{k}$ are appreciable, but not sufficient to account for the variations that occur. Each run in itself is remarkably in agreement with a second-order change. There is, however, within these runs a relation which was at first thought significant, but, after succeeding runs, was considered as uncertain because it does not hold invariably. In the first five runs the increasing values of the constant are in the same order as the decreasing values of p_∞ (i.e. ozone concentration). Thus high ozone concentration seemed to give a low value of the constant.

Run 2 contains somewhat more information than the others, and this will be mentioned in more detail later.

With Run 6 the correction for manometer movements had been eliminated by reconstructing the manometer of capillary tubing. Superheating was attempted for the first time, but was unsuccessful. The p_∞ is therefore a calculated value. The very high rate is explained in the discussion of Run 7.

Run 7 represents the first run in which the value of p_∞ was obtained experimentally by the method of superheating explained above. This run, with Runs 6 and 8 also, have, however, a very much higher rate than the average. This is due to an unknown impurity which enters from the use of fresh sulfuric acid in the electrolysis apparatus. This is checked by Runs 22 and 23.

It is an effect which disappears with the use of the acid as evidence by Run 9. These two runs show one other interesting feature, namely, the constant increases with time. This has the following explanation. The heat of decomposition of ozone is large, amounting to 34,500 calories per mol[8]. The heat liberated in the chamber, if the reaction is fast, may then be sufficient to maintain a small temperature difference decreasing with time, above 100°. For these fast rates there is reason to believe that this temperature effect is appreciable. The change in pressure caused thereby when superimposed upon the normal second-order rate will later be shown to affect the pressure change in such a way that the specific reaction rate constant calculated as second-order will increase with time. This is exactly what is found in Runs 7 and 8. It must be mentioned, however, that a change in order caused by the catalyst might be expected here anyway; but a catalyst does not necessarily change the order. And, moreover, while the variation is in the direction of a first-order change, the curve obtained is not a picture of a typical first-order change calculated as of the second-order, but is a picture of the temperature effect mentioned just above. Conclusions such as these, which may be drawn from the general form of the curve, will be spoken of further.

With Run 9 the catalytic impurity has disappeared from the ozone, and an excellent second-order change is found. The cooling mentioned was not a drastic cooling. It was employed to lower somewhat the temperature of summer tap water.

The conditions under which Runs 10 and 11 were made were the same as those for Run 9, and they agree well with this run.

Run 12 is the first run in which ozone made in the corona was used, and it shows a good agreement with Runs 9, 10, and 11.

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[8] Jahn, Zeit. f. anorg. Chem., 60, 337 (1908).

Run 13 is a duplicate of Run 12 and agrees well with all of the four preceding runs.

In Run 14 the value of $\underline{k}$ has increased. The flow had been increased a little, thereby lowering the ozone concentration.

Run 15 is again an excellent second-order change and is important in that its rate did not increase, though its initial concentration is low as a result of the decrease in voltage on the corona ozonizer.

In contrast Run 16 shows a marked increase in rate. The concentration has been further decreased due to still lower voltage.

Run 17 shows a high rate for electrolytic ozone (compare early runs with this gas).

Run 18 shows a higher rate than 17 and the concentration has fallen because the cooling was less strong.

Run 19, however, shows a low rate. It will be noted that the apparatus had stood idle for some time.

Run 20 shows a somewhat high rate, yet considering that p_{∞} was calculated, it agrees very well with Run 18.

Run 21 agrees well with Run 17. Thus a comparison of Runs 20 and 21 with 18 and 17 shows that the sulfuric acid lubricant had exercised no large effect. And Run 21 is incidentally a run in which a test was made for complete decomposition of the ozone after superheating.

Runs 22 and 23 have been referred to above as also showing the extraordinary high rate caused by impurity from the use of new sulfuric acid in the ozone generator. Both show the temperature effect upon the constant referred to previously.

In Run 24 calcium chloride was first used as a drying agent. The run shows a high rate for a normal corona ozone mixture, as may be seen by comparison with Runs 12-16.

In Run 25 the rate dropped while the concentration of ozone also dropped greatly, thus agreeing in this respect with Run 15.

Run 26 reproduces 25 well. Neither the preliminary sweeping of the chamber nor the change of the entire manometer produced any decided effect.

Run 27 reproduces 26 well. However, the rates of these runs are higher than the rates found in Runs 12-16.

In Run 28 the ozone concentration was decreased by increasing the gas flow through the ozonizer. The rate is not constant over the run in this case. As will be shown later, an error in the final pressure large enough to account for this variation in the constant is of a magnitude which renders it improbable. It is probably not justifiable to draw any conclusion from this run as to the behavior of the rate with low ozone concentration, although the rate does not appear to have increased.

Run 29, in which conditions of 27 were returned to, checks it very well.

Run 30 does not give the same result as 29, although made under the same conditions except for the change of stopcock lubricant (vaseline now being used), and the rinsing of the apparatus carried out before the run.

Run 31 is high but constant.

Run 32 is lower and constant, and in fair agreement with Run 24.

Run 33, performed using long sweeping out with oxygen as a preliminary measure to remove any residual nitrogen, was made to see if a decrease in rate could be obtained thereby. None was found. The rate is constant and falls between Runs 31 and 32 in magnitude.

Run 34, performed to see if the oxidation of traces of nitrogen to nitrogen pentoxide in the corona could be the cause of the acceleration of the rates in fast runs, with a very low voltage to reduce any nitrogen oxidation, gave a rate that was much higher rather than lower. It is in agreement with that for low ozone concentration obtained by low voltage on the ozonizer.

Runs 33 and 34 had indicated an increase in rate with decrease in voltage. An increase in flow in Run 28 had not appeared to give this effect. Run 35 was performed with high voltage to see if a low rate would be found. The rate apparently fell, but was not constant. The run, however, was investigated over 85% of its course, which is more than in most cases, to discover whether any appreciable "heat piling-up" occurred in the chamber. Thus if the exothermic decomposition maintained a certain temperature greater than 100°, might not the chamber be at a slightly different temperature when containing 2% ozone during a decomposition, if originally there were 3% ozone present, than if originally there were 4% ozone present, due to the greater heat piling-up in the case of the higher concentration? If a run were carried out over a certain portion of a quantity of ozone, and then the temperature lowered a few degrees for a short time, the remaining ozone then could be raised to 100° again and a second run carried out. Discontinuity between the two halves would result if there had been a heat piling-up; that is, the temperature at the end of the first portion would have been something above 100°, while that at the beginning of the latter portion would be 100°. Such a test made in Run 35, which consists of two parts, showed no piling-up effect. Similarly Run 2, due to an accident, was carried out in closely the same way with respect to lowering the temperature when partly over; and it, too, shows no discontinuity.

In Run 36 the conditions were the same as in Runs 31 and 32, except that electrolytic oxygen was supplied to the ozonizer at a low gas flow instead of Linde tank oxygen. The rate is constant but high.

In Run 37 Linde oxygen was again used, but the concentrated sulfuric acid drying agent was replaced by fresh material from the same supply bottle. The rate decreased with time. Here again as in Run 28 and others in which the constant varied, this variation might be caused by an error in the final pressure; but the magnitude of the error necessary for this renders it very improbable.

Summarizing, the results show variations in the value of the constant between experiments, which is remarkable when the adherence to the second-order expression within each run is considered. In only a small minority of the runs is this second-order character missing. It is of course clear that positive catalytic influences entered or increased as the experiments progressed, for chronologically the apparent specific rate showed a definite increase over the thirty-seven measurements. In part this was probably due to the new drying agent introduced at Run 24 and to the vaseline lubricant introduced at Run 30. But the important variations are independent of these, and, for example, are exhibited by Runs 17 and 18 or Runs 13 and 14, just as by Runs 31 and 32 or Runs 31 and 36. These are the difficulties with which we are most concerned, and which are apparently to be traced to the processes taking place when the gas is made. The specific second-order rates observed in the early experiments using both sources of ozone (Runs 10-15) are practically the same as the lowest rates that have been observed by earlier experimenters.

Discussion of Possible Sources of Error

One of the possible sources of error which presented itself in this work has been sometimes disregarded in the study of gaseous reactions in which the changes were followed by pressure measurements. If the reaction is strongly exothermic, it must be shown that the reaction mixture is really held at a constant temperature by the bath in which the chamber is placed. In the case of this experimental work calculation showed that the heat liberated by the decomposing ozone was sufficient to make possible an elevation of the temperature by an amount which would cause an appreciable effect upon the pressure readings, this effect obviously decreasing with time, approaching zero as the ozone concentration approached zero.

Experiments were made in which heat was liberated electrically in the center of the reaction chamber by a small heating wire, at a rate calculated to correspond approximately to 5% ozone decomposing at 100°. The pressure changes were followed. These were not entirely satisfactory experiments. Liberating heat in the center of the chamber did not simulate the conditions of homogeneous ozone decomposition. Qualitatively they were of some value, as they represented the worst that might occur. The actual effects would be considerably smaller.

The pressure changes found in these experiments were sufficiently large to influence our results had they occurred in the decomposition experiments. It was therefore necessary to determine whether or not the ozone itself was causing an elevation of the temperature in the chamber. The absence of this effect was demonstrated by showing that the result of superimposing such an effect on a second-order change is to cause the constant calculated as second-order to be initially low (by an amount being greater the greater the initial ozone concentration) and to increase with time, approaching the true value of the specific reaction rate as the ozone concentration approaches zero.

This can be shown as follows. The temperature increment above 100° is proportional to the rate of heat liberation so long as the increment is small. The experiment mentioned just above corroborated this. And the pressure increment due to it is proportional to it. Therefore

$$\Delta p = \beta p_{O_3}^2 \tag{7}$$

for the rate of heat liberation is proportional to the rate of reaction. Hence the observed pressure difference p of the manometer columns at any time is equal to Δ p plus one third of the pressure of the oxygen in the chamber from the ozone which has decomposed. Therefore the true value of the ozone pressure at any time is given by

$$2\left[p_\infty - (p - \Delta p)\right] = 2\left[p_\infty - (p - \beta p_{O_3}^2)\right] = p_{O_3} \tag{8}$$

But when this effect is neglected, the value of the rate which is set proportional to the square of the ozone concentration is $+2\frac{dp}{dt}$ since then $2(p_\infty - p) = p_{O_3}$ and

$$+ 2\frac{dp}{dt} = -\frac{dp_{O_3}}{dt} = k \cdot p_{O_3}^2$$

Hence it is the new value of $+2\frac{dp}{dt}$ that is desired. Differentiating (8) we have

$$-2\frac{dp}{dt} + 4\beta p_{O_3}\frac{dp_{O_3}}{dt} = \frac{dp_{O_3}}{dt}$$

or

$$+ 2\frac{dp}{dt} = (1 - 4\beta p_{O_3})\left(-\frac{dp_{O_3}}{dt}\right) = k(1 - 4\beta p_{O_3}) p_{O_3}^2 \tag{9}$$

This shows that such an effect gives a value for the constant which is always smaller than the true value, approaching it, however, (a finite constant value) as the ozone concentration decreases.

The possibility that this heating effect, when superimposed on a first-order change, can produce the effect of a second-order change may be disposed of by similar calculations. Thus equation (8) for this case becomes

$$2\left[p_\infty - (p - \Delta p)\right] = 2\left[p_\infty - (p - \beta p_{O_3})\right] = p_{O_3} \tag{8a}$$

since now the rate of heat liberation is proportional to the first power of the ozone concentration. Differentiating

$$-2\frac{dp}{dt} + 2\beta\frac{dp_{O_3}}{dt} = \frac{dp_{O_3}}{dt}$$

or

$$+2\frac{dp}{dt} = (1-2\beta)\left(-\frac{dp_{O_3}}{dt}\right) = k(1-2\beta)p_{O_3} \qquad (9a)$$

Thus a first-order change remains first-order, the numerical value of the constant being changed, but constant over the entire run. Therefore a first-order change containing this heat effect, but calculated as in this work as a second-order change, could never give a constant quantity for the proportionality factor in the second-order expression.

Nor can a third-order change containing this heating effect explain the facts. For it similarly

$$2\left[p_\infty - (p-\Delta p)\right] = 2\left[p_\infty - (p-\beta p_{O_3}^{\,3})\right] = p_{O_3} \qquad (8b)$$

And differentiating

$$-2\frac{dp}{dt} + 6\beta p_{O_3}^{\,2}\frac{dp_{O_3}}{dt} = \frac{dp_{O_3}}{dt}$$

or

$$2\frac{dp}{dt} = \left(-\frac{dp_{O_3}}{dt}\right)(1-6\beta p_{O_3}^{\,2}) = k(1-6\beta p_{O_3}^{\,2})p_{O_3}^{\,3} \qquad 9b)$$

Thus a third-order change with this effect superimposed gives a value for the proportionality factor in the third-order expression which behaves similarly to to the case of the second-order change (i.e. a value of the calculated constant which increases throughout a run approaching the true value as a limit), only the effect is much more pronounced.

There is another effect which will produce an increasing constant. It is the simultaneous occurrence of a first-order change with the second. It can be shown that such gives a value of the constant which increases as the ozone concentration decreases, but approached infinity and not a finite value.

For

$$-\frac{d p_{O_3}}{dt} = k_2 p_{O_3}^2 + k_1 p_{O_3} = \left(k_2 + \frac{k_1}{p_{O_3}}\right) p_{O_3}^2 \qquad (10)$$

Hence the value obtained by assuming a second-order change, where both a first and second really occur, gives a value of the constant that approaches infinity with time. Incidentally, this is a graphical way of recognizing a simultaneous first and second-order change, using the method of plotting described above. It illustrates the interpretation of the run that the plot provides.

There is another possible source of error which it seemed essential to evaluate and study. If, in spite of tests made in repeated superheating, an error was coming into the final pressure, which value constitutes the only measure of the ozone concentration, this might have the effect of changing the calculated specific rate in just such a way as to explain the deviations found. Therefore calculations were made to determine what effect an error in p_∞ would have upon (1) the numerical value of the constant, and (2) upon the constancy of the constant within the run. This effect is illustrated in what follows. Let q be the quantity obtained using the observed pressure values in the expression

$$q = -\frac{dp}{dt}\frac{1}{p^2} \qquad (11)$$

Then the true value for the specific reaction rate, since the values of p are all too small or too large by a constant numerical amount , is given by the expression

$$k = -\frac{dp}{dt}\frac{1}{(p \pm \alpha)^2} \qquad (12)$$

It is to be noted that the rate of change of the pressure remains the same. Hence these two quantities, the true value of k and the apparent value of q obtained in the calculations, are related to one another by the expression

$$q = k\left(\frac{p \pm \alpha}{p}\right)^2 \qquad (13)$$

Throughout any one run α is a constant. But clearly q changes within a particular run as the pressure changes. Therefore the amount by which q differs from k depends upon the value of α for the particular run and upon the particular pressure to which the calculation of q corresponds within the run.

A little more than two thirds of the course of the decomposition was followed in some of these experiments, that is, the last observed pressure was roughly one third the initial pressure. In such cases then

$$q \text{ (at start)} = k \left(\frac{p_0 \pm \alpha}{p_0}\right)^2 = k \left(\frac{3p \pm \alpha}{3p}\right)^2 \qquad (14)$$

$$q \text{ (at finish)} = k \left(\frac{p \pm \alpha}{p}\right)^2 \qquad (15)$$

where p is the last observed pressure during the run. α has been designated as the difference between the true pressure and the observed. If this is positive, q is always greater than k, if negative it is always smaller, the effect becoming more pronounced in both cases as the pressure decreases. In order that q be twice as great or one half as great as the true value of k at the last observation of the pressure, α must assume a value corresponding to the relations

$$\left(\frac{p+\alpha}{p}\right)^2 = 2 \qquad \text{or} \qquad \alpha = 0.4\,p \qquad (16)$$

$$\left(\frac{p-\alpha}{p}\right)^2 = \tfrac{1}{2} \qquad \text{or} \qquad \alpha = 0.3\,p \qquad (17)$$

And the value of q at the start of the run for these two cases is

$$q = k \left(\frac{3p + 0.4p}{3p}\right)^2 = 1.3\,k \qquad (18)$$

$$q = k \left(\frac{3p - 0.3p}{3p}\right)^2 = 0.9\,k \qquad (19)$$

Thus, to cause a relative variation over an entire run of from 1.3 to 2.0 in the value of k, the error α would have to be $0.4 \frac{p_0}{3}$ or $0.13\ p_0$. And to cause a relative variation over an entire run of from 0.9 to 0.5 in the value of k,

the error δ would have to be $0.3\frac{p_o}{3}$ or $0.1\ p_o$. By an entire run is meant two thirds of the decomposition.

From these considerations it follows that the variations which were observed in the constant between the several runs can not be accounted for by an error in the final pressure read after superheating. First, in all but runs of the very lowest concentration it is known quite surely from experiment that the error in the final pressure is not sufficiently large; second, the calculations show that a characteristic of a value of q which is appreciably different than that of the true value k, is that it be not constant but that it vary in a definite and marked way within the run. When the correction is positive the calculated values of q are larger than k, and they increase within the run as the pressure decreases. When the correction is negative, the calculated values are smaller than k, and decrease within the run as the pressure decreases. No such correlation between the value of the constant and its variation is to be found in the thirty seven experiments made. Incidentally, the extreme constancy of q in the majority of runs is an excellent check on the accuracy of the observed final pressure after superheating as corresponding to complete decomposition.

There is a possibility that, even if the chamber was being held at a somewhat higher temperature than the bath, this fact might not show in the graph in the way stated above. If a piling-up of heat occurred in a very special way, so as to just neutralize the effect mentioned in the previous paragraphs, then the calculated constant might be practically constant over the entire run, but of an incorrect numerical value. This rather improbable assumption would require, for example, that the difference in temperature of the chamber from 100° at the moment when, having started with three percent ozone, the decomposition passes the two percent concentration mark, is different (less) than this

difference at the moment when, having started with four percent ozone the decomposition passes again the two percent concentration mark. That is, a piling-up more pronounced for the higher concentrations would be observed.

Although the many runs, when considered together, render this improbable, it was felt necessary to show in some particular way that there was no such piling-up effect. Runs 2 and 35 are given as evidence. In these runs, when the middle of the decomposition was in progress, the temperature of the bath was lowered many degrees and then brought back to 100°. If the effect had been present in the run, this would have erased it. A different numerical value for the constant would be found for the remaining portion of the run than for the first part, and a discontinuity in the pressure change with time would be observed at this point. These effects were not found. The graphs of the pressure change with the time, and of the reciprocal of the pressure against the time for Run 35, which was performed especially to study this effect, are given in Figures 4 and 5. It happened that in this run the constant showed an increase with time, as is evidenced by the fact that the curve in Figure 5 is not a straight line. But this does not lessen the value of the two curves for this particular use, since they show no discontinuity at the point where the first half of the run ended and the second half began. ~~Since it was in the vicinity of this point that the two curves were of interest, the early and late portions of the run, which were not conveniently included on the sheet, are not shown.~~ The second half was placed on the paper by extrapolating the first half a short distance, until the first pressure observed in the second half

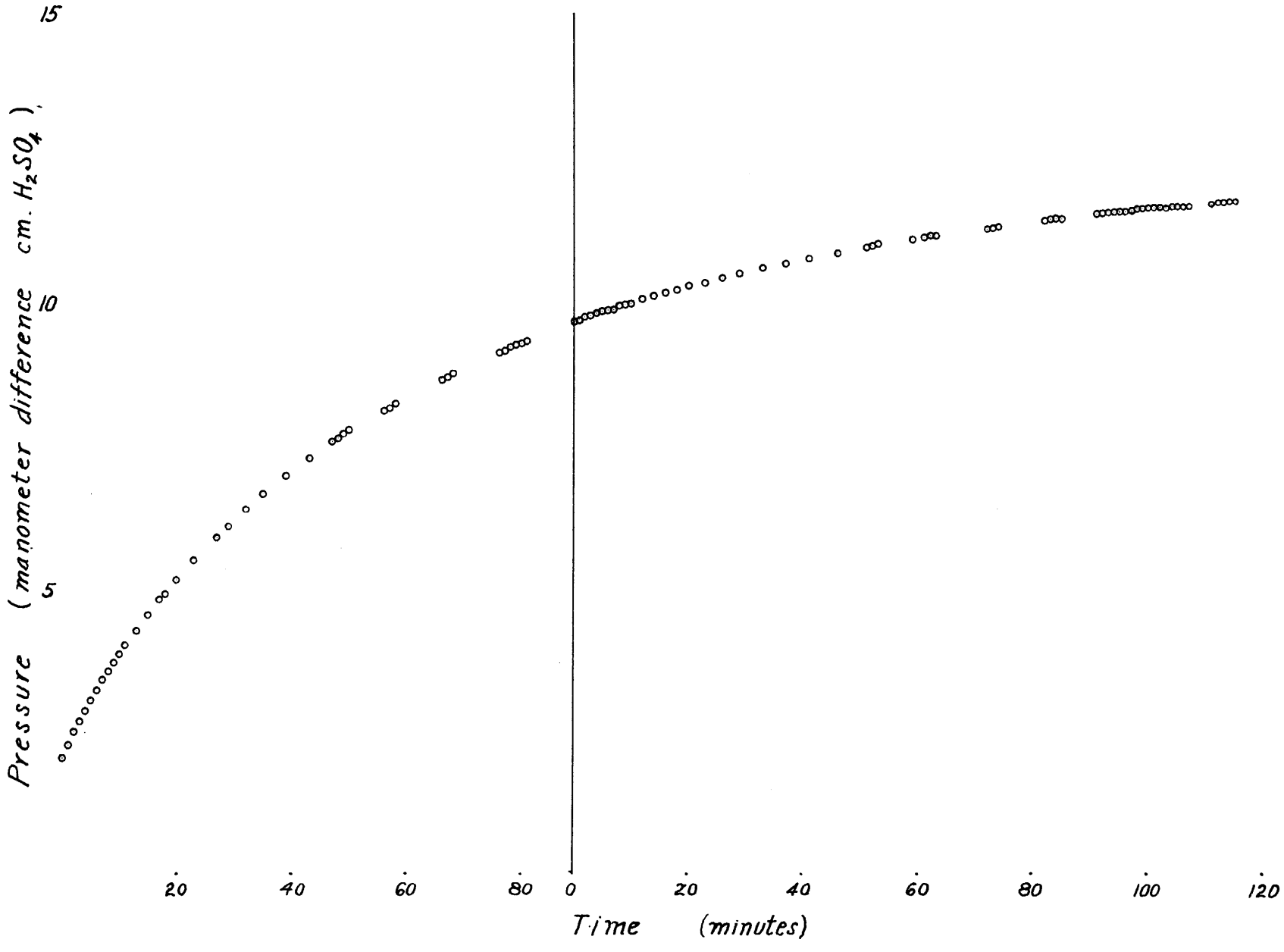
15
10
5
Pressure (manometer difference cm. H_2SO_4)
20
40
60
80
0
20
40
60
80
100
120
Time (minutes)

Figure 4.

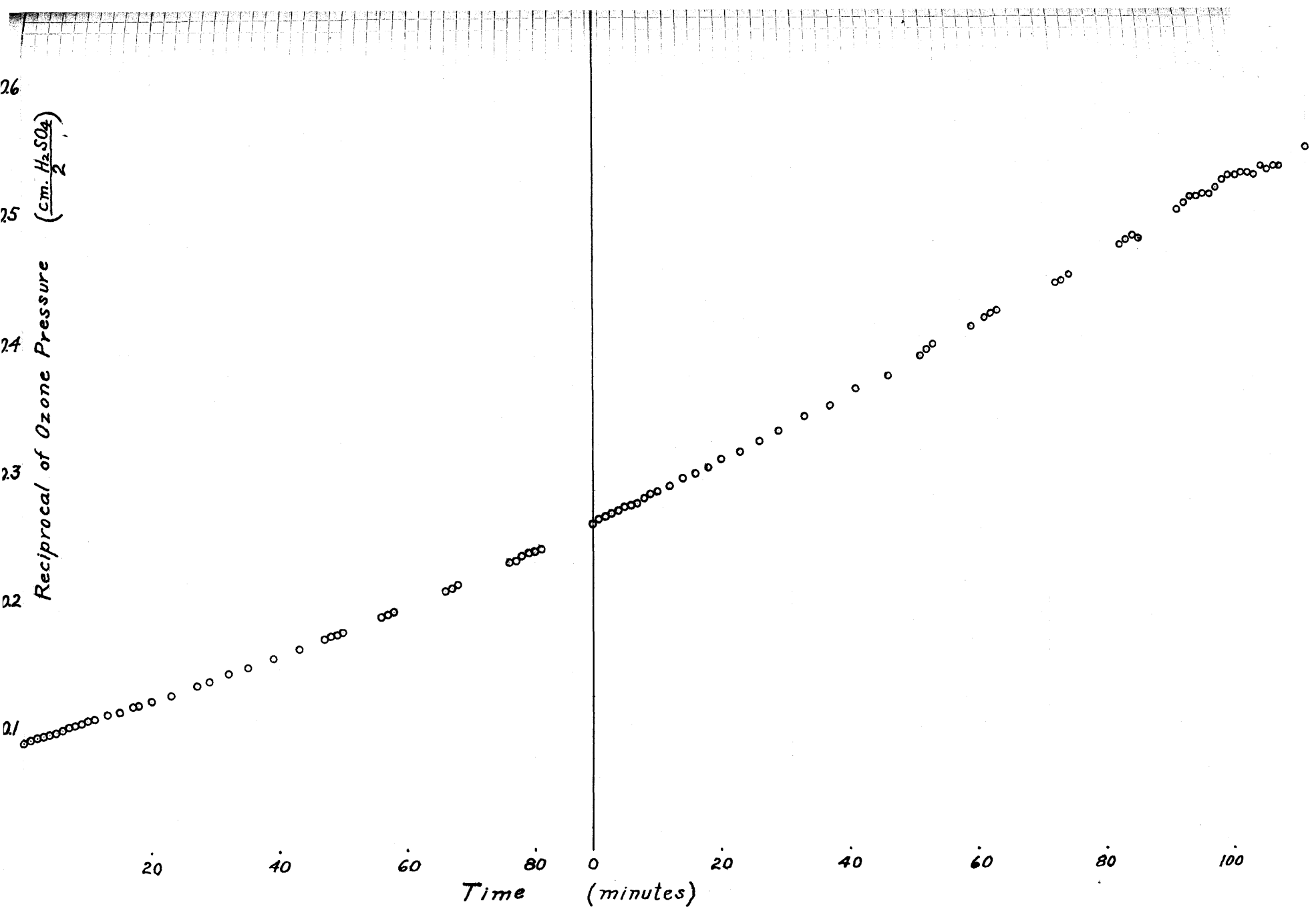
2.6
2.5
2.4
2.3
2.2
2.1
Reciprocal of Ozone Pressure $\left(\frac{cm.\ H_2SO_4}{2}\right)$
20
40
60
80
0
20
40
60
80
100
Time (minutes)

Figure 5.

was reached, the second half being started here and continued from this point on in time. This seems justifiable, since this is really the point the reaction would have reached in this shorter time (actually eight minutes in this case), if the temperature had not been lowered. From the thirty seven runs considered together, and from Runs 2 and 35 in particular, it is concluded that there exists no heat-piling-up effect in the reaction chamber.

Summary of Part II

The decomposition of ozone at 100° is a change of the second-order.

Values for the specific rate have been obtained in a series of thirty seven determinations. These show a variation that practically covers the region over which the values of earlier experimenters lay scattered. Nevertheless, in a large majority of these runs the decomposition adheres strictly to the second-order expression.

The decomposition of ozone proceeds at different specific rates even for consecutive samples of the gas, from causes which can not be traced to the conditions of the walls of the containing vessel, nor to the method of drying the gas. The causes of these variations are contained in the gas itself, and are probably connected with the method by which the gas is made.

Errors which may enter into this method of measuring the rate of reaction have been described and analyzed. Since the method is considerably used in studying gas reactions involving a change in the number of molecules, and since the errors to which it is subject do not seem to have been sufficiently emphasized heretofore, these results have been included.

Some useful graphical methods for the interpretation of experimental data, such as collected in the above work, have been devised and applied.

PART III

Experiments Using a Modified Static Method

Introduction

The static method of measuring the rate of ozone decomposition, when carried out at one total pressure can yield information concerning only the character of the course of the reaction. The effect of oxygen pressure can hardly be tested, because the ozone which is available is limited by our ordinary methods of preparation to very low concentrations, and the oxygen concentration is therefore always nearly constant. As described in the introduction earlier investigators[1,2,3] have made use of the static method at various total pressures, thus affording comparisons of the rates of decomposition under different oxygen concentrations. This is, however, limited by two difficulties. First, as seen from Part I, as well as from all earlier work, consecutive samples of ozone decompose under apparently the same conditions at different rates. This makes comparison between consecutive runs somewhat uncertain. Secondly, when original ozone is put into reaction vessels at different total pressures, not only is the partial pressure of oxygen now different from that in the experiments performed under one atmosphere of total pressure, but similarly the partial pressure of every other molecular specie present has been changed in the same way, thus the partial pressure of the ozone and also, it must be noted, the partial pressure of any catalytic impurity.

These limitations apply to the experiments of Perman and Greaves[4] and of Griffith and McKeown[7], but the static experiments of Jahn using the Warburg differential ozonometer are free from the latter difficulty, though less so from the former. It seems doubtful whether a reaction chamber, which is itself

a silent discharge ozonizer, can ever produce the same character of ozone twice in succession. The very nature of the silent discharge would lead one to believe that the variableness of it and the effect it may have on gases occluded in the walls would yield, upon consecutive ozonizations, ozone of different characteristics. That this is undoubtedly true is borne out by Warburg's careful early measurements.

The work of Chapman and Jones[6] had indeed avoided probably both of the two difficulties mentioned above, for in this case the rates of decomposition of two samples of the same ozone were compared. To one of these oxygen had actually been added.

The apparent discrepancy between the work of Jahn and of Chapman and Jones was not necessarily a real one, since the experiments were for the most part different. Jahn, in all his experiments except those in which ozone was diluted with air, measured the effect of total pressure, while Chapman and Jones measured the effect of added oxygen. While a possible explanation of Jahn's results was contained in his hypothesis, in which oxygen behaves as a negative catalyst according to the interesting mechanism described by him, a wholly different explanation could be given on the assumption of the presence of some other negative catalyst.

It appeared important to reproduce essentially the static experiments of Jahn and of Chapman and Jones by a method which need possess only sufficient accuracy to differentiate between changes in rate of the order of one and two fold, in order to explain if possible the discrepancy between the results of the two investigations.

To do this, the work described in the following pages was carried out. The apparatus was made as simple as possible. Especially the effort was made to avoid the need of comparing consecutive samples.

Dependence of the Rate on the Total Pressure.

Apparatus and Method

The apparatus and procedure may be described in a few words. Four bulbs of pyrex glass, of known volume and nearly alike, were sealed together in series by means of connecting constricted capillary tubes. One end of this bulb train was sealed by means of another capillary to a course of ozone supply. The other end was sealed by means of still another capillary to a system of glass tubing which possessed in it a mercury manometer, a connection to a water jet pump, and an outlet tube from which the ozone could pass to the room by bubbling through concentrated sulfuric acid. This bubbling tube was sealed to the system through a constricted capillary. Figure 6 illustrates the apparatus.

The procedure consisted in sweeping out this train with ozone until all air was removed, the issuing gas escaping at the bubbler. After a time longer than that necessary to sweep the air from the system, the flow of ozone was stopped and the capillary at a sealed off before the flame. The capillary f was next sealed. Then by means of the water pump, gas was removed from the system until the pressure of ozonized oxygen in the four bulbs was approximately 560 mm. Hg. With stopcock g closed, the capillary at c was sealed. Then the pressure in Bulbs III and IV was further reduced to approximately half the value of that remaining in Bulbs I and II, and at this point the capillary at e was sealed off. Capillaries b and d were now sealed, leaving all four bulbs separated, I and II being at a relatively high pressure, while III and IV were at a pressure roughly one half this.

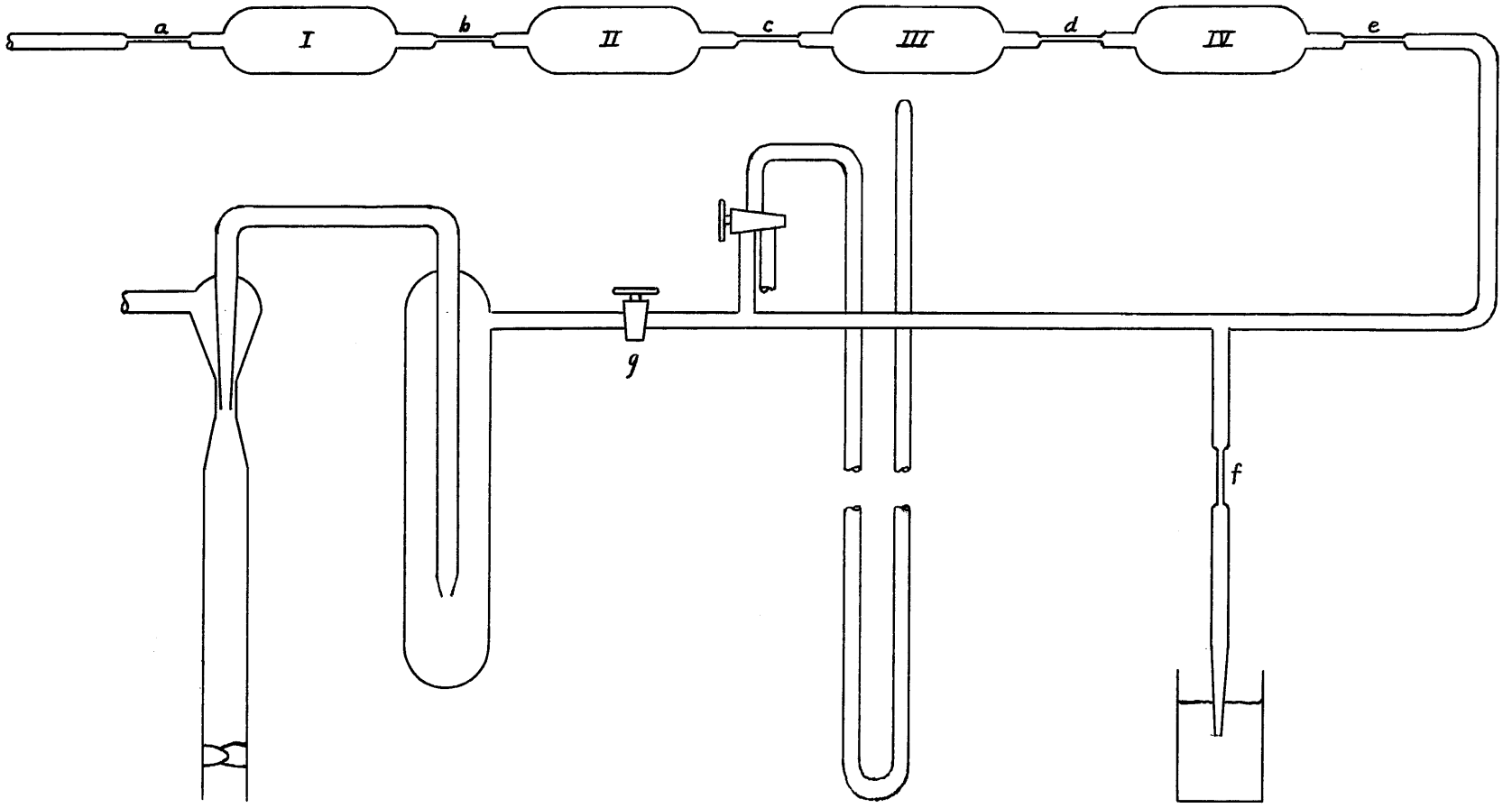

Figure 6.

Bulbs II and III were then placed in a clamp rack and immersed simultaneously in a bath of boiling water where they were allowed to remain from one half to three quarters of an hour, dépending on the experiment. The bath, which was heated by an electric hot-plate, was almost completely covered, allowing very little diffuse light to enter. Bulbs I and IV were held as controls in a bath of tap water.

After the time interval of reaction, Bulbs II and III were removed simultaneously and chilled in tap water, then placed with I and IV. After more than sufficient time for complete cooling of the bulbs (usually about twenty minutes) the ozone in each was allowed to react with neutral 2% potassium iodide solution by crushing one capillary tip under the surface and letting the solution be forced in until pressure equilibrium was reached. The absorption was carried out with gentle shaking.

By cutting off the upper tip the solution of liberated iodine in potassium iodide was run out, and the bulb rinsed. This solution was then made acid with dilute sulfuric acid and titrated against 0.01 n. sodium thiosulfate.

Results

The data obtained using the above procedure gave two concentration values over a decomposition for the same sample of ozone at two different pressures, the two portions of the gas being at the high temperature for the same length of time.

Assuming that the reaction has followed approximately a second-order course over the time interval (an assumption amply justified by all earlier work), we may calculate the value of the specific second-order rate from the following familiar expression

$$k_2 = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_o}\right)$$

where Bulbs I and IV each yield a C_o value, while Bulbs II and III give each the respective value of C.

Our interest lies in the comparison of the ratio of these two values in each experiment with the ratio of the corresponding total pressure, or better, its reciprocal.

Six experiments of this type were performed. The following table gives the significant data of each consecutively.

Table III

Expt. no.	Reaction time (min.)	Initial conc. in Bulb I $\frac{\text{mols.}}{\text{cc.}} \times 10^6$	$k_2 \times 10^{-2}$ cc/mol. sec. p_1	p_2	$\frac{k_2 p_2}{k_2 p_1}$	p_1 (At room temp.)	p_2	p_1/p_2	$\frac{k_2 p_1 \times p_1}{k_2 p_2 \times p_2}$
1	37	1.73	2.85	5.71	2.0	556	263	2.11	1.05
2	37	1.44	2.67	6.41	2.4	556	263	2.11	0.88
3	30	1.57	1.50	2.73	1.8	556	250	2.22	1.22
4	40	2.15	1.55	2.83	1.9	552	248	2.23	1.22
5	45	0.58	2.95	10.30	3.4	553	240	2.30	0.66
6	45	0.65	2.60	6.55	2.5	553	239	2.31	0.92
								Mean	1.05

The fourth and fifth columns show clearly the effect of the total pressure, the increase in rate with decreasing pressure. The question whether the increase is inversely proportional to the total pressure is answered in the last column where the ratio of the two products of the rate by the corresponding pressure gives a mean value very close to unity. In experiment 5 the ozone concentration was so low that the probable error is large, especially so in the low pressure bulbs, where the concentration of ozone was very small. It will be seen that the low pressure value of the rate in this run is high. It is, however, higher than would be expected even with the large error, and so the

result must be regarded as uncertain. Run 5 was therefore omitted in taking the mean of the final column; including it would, however, only bring the ratio nearer unity.

There are certain remarks that should be made concerning these experiments, in order to give each its full significance. Experiments 1 and 2 were carried out with ozone prepared from Linde tank oxygen by the silent discharge. The gas was dried once before entering and once after leaving the ozonizer by concentrated sulfuric acid.

Experiments 3, 4, 5, and 6 were performed at a later time, after most of the other experiments described in this Part. They were carried out with ozone prepared from oxygen produced electrolytically from a 12% solution of pure sodium hydroxide. The oxygen was never in contact with anything other than cleaned glass surfaces and dilute and concentrated pure sulfuric acid, after being evolved from the caustic solution. The drying was accomplished without bubbling by extended exposure to surfaces of concentrated sulfuric acid. The ozonizer was of somewhat improved mechanical construction, but in principle the familiar silent-discharge ozonizer. This apparatus is described in Part IV of this thesis, and illustrated in Figure 9 .

The remarkable variation in the ozonizability of the caustic oxygen, which is discussed more fully in Part IV, is clearly seen by a glance at the initial concentrations of 3 and 4, as compared to those of 5 and 6. All four were produced under the same electrical conditions and the same current imput in the generator, thus the same rate of gas flow. But the former two were carried out not long after the electrolyte had been prepared, the

latter two after the apparatus had remained idle for a month. The replenishing with distilled water done after experiment 6 (i.e. the addition of a quantity of distilled water roughly 5% of that in the entire electrolyte, this being the extent of the depletion) brought back in a large measure the ozonizability of the oxygen.

Since these experiments were performed in order to make definite our opinion as to the effect of total pressure on the second-order rate, it is well to briefly summarize the work done upon it. Jahn[1] had carefully tested this using the differential ozonometer, and at four pressures had shown satisfactorily the inverse proportionality of the second-order rate and the total pressure. Our experiments are taken as confirming this fact by a different method and with different ozone. The failure of Perman and Greaves[4] and of Griffith and McKeown[7] to confirm this quantitatively is probably due to the presence of a positive catalyst in their ozone, which is indicated by the failure to obtain second-order rates, finding rather an increasing value of the calculated second-order constant.

A remark must be made regarding the values of the pressures given in Table III, and in all of the experiments described in Part III. As the heading of the column indicates, they are for room temperature; that is, measured at the time the bulbs were filled. Since it was the pressure ratio that was of interest in these experiments, no reading of the room temperature was taken, so that the actual pressures under which the decomposition took place may be obtained only approximately by applying a factor 373/295 to the observed values. The interest in the pressure during the reaction comes

about of course through the effect of the total pressure, and is important in comparing the rates observed in these experiments with those found in the work of Part II as well as those found by earlier investigators. However, the accuracy of the pressures at 100° obtained by assuming the room temperature to be 295° are entirely satisfactory considering the accuracy with which the constant itself is measured.

The average value of the rates given in Table III for the high-pressure bulbs, when corrected to one atmosphere pressure at 100°, is 2.1 cc/mol sec., which is in good agreement with the low rates found using the static method of Part II.

Dependence of the Rate on the Partial Pressure of Oxygen

Apparatus and Method

Three determinations were made of the effect of added oxygen. In these a fifth bulb, as illustrated in Figure 7, was used: it served as the container for the oxygen. The experimental procedure was much the same as in the six runs mentioned in the preceding section.

Prior to the filling of Bulbs I, II, III, and IV with ozone, Bulb V was filled with oxygen by sweeping out as in the preceding experiments, the gas passing first through I, II, and III, and finally out through the capillary at j, bubbling through sulfuric acid. Stopcock i was lubricated and sealed with sulfuric acid. Bulb V having been filled with oxygen, this stopcock was closed and the capillary at j sealed before the flame.

Bulbs I, II, III, and IV were then filled with ozone in the same manner as in the preceding experiments. When they had been swept completely with ozone, and the system sealed at a and f, the pressure in all four bulbs was reduced to approximately 300 mm. Hg. The capillary at c was next sealed. Then the stopcock i was carefully opened, allowing pressure equilibrium to be established between Bulbs V, III, and IV, thus injecting more oxygen into III and IV, and as a matter of fact nearly doubling their oxygen concentration. The capillaries at b, g, and h were then sealed, separating all four bulbs. From this point the treatment was the same as in the preceding six runs, and therefore need not be referred to here.

The first determination was performed using Linde tank oxygen, dried by concentrated sulfuric acid. The second and third were performed with electrolytic oxygen from the caustic solution. In all cases ozonization was by the silent discharge.

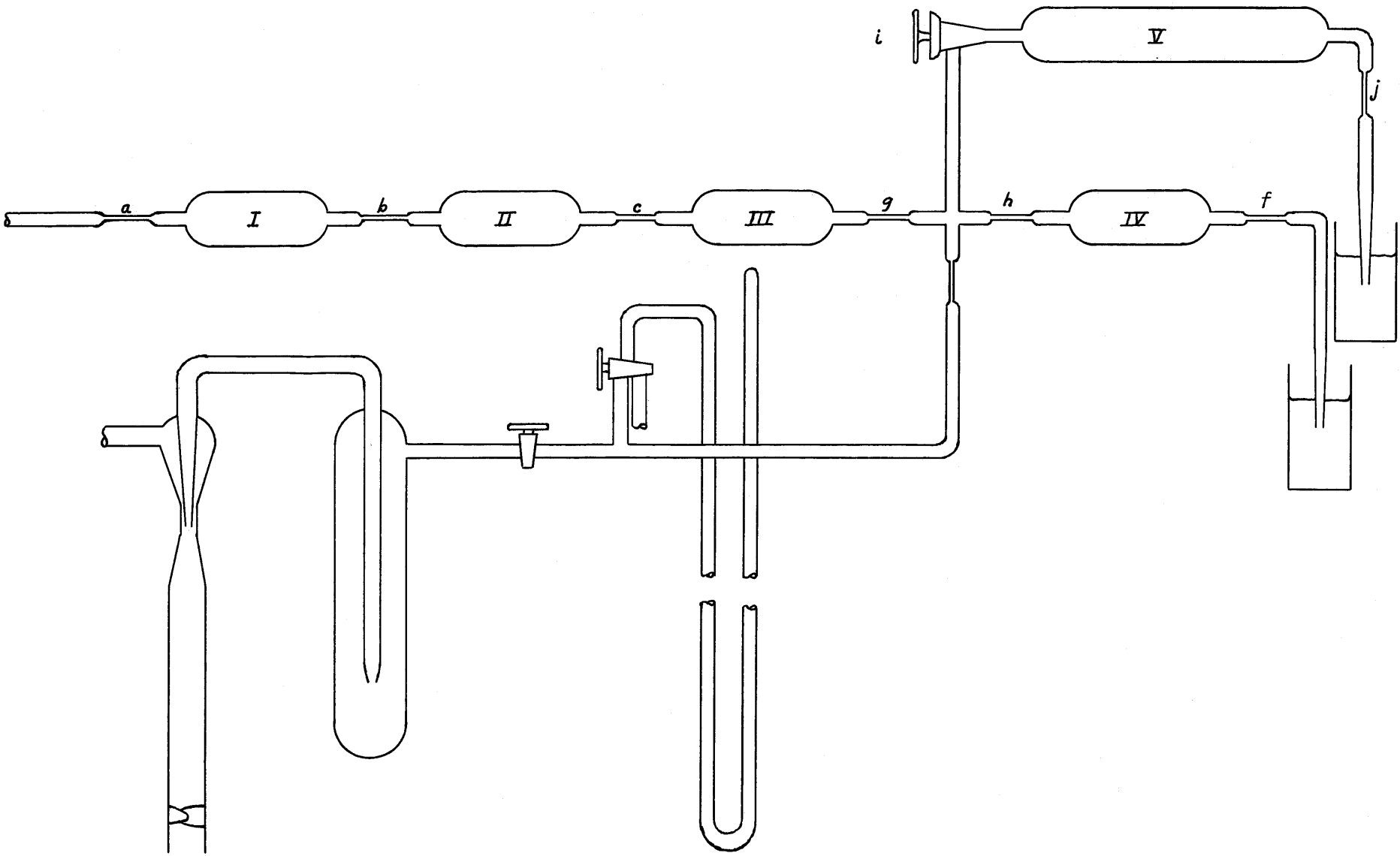

Figure 7.

The results of these experiments are collected in the following table.

Table IV

Source of oxygen	Reaction time (min.)	Initial conc. Bulb I (mole/cc.)	$k_2 \times 10^{-2}$ (cc/mol.sec.) original gas	$k_2 \times 10^{-2}$ (cc/mol.sec.) oxygen added	Total pressure (room temperature) I + II	III + IV
Linde tank	37	1.27×10^{-6}	4.05	4.45	296	499
Electrolytic	45	1.29×10^{-6}	2.22	1.74	289	523
Electrolytic	45	1.19×10^{-6}	2.59	2.06	289	524

The table shows in the first experiment within the limits of error no effect of added oxygen, or perhaps a slight acceleration. It must be mentioned, however, that two counteracting effects of the added oxygen will later prove to be the probable description of this result.

On the other hand the runs with electrolytic caustic oxygen evidence a definite retarding effect, although not that called for by the hypothetical mechanism involving the inverse first power of the oxygen. In these cases also, however, two partly counteracting effects due to the added oxygen undoubtedly were present.

While the errors in this experimental method are sufficiently large to seriously limit the quantitative value of the results, these determinations do nevertheless roughly agree with the four experiments made by Chapman and Jones[6]. But the three experiments given above indicate the importance of some other effect than that due to the oxygen alone. It is believed that this will lead to a reconciliation of the results of the important experiments of the earlier investigators with those to be described later in this thesis, as well as with the results of other investigators as described under Part I.

Further Experiments on the Effect of Total Pressure

In the first six experiments on the influence of the total pressure the pressure was in all cases reduced by withdrawing from Bulbs III and IV a portion of the ozone. The experiment described here was performed as the inverse of this: that is, the pressure in Bulbs III and IV was increased over that in Bulbs I and II by forcing in ozone.

Procedure

The method was identical with that used in the experiments on the addition of oxygen, except that Bulb V in this case contained ozone and this was forced into Bulbs III and IV. Thus the only difference was that the ozonizer was running during the filling of Bulb V.

Result

The result can best be expressed as another row of the Table on page 49.

Table V
Linde tank oxygen

Reaction time (min.)	Initial conc. Bulb I (mols/cc.)	$k_2 \times 10^{-2}$ (cc/mol.sec.) p_1	p_2	$\frac{k_2 p_1}{k_2 p_2}$ p_1	p_2	p_2/p_1	$\frac{k_2 p_2 \times p_2}{k_2 p_1 \times p_1}$
31	0.71×10^{-6}	5.03	3.14	1.60	250	475	1.90	1.19

Considering the errors inherent in the method, the results of this experiment are in good agreement with the six others performed on the effect of total pressure.

Furthermore the numerical value of these rates corrected to one atmosphere pressure at 100° agree well with those found in the preceding experiments. Their average here is 2.29×10^2 cc/mol. sec.

Another experiment was carried out in much the same way as the preceding one; but the attempt was here made to determine the effect of first decomposing part of the ozone in Bulb V before adding it to Bulbs III and IV.

Procedure

Bulb V was encased in a steam bath, and after the same procedure as in the last experiment up to the complete filling of the system (except that the capillary at j was not sealed), and the sealing of the capillaries at a and f, the steam bath around Bulb V was heated to 100°. After allowing the increase in volume at constant pressure to occur through the outlet of Bulb V, the capillary at j was sealed, and Bulb V held at 100° for approximately half an hour. It was then cooled by passing air through the steam jacket. The pressure in the four bulbs was reduced to 181 mm., and after sealing the capillary between Bulbs II and III, the partially decomposed ozone was allowed to enter Bulbs III and IV from V, until pressure equilibrium was reached. From this point the procedure was as described before.

Result

The result can best be expressed as still another row of the Table on page 49.

Table VI
Linde tank oxygen

Reaction time (min.)	Initial conc. (Bulb I (mols/cc.)	$k_2 \times 10^{-2}$ (cc/mol. sec.) p_1	p_2	$\frac{k_2 p_1}{k_2 p_2}$	p_1	p_2	p_2/p_1	$\frac{k_2 p_2 \times p_2}{k_2 p_1 \times p_1}$
30.5	0.70×10^{-6}	4.48	4.40	1.02	181	383	2.12	2.08

The values can not be interpreted from the present point of view regarding the decomposition. The preceding experiment (Table V), using the same kind of oxygen, had given the total pressure effect satisfactorily by the same procedure.

That the failure to observe such in this case was the result of positive catalyst getting into the ozone of Bulb V in some unknown way is supported by the following facts. The initial concentration of the ozone in Bulb V is known from the analysis of Bulb I, and the difference in pressure and temperature. This was approximately 2.33×10^{-6} mol/cc. Now in the half-hour decomposition interval this would normally decompose by an amount something less than half its original value. From a comparison of the analysis of Bulb IV and Bulb I and their corresponding pressures, the concentration of the ozone after decomposition in Bulb V can be calculated. This proves to be 0.65×10^{-6} mols/cc. Calculating the specific second-order rate for this decomposition in Bulb V at 100° and atmospheric pressure, one finds the value 5.44×10^{2} cc/mol.sec. This is approximately four times as fast as the decomposition in Bulbs I and II, which was 1.35×10^{2} cc/mol sec. when corrected to atmospheric pressure.

These calculations demonstrate the presence of a positive catalyst in the ozone in Bulb V and hence account for the failure of the rate in Bulbs IV and III to be retarded by the injected gas mixture.

Experiments on the Order of the Decomposition

With the experimental arrangement used in the preceding experiments it was also possible to make observations upon the order of the decomposition. Although not so well adapted to this as the method described in Part II of this thesis, and, in fact, possessing certain particular difficulties, it was nevertheless felt worth while to make such measurements using this different method. These experiments are described below.

Procedure

In the first four experiments the same apparatus was used as in the first two experiments on the effect of total pressure. All four bulbs were filled to the same pressure with ozone. Keeping Bulb I immersed in tap water as a control, Bulbs II, III, and IV were immersed in boiling water, each for a different time interval, and after being removed from the 100° bath, they were chilled in tap water. The contents of all four were analyzed as described in the preceding experiments. With Bulb I, therefore, each of the other three gave an initial and final concentration value over a particular time interval, and permitted thus the calculation of three values of the specific rate.

Results

The results of these four experiments are given in the following table.

Table VII

Reaction time (min.)	C x 10^7 (mols/cc.)	k_2 x 10^{-2} (cc/mol.sec.)	k_1 x 10 $sec.^{-1}$
	Experiment I. Pressure = 49 cm. at 100°		
0	13.48	-	-
15	9.83	3.43	2.31
30	6.83	4.02	2.26
45	4.48	5.52	2.45
	Experiment II. Pressure = 52 cm. at 100°.		
0	14.38	-	-
10	9.26	6.36	4.38
25	8.81	2.92	1.96
60	5.32	3.28	1.66
	Experiment III. Pressure = 70 cm. at 100°.		
0	14.05	-	-
15	10.10	3.07	2.19
40	6.78	3.18	1.82
105	3.44	3.48	1.33
	Experiment IV. Pressure = 73 cm. at 100°.		
0	12.34	-	-
14.5	5.67	10.97	5.37
39.5	5.86	3.80	1.89
83.5	3.25	4.53	1.60

The results do not, indeed, show any better agreement with the second order than with the first. However, the average value of the constant*, when the separate values are corrected to atmospheric pressure, although high gives a value which is in the range of values found in the work of Part II by the static method. It is somewhat higher than the majority of the values found in the preceding experiments, in which this method was used.

It was obvious that difficulties in the method prohibited its use in this form as a method of determining the order. The variations in these experiments, however, were not very surprising. Several errors enter into the procedure, perhaps the most important of which are: the error in the time, particularly for the shortest interval, i.e. Bulb II; and the errors introduced during the sealing of the capillaries before the flame. Serious trouble would occur if the system on each side of a capillary were not at the same temperature throughout the operation. Therefore it was necessary to be careful in the use of the flame while sealing the capillaries. A small pointed flame was used. Also there was the possibility of introducing decomposition products of the hot glass into the reaction space. While trouble from the sealing might be common to all the experiments using the four reaction bulbs in this way, it would be made most apparent in the calculations of the order.

In spite of these serious possibilities, it was felt that the particular variations indicated a still more fundamental difficulty; namely, a series of rapid variations in the character of the ozone. That is, it appeared as if the ozone entering the bulbs changed erratically and within wide limits many times perhaps during the time required for the filling of a single bulb; thus resulting in an unequal distribution of kind throughout the bulbs.

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*An unknown source of error entered in the second value of Run IV, and this value was accordingly omitted in computing the average.

To test this hypothesis a method was devised to eliminate such unequal distribution of the gas. The four bulbs were set up in parallel using at both ends glass manifolds, each possessing one inlet and four outlets. The four outlets were sealed to the ends of the four bulbs by means of equal lengths of capillary tubing all of the same bore. This tubing was thin wall and all eight pieces could be taken from the same piece of original tubing of about one foot in length. The joints were carefully made to avoid any contrictions, the capillary tubes flaring immediately to a much larger bore as soon as the constant bore portion met the joint.

As a second precaution a bulb of one liter capacity was introduced in the ozone supply line, as a volume in which rapid variations would be erased by mixing and a fairly representative mixture be delivered from this to the reaction bulbs.

The use of the bulbs in parallel represented the expenditure of considerable effort in view of the fact that the manifold and four bulbs had to be sealed together in a single and rather fragile unit before being sealed into the ozone train. The unit was mounted in a vertical position. The apparatus of course had to be cut in pieces again during a run. Two runs were made with this apparatus.

The procedure of filling the bulbs to the required pressure with the ozone mixture was carried out in about the same way as with the bulbs in series. After the system was swept clear and filled with ozone and the exit capillary sealed, the four upper capillaries were sealed and the pressure reduction made. Then the four lower capillaries were sealed, isolating each bulb. Especial care was taken in sealing the capillaries as a result of a growing appreciation of its importance. The remainder of the procedure was the same in detail as that used in the earlier experiments.

The results of these two experiments are given in Table VIII.

Table VIII.

Reaction time (min.)	C x 10^7 (mols/cc.)	k_2 x 10^{-2} (cc/mol. sec.)	k_1 x 10 sec^{-1}
	Experiment I. Pressure = 70 cm. at 100°		
0	10.52	-	-
15	9.08	1.69	0.099
40	7.38	1.70	0.089
100	5.07	1.70	0.073
	Experiment II. Pressure = 70 cm. at 100°.		
0	15.15	-	-
15	12.36	1.65	0.135
40	10.06	1.39	0.102
100	6.60	1.43	0.083

The improvement in technique is evident in the results. It will be noted that the initial concentration in the two runs is different, and that the test of the order thereby afforded shows the order to be the second. Thus both the constancy of the specific rate in the runs and the agreement between the runs contrasts with the marked trend of the calculated first-order coefficient in each run and the lack of agreement between the runs. The average value of the second order specific rate corrected to one atmosphere pressure is 1.59 x 10^2 cc/mol.sec.-in good agreement with the lowest rates found heretofore.

These experiments demonstrated the practicability of proving the second-order character of the reaction, if the large errors inherent in the method were minimized as far as possible.

It was felt that besides the general improvement in technique, the interposition of the mixing bulb had largely accounted for the improvement, and that the difficult parallel arrangement of the bulbs was not so essential. To test this, an experiment was performed using the mixing bulb, but with the four reaction bulbs in series. The procedure was the same as in the earlier runs with the bulbs in series. Unfortunately during the immersion in the boiling water a large crack developed in Bulb II and some water entered. Bulbs III and IV, however, afforded two determinations.

The results are given in the following table.

Table IX

Reaction time (min.)	C x 10^7 (mols/cc)	k_2 x 10^7 (cc/mol.sec.)	k_1 x 10 $sec.^{-1}$
	Pressure = 70 cm. at 100°		
0	13.86	-	-
15	-	-	-
40	8.57	1.85	0.120
100	5.27	1.96	0.096

Thus the results strengthened the belief that with the mixing bulb the reaction bulbs in series gave satisfactory results. For here again, not only do the two values for the second-order rate agree with one another, while those for the first-order do not, but the former also agree with the six values of the second-order rate found in the preceding experiments using the bulbs in parallel.

The apparent dependence upon the initial concentration of ozone, indicated by the total pressure experiments, held sharply in mind the question as to whether this was due to the method of production of the ozone, and therefore to some unknown impurity in the ozone, or whether this dependence were actually and solely on the initial concentration of the gas. The latter seemed improbable from almost any point of view, and yet it certainly required testing. An experiment was devised to give an answer to this question. At the same time it yielded further evidence as to the concordancy of results and the agreement of the rates with the earlier values.

The procedure was that of the regular series arrangement. Four new bulbs replaced the old ones, whose ends had become badly crystallized or burnt from repeated working in the flame. After the bulbs were filled and separated, Bulb I was kept as the control. Bulbs II, III, and IV were immersed in boiling water for lengths of time totalling 100 minutes in each case, but Bulb II was withdrawn twice and immersed for 10 minutes each time in tap water before replacing in the boiling water, the ozone in it being thus decomposed in three separate stages of 25, 25, and 50 minutes respectively. Bulb III was treated in a similar manner: it was withdrawn only once, the ozone in it being decomposed in two separate stages of 40 and 60 minutes. Bulb IV remained in the 100° bath for 100 minutes continuously.

If the decomposition depended upon the character of the initial ozone, then in all three bulbs the decomposition should have proceeded the same amount, that is, with the same specific rate over each of the six separate decomposition stages represented. But if on the contrary the specific rate really depended

on the initial ozone concentration, then all three stages in Bulb II would proceed at different specific rates, as would also the two stages in Bulb III, with the result that Bulbs II, III, and IV should show different amounts of decomposition over the 100 minutes common reaction time.

The results of the experiment are given in the following table.

Table X

Reaction time (min.)	$C_o \times 10^7$	$k_2 \times 10^{-2}$
	Pressure = 70 cm.	
0	12.74	-
25+25+50 = 100	5.78	1.58
40+60 = 100	5.68	1.62
100	5.75	1.59

Clearly the cooling the reheating did not influence the specific rate, and thus it was not dependent on the initial ozone concentration. For by cutting down the initial concentration by three subsequent decompositions, the reaction proceeded at the same rate as three in which the initial concentrations were the same.

These experiments yielded the same numerical value for the specific rate as the preceding ones, a value which is closely that of the lowest that has been observed.

Summary of Part III

A method has been described by which the decomposition of ozone at two different total pressures may be compared for the same sample of ozone. By the same method the effect of added oxygen may be studied.

Using this method the inverse proportionality of the second-order rate with the total pressure, found by Jahn[3], has been again observed in a series of seven measurements.

The effect of added oxygen has also been studied and the results, while qualitatively in agreement with the observations of Chapman and Jones[5] that oxygen exercises only little retarding effect, indicate that the conclusion drawn by Chapman and Jones that oxygen exercises no retarding effect on the decomposition is unjustified; and that there probably are important impurities in most oxygen. That pure oxygen accelerates the reaction inversely as its partial pressure as concluded by Jahn still remains a possibility. For the answer to this question some other method would be more suitable.

The specific second-order rate depends on the initial pressure of the oxygen-ozone mixture and not on the initial concentration of the ozone. Thus, after decomposing a fraction of a certain quantity of ozone, and after cooling to room temperature, the gas so obtained showed in a subsequent decomposition the same specific second-order rate as was observed during the decomposition of the first fraction.

The best values of the specific second-order rate obtained while using this method to study the problems discussed above agree, when corrected to atmospheric pressure, with the best values obtained in the research of Part II - a specific rate of approximately 200 cc/mol.sec.

PART IV

Experiments Using the Dynamic Method

Introduction

The static method of studying the rate of change of concentration in chemical kinetics has been widely used, while the dynamic method has been only rarely applied. There are advantages and difficulties in the use of each, but there are conditions under which one is more satisfactory than the other. The difficulties in the latter are for the most part practical ones, and the method, where it can be successfully applied, would generally be useful. It is, however, hardly applicable to any except gas reactions.

The dynamic method is briefly described by the following. The reactants are led at a known rate through the reaction chamber held at the desired temperature. A steady state is thus set up, and concentration measurements, one before entering and one after leaving the reaction chamber, give the concentration decrease in a known time interval. By changing the rate of flow a similar set of data may be obtained for another time interval, and so on, thus finally obtaining all the data that the static method generally yields. However, one important difference is the steady-state condition, set up for a measurement. Divergences from constant composition and character of the reactants in this method become immediately apparent, while many static experiments may be necessary to disclose them. Further, small deviations are smoothed out in the average which the dynamic method really gives. Changing conditions of the walls of the reaction chamber, and in fact any changes appreciably affecting the rate of the reaction become apparent by their alteration of the steady-state condition. The circumstances under which the method may be applied are such as to permit a much more rapid accumulation of data than is generally possible with the static method.

With these remarks its particular advantages in this research become apparent, and the difficulties encountered in applying it should now be discussed. As remarked heretofore, however, these difficulties are chiefly of a practical nature. They will be discussed under the description of apparatus, where they naturally arise.

Apparatus

The reaction chamber was made of a tube of pyrex glass, and is shown at A in Figure 8. It was approximately 1.5 cm. in diameter and 26 cm. long over the constant bore portion, being 34 cm. from d to e. The connecting tubing was 0.3 cm. bore. The volume of the reaction vessel and 43 cm. of connecting tubing was found to be 46.0 cc. $\pm$ 0.2 cc.

The reaction chamber was contained in a larger pyrex tube B of 3.4 cm. inside diameter and 54 cm. long, near the lower end of which was wound a nichrome heating coil E over a single layer of asbestos paper and covered with heavy asbestos insulation. The tube B was nearly filled with paraffin.

C was a mercury regulator of small bore pyrex tubing with the familiar fine thread screw adjustment contained in a brass cap of the head. This regulator controlled the heating current in the coil E in the following way. The main current, sufficient to hold the bath nearly to the desired temperature, passed through a small exterior resistance, and the relay served to make or break a shunt across this resistance. A thermometer D registered the temperature of the bath.

It is clear from the figure that strong convection currents were continually present in the paraffin, and hence there resulted some un-uniformity of temperature. These conditions were, however, practically constant. The thermal regulator held the thermometer within $\pm$ 0.4°, and as will be seen, these conditions sufficed entirely for the purpose of the experiments.

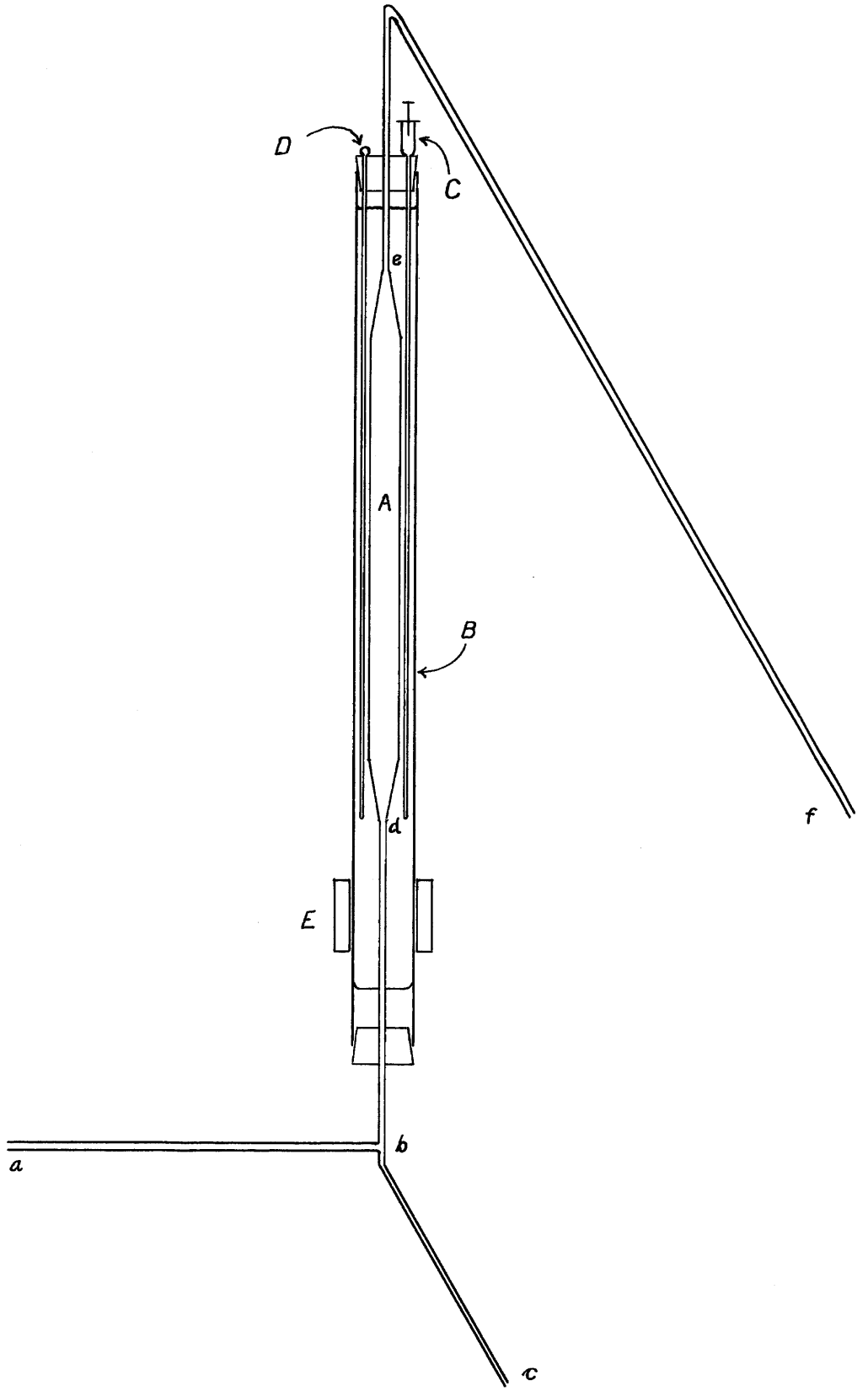

Figure 8.

Coming now to the main difficulty in the dynamic method, the conditions of flow in the reaction chamber can not indeed be determined in a moment. The assumption made, however, is that the time of passage of any one molecule through the reaction chamber is given by the quotient of the volume of the chamber by the rate of gas flow, and this is the assumption made also in the previous researches that have used this method. It should be especially noted that this can not be an average time but an actual time for each molecule. That this assmption will depend on the shape of the vessel and on the rate of flow is immediately evident, but to show that there are conditions under which it is valid is much more difficult. The justification for the assumption in this work is given in the following paragraphs.

The walls of the reaction tube were made of a shape approximately that of stream lines to avoid turbulence and stagnant spaces. The rate of flow was, moreover, always low, being in all cases less than twice the volume of the tube per minute. Still a further consideration showed that even without turbulence our conditions would hardly be realized unless some effect overweighed the variation of velocity with the distance out from the center. For lamina flow of a continuous fluid in a tube the variation of velocity from the axis outward is a parabolic function of the distance, the velocity decreasing to zero, of course, immediately at the walls. Under this distribution of velocities, molecules at different distances from the center would occupy different times in passing through the tube.

It was felt, however, that the assumption was valid. Clement[2] had indeed made an assumption under conditions where it could hardly hold, and as mentioned in Part I, divergences of his observations from those of other investigators are probably due in a large measure to this. Jahn[3] made the assumption under different conditions where it would surely be expected to hold, and with successful results.

The effect that overweighs the difference in velocity of the various cylindrical layers as one goes outward from the axis is found in the diffusion of the molecules. Thus, under the present conditions an oxygen molecule on the average moves from the axis to the wall many times during its transit. Einstein[9] has given a derivation for the relation between the average displacement $\overline{\Delta x}$ for a molecule and the time. Thus

$$\overline{\Delta x} = \sqrt{\frac{4D}{\pi}}\, t$$

where D is the coefficient of diffusion defined by the equation

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

C designates concentration. The self diffusion coefficient for oxygen at ordinary temperatures is 0.2 sq. cm./sec. Solving for t for a distance of one centimeter, which is somewhat greater than the radius of the tube, we find the time required to move on the average a distance of one centimeter is two seconds, which is small compared with the 50.5 seconds required for a molecule to pass through the reaction tube on the basis of the assumption and for the fastest rate of flow commonly used in these experiments.

A further difficulty, however, arises from this diffusion effect occurring in and opposite to the direction of motion. This causes some of the molecules to pass through the bulb in a shorter time than the average, while others take a longer time. These two effects tend to counteract one another. That they do not completely do so is because the decrease in concentration with the time is not linear. The error introduced by the failure to compensate is neglected in this work.

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[9] Einstein, Ann. d. Physik, 17, 558 (1905).

Summarizing briefly, the apparatus illustrated in the figure, used with the rates of gas flow employed in these experiments, approximated the conditions of uniform cloud bank flow of the ozone within a space enclosed by walls of constant temperature. That these conditions were not rigorously attained did not prohibit the employment of the apparatus in answering the particular questions of interest.

Sources of Oxygen and Ozone

The experimental work using the dynamic method was carried out with two different sources of oxygen and ozone. In the development of each two new pieces of apparatus were devised.

The first was an oxygen generator in which the electrolyte was a 12% pure sodium hydroxide solution. This, with the drying train and silent discharge ozonizer connected with it, served also as a source of ozone in the work of Part III, as has been mentioned before. The new features of this electrolytic generator lay in the stirring of the electrolyte, which was accomplished without outside mechanical stirring and without any admixing of the gases. This permitted using high currents, yet avoiding the natural tendency of such cells to polarize as a result of the concentrating of the sodium hydroxide about the cathode and pure water about the anode. The present cell may be run continuously at 12.5 amperes without any change in resistance except a slight initial effect as the bath warms, and without any serious heating. Prolonged tests have not been made with higher currents; so the limit may be considerably higher. This generator served as the source of oxygen for one of the kinds of ozone, the oxygen being dried over concentrated sulfuric acid and ozonized by the silent discharge. The apparatus is illustrated in Figure 9. In speaking of this ozone hereafter it will be referred to as "caustic ozone", and the oxygen from which it is prepared, as "caustic oxygen".

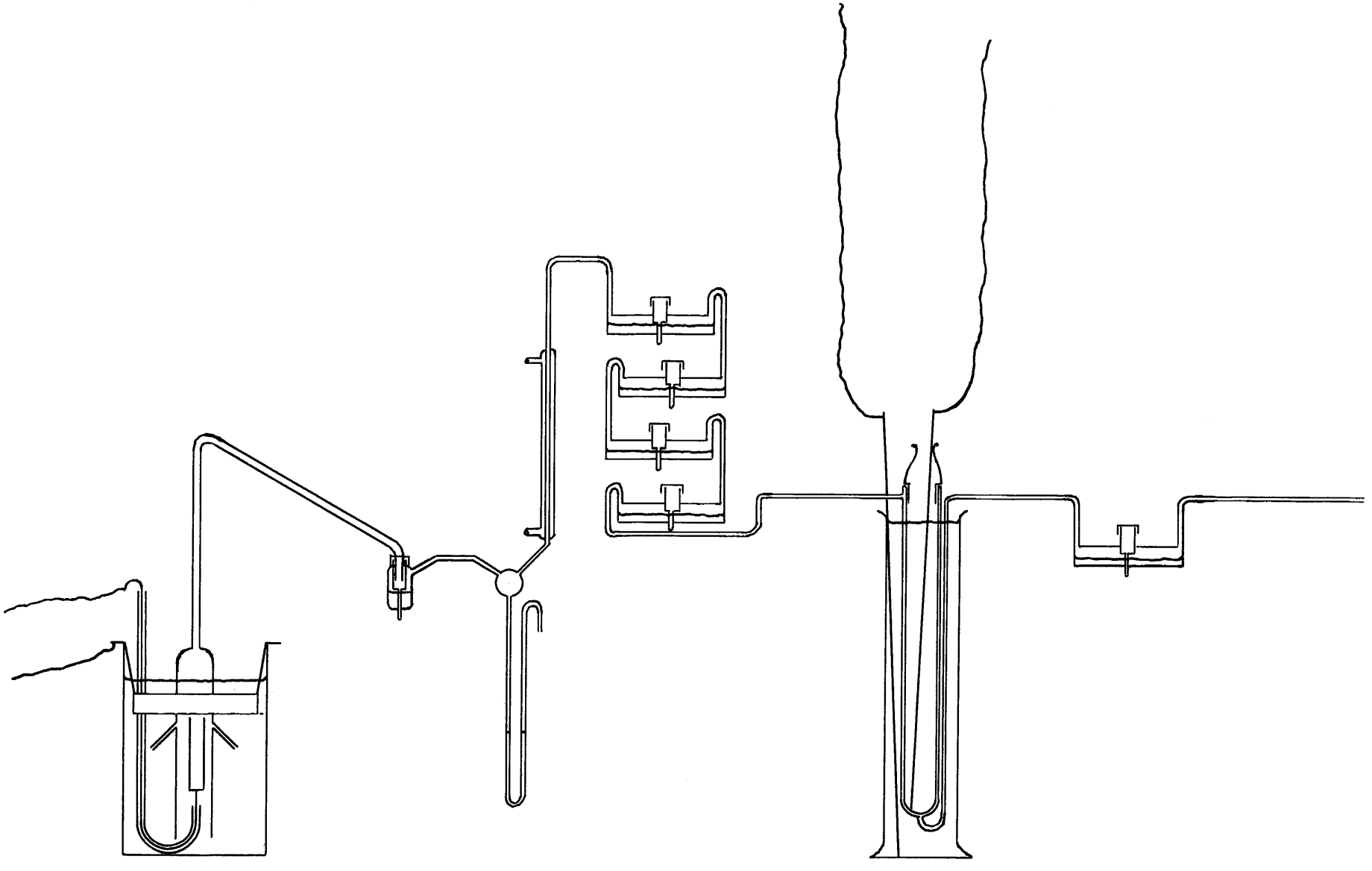

Figure 9.

The other source of ozone was an electrolytic ozone generator using a dilute sulfuric acid solution, with lead electrodes. The development of an inexpensive water-cooled lead anode of small surface constituted a chief advance in this piece of apparatus. The cathode being a lead collar of large surface, no difficulties from concentration polarization were encountered; and the generator worked steadily without any change of resistance or serious heating at a current of 10 amperes. Greater currents could undoubtedly be employed. This ozone was dried over concentrated sulfuric acid. Figure 10 illustrates the apparatus. In speaking of this ozone hereafter it will be referred to as "acid ozone".

Experimental Method

In carrying out the measurements on the fraction decomposed in passing through the decomposition chamber, when using the "caustic" oxygen, the oxygen was first started through the apparatus to clear it of any air that might have diffused back through the line. After this had been accomplished the discharge was started in the ozonizer, and the drying bulb and reaction chamber swept out with ozone.

With the "acid" ozone the entire system was simply swept out with the ozone until clear.

With the paraffin bath at constant temperature and the rate of gas flow constant, if the concentration of the ozone entering the chamber is constant, a steady state obtains in a few minutes at the rates actually employed. A set of data may then be obtained immediately by determining the concentration of the ozone entering and leaving the reaction chamber. This set may be checked by taking a similar set a few minutes later when the steady state has again been reached. To obtain a second determination either the initial concentration may be changed or the rate of flow.

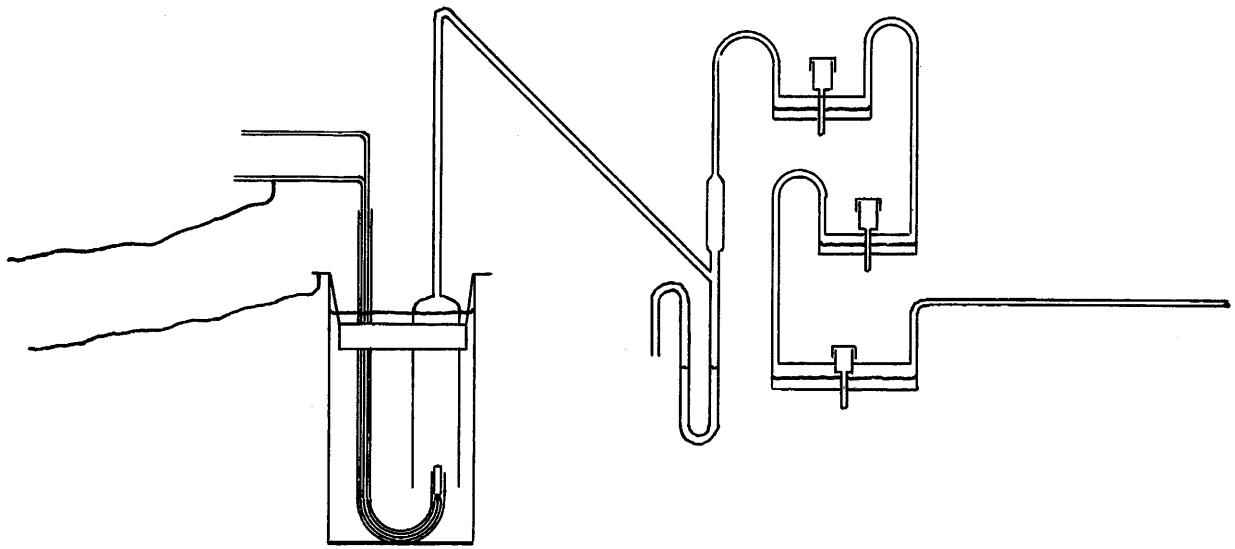

Figure 10.

Analytical Procedure

Analyses were made in an unusual way which requires justification. From the figures it is clear that the pressure in the apparatus was never much over one atmosphere, for at several points the system is sealed only by a small trap of concentrated sulfuric acid, as in the drying tubes, or of water at other points. There being no marked constrictions in the line, the resistance offered to the gas flow was very small. The control of the flow of gas either out at c or at f was had by simply stopping the other exit with a bit of distilled water. This held itself in place at the respective orifice by capillarity, and the gas flow took place entirely through the other.

The ozone was absorbed in the usual way in neutral potassium iodide solution, which after subsequent acidification was titrated against standard thiosulfate solution. But in taking the sample, the gas was allowed to flow quietly into a long test tube containing the potassium iodide solution, the orifice being approximately two centimeters above the surface. The remaining volume of the tube was considerably larger than the volume of the sample collected (known from the rate of flow and the time) and the sample was thus collected by the upward displacement of air. After this, the tube was covered, and absorption allowed to continue for some time (half an hour or greater). During the collection of the sample the surface of the solution was gently agitated by a small motion of the lower part of the tube.

A visual proof that the ozone was displacing the air upward and not itself escaping from the tube could be obtained from the movement of the cloud that forms over the potassium iodide solution characteristic of the absorption of ozone. It showed no marked turbulence in the tube. The gentle agitation of the solution was maintained during absorption to prevent the excessive concentration of

hydroxyl
/ion at the surface, for under conditions of strong alkalinity the number of oxygen atoms in the ozone molecule that are available for oxidation becomes greater than one.

To be certain, however, that this method was yielding results sufficiently accurate to be useful, a comparison of it against absorption by bubbling the gas through potassium iodide solution was made using a separate ozonizer connected with a tank of oxygen. The flow was made 40 cc./min. which is a little greater than the highest generally used in the experiments.

While no specially devised bubbling tube was used in the absorption by bubbling, thus rendering the results probably a little low for this method, the conditions sufficed for the test of interest; namely, that the new method was giving values comparable with the correct ones. The results showed this, and in fact gave slightly higher values for the new method, probably for the above reason. In each comparison a sample was first taken by bubbling, then one by the new method, and again one by bubbling. The middle value was then compared with the mean of the other two. The error in the time over which the sample was taken was appreciable, amounting possibly to $\pm$ 2%. The following table gives the results of these comparison analyses.

Table XI

Analyses of Samples

Cc. thiosulfate Without bubbling	Mean of two with bubbling	Difference	Percent deviation
18.68	18.59	+0.09	+0.5
15.36	15.13	+0.23	+1.5
16.72	16.08	+0.64	+4.0
19.11	18.62	+0.49	+2.6
17.87	17.92	-0.05	-0.3
16.37	16.24	+0.13	+0.8
17.34	16.99	+0.35	+2.1

This data sufficed to show that the new method gave results sufficiently close for rough quantitative answers which were all that were desired. This data was taken at the start of the work. With experience the technique has been bettered uhtil it seems probable that the method is satisfactory for the quantitative determination of ozone.

Preliminary Results

The character of the decomposition of ozone obtained by the silent discharge ozonization of oxygen from caustic solution was first investigated. As the work progressed, it became clear that with apparently identical conditions of gas flow and of potential on the ozonizer, the ozonizability of the oxygen was varying in a remarkable way. Thus in one experiment, when the concentration was measured at frequent intervals after starting the generator and ozonizer, a three-fold decrease was observed, which reached an almost constant value in about two and one half hours. One of the many conditions which change during

such a time is the temperature of the ozonizer baths. Measurements of the concentration similar to those just described, but with the large outer bath heated before starting to a temperature somewhat higher than that which it had reached at the conclusion of the last mentioned measurement, showed that, although the initial concentration in this experiment was much lower, the steep decrease with time was by no means erased. And the lower initial concentration may have been entirely due to the normal decrease with the use of the electrolyte that is described below. The final value approached in each case was approximately the same. In the first experiment cooling the outer bath of the ozonizer by means of ice to practically its initial temperature again, caused only a very slight increase in the concentration.

These results are described here because of the close connection they undoubtedly have with the processes occurring during ozonization, and with the variation of the rate of decomposition with initial concentration of the ozone discovered in this research.

The effect of the changing concentration of the ozone delivered by the ozonizer upon the rate of decomposition as measured in the reaction apparatus, was observed at the beginning of these experiments. In a series of five runs, which must now be regarded as preliminary, the marked increase in the calculated second-order rate with decreasing concentration was confirmed, as well as its considerable independence of the voltage at which the ozonizer was operated.

There was discovered one factor which exercised a large effect on the ozonizability of the oxygen and the corresponding rate of decomposition of the ozone. As the electrolyte in the generator was depleted of water, the ozonizability of the oxygen decreased and the second-order rate of decomposition of the resulting ozone increased correspondingly. By replenishing the

electrolyte with distilled water at a later date (actually a small addition of about 5% of the total water in the electrolyte), the ozonizability of the oxygen underwent a marked increase, of the order of 200-300%. At the same time the second-order rate underwent a decrease.

It seems unnecessary to tabulate here the data accumulated in the preliminary experiments, which served only as guides to the further work.

But it was clear that the "caustic" oxygen generator was delivering oxygen whose ozonizability was variable, and that the resulting ozone possessed a correspondingly variable degree of stability. This remarkable relation between the ozonizability of the oxygen and the stability of the resulting ozone was evidently connected fundamentally with the process of the formation of the ozone. For with the same ozonizer potential and the same gas flow, when the character of the gas was such that a large fraction could be converted into ozone, the resulting ozone was very stable. It seems certain, therefore, that an understanding of the mechanism of the decomposition will bring with it an understanding of the formation processes. It will be remembered from the work of Part II, and it will also be shown to have been again observed in this present work, that the property possessed by low concentration ozone of being singularly unstable is characteristic of electrolytic ozone as well as of that made in the silent discharge.

Results

Finally, using the reaction apparatus illustrated in Figure 8, the character of the ozone obtained by the action of the silent discharge on the "caustic" oxygen was studied in a series of experiments at a temperature of approximately 140°. Nine series comprising a total of forty-five determinations of the drop in concentration in the reaction chamber over known time intervals were made, exclusive of some at concentrations too low to be satisfactorily analyzed.

The following table summarized the results. C_0 represents in each case the concentration entering the reaction chamber, and was taken directly after C, which represents the concentration leaving the chamber. Over this interval of two to four minutes the concentration of the generated ozone does not change appreciably except under the unusual conditions occurring directly after starting the apparatus that have been mentioned. By k_2 is designated the calculated specific rate, on the assumption that the decomposition had proceeded over the time interval according to the second-order. For the purpose of studying the large effects that were of particular interest the conditions of gas flow were assumed to be strictly those of uniform cloud bank motion and the change in volume on decomposition was neglected. Clearly the pressure under which the reaction took place was always that of the atmosphere. The magnitude of the variations being studied did not justify making barometric correction.

Table XII

Date	Reaction time (sec.)	$C_o \times 10^7$ (mol/cc.)	$C \times 10^7$ (mol/cc.)	$k_2 \times 10^{-4}$ (cc/mol sec.)
1925				
Dec. 31	101.0	12.04	3.76	1.81
	"	10.90	3.45	1.96
	"	9.23	3.14	2.09
1926				
Jan. 1	40.4	10.50	5.45	2.18
	"	9.61	5.11	2.27
	50.5	8.50	4.01	2.61
	"	8.10	3.97	2.55
	67.3	7.59	3.05	2.92
	"	7.36	3.05	2.85
	101.0	7.27	2.38	2.80
	"	7.30	2.49	2.62
Jan. 4	101.0	14.81	4.48	1.54
	"	13.46	4.02	1.73
	"	11.92	3.80	1.78
	"	10.87	3.58	1.87
	"	9.55	3.24	2.02
	"	8.70	2.96	2.22
Jan. 5	101.0	12.45	3.80	1.78
	"	12.59	3.85	1.79
	"	11.00	3.58	1.87
	"	9.95	3.40	1.92
	"	9.12	3.05	2.16
	"	8.56	2.98	2.17

Table XII (Cont.)

Date	Reaction time (sec.)	$C_o \times 10^7$ (mol/cc.)	$C \times 10^7$ (mol/cc.)	$k_2 \times 10^{-4}$ (cc/mol sec.)
Jan. 8	202.0	14.59	2.41	1.72
	"	13.00	2.43	1.66
Jan. 9	67.3	11.29	4.63	1.90
	"	10.03	4.29	1.98
	"	8.73	3.81	2.20
	"	8.58	3.50	2.52
	"	9.47	3.86	2.28
	"	9.69	3.75	2.43
	"	9.73	3.91	2.28
Jan. 14	50.5	11.48	5.50	1.87
	"	11.20	5.52	1.82
	"	3.81	2.40	3.06
	"	3.52	2.20	3.38
	"	7.62	3.71	2.74
Jan. 15	50.5	1.20	0.915	5.13
	"	1.20	0.915	5.13
	"	1.19	0.905	5.25
Jan. 17	50.5	10.29	5.37	1.72
	"	9.51	5.38	1.60
	"	8.95	5.12	1.66

The table is arranged chronologically. In spite of this, the marked variations with the concentration are readily apparent, the specific rate decreasing as the initial concentration increases. This then is a phenomena quite apart from the change in rate with the total pressure of the gas mixture studied in Part III. It is the effect, made perfectly clear now, which was indicated early in the work of Part II and which has undoubtedly been the chief cause of the variations in absolute rate found in the experiments of Part III.

The variations are, however, not yet entirely ordered, as is evident when the values of the rates found for the same initial concentration are compared. There is still a large variation in these. That the order during a particular run is not exactly the second seems probable on the basis of the explanation of the decomposition that will be given below, and may explain in part some of the variations in the rate for the same initial concentration over different time intervals. But still further, for the same initial concentration and the same time interval the values of the constant show rather marked variations.

At this point, therefore, it seems best to introduce the description of ozone decomposition, which it is now believed accounts satisfactorily for the multitude of observations that have been recorded on this interesting reaction.

The Reaction Mechanism

The decomposition is of the second-order and is described by the mechanism first given by Jahn:

$$O_3 \rightleftharpoons O_2 + O \text{ (fast; equilibrium far to left)}$$

$$O_3 + O \longrightarrow 2O_2 \text{ (measurably slow; to completion)}$$

It is a reaction very susceptible to catalytic influences, probably in a large measure through their effect upon the concentration of monatomic oxygen. Such influences while tending to change the order of the reaction, may nevertheless change the apparent rate two or three fold without greatly changing the order of the decomposition. The reason for this arbitrary statement is to be found partly in the mechanism of the dissipation of the heat of decomposition, which in this reaction is very large. Upon this also depends the explanation of the failure of the observed temperature coefficient to agree with that calculated from the increase in heat content during the first reaction given above, since now with the heat of dissociation of oxygen available (from the work of several investigators[10]), it is possible to calculate thermochemically this change in heat content. The temperature coefficient so found is approximately 3.4 fold for 10 degrees rise at 100°, while the observed value is 2.5 fold. The discussion of this subject can not be taken up here, however.

The variations in the results compiled in Table XII are therefore felt to be due to the presence of varying amounts of positive catalyst contained in the ozone and introduced originally in the process of the oxygen generation. In order then to inquire as to the best value of the uninfluenced second-order specific rate of ozone decomposition at this temperature, the values calculated for the highest initial concentrations should be considered. For the introduction

[10] Warburg, Z. Elektrochem., 26, 58 (1920);
Born and Gerlach, Z. f. Physik, 5, 440 (1921);
Wulf, Jour. Amer. Chem. Soc., 47, 1944 (1925);
Birge, Bull. Amer. Phys. Soc., Mar. 6, 1926, pg. 8.

of a first-order rate into one of the second-order produces an effect which grows relatively less as the concentration is increased, because the concentration enters in the second power in the second-order mechanism. Furthermore, high initial concentrations indicate, as described above, ozone more free from catalytic contaminations than ozone of low initial concentrations.

From this point of view the results may be compiled graphically in a helpful manner. It is of interest to know what specific second-order rate would be characteristic of ozone of indefinitely high concentration. In Figure 11 the data of the table has been plotted, placing the values of the second-order rate as ordinates against the reciprocal of the concentration as abscissae. Thus the intercept on the axis of ordinates of the best curve drawn through the data should indicate the value of the specific second-order rate at infinitely high concentration of ozone.

The extent of the variations of the rate for the same concentration is made evident in the graph. In the range of concentrations from 9-10 x 10^{2} mol/cc., for instance, (i.e. ordinates 0.1 and 0.111) where the variation is greatest, the rate varies almost two fold. It is, however, fair to say that the graph gives a definite indication of the value of the rate at infinite ozone concentration. The majority of the points lie in the concentration range of 7 - 14 x 10^{-2} mol/cc. The two points further to the right are in the vicinity of 3.6 x 10^{-2} mol/cc, while those to the extreme right are at 1.2 x 10^{-2} mol/cc. The accuracy of measurement at these concentrations is much less than at the higher ones. This was the chief reason for avoiding them in the measurements. They come in now, however, in an important

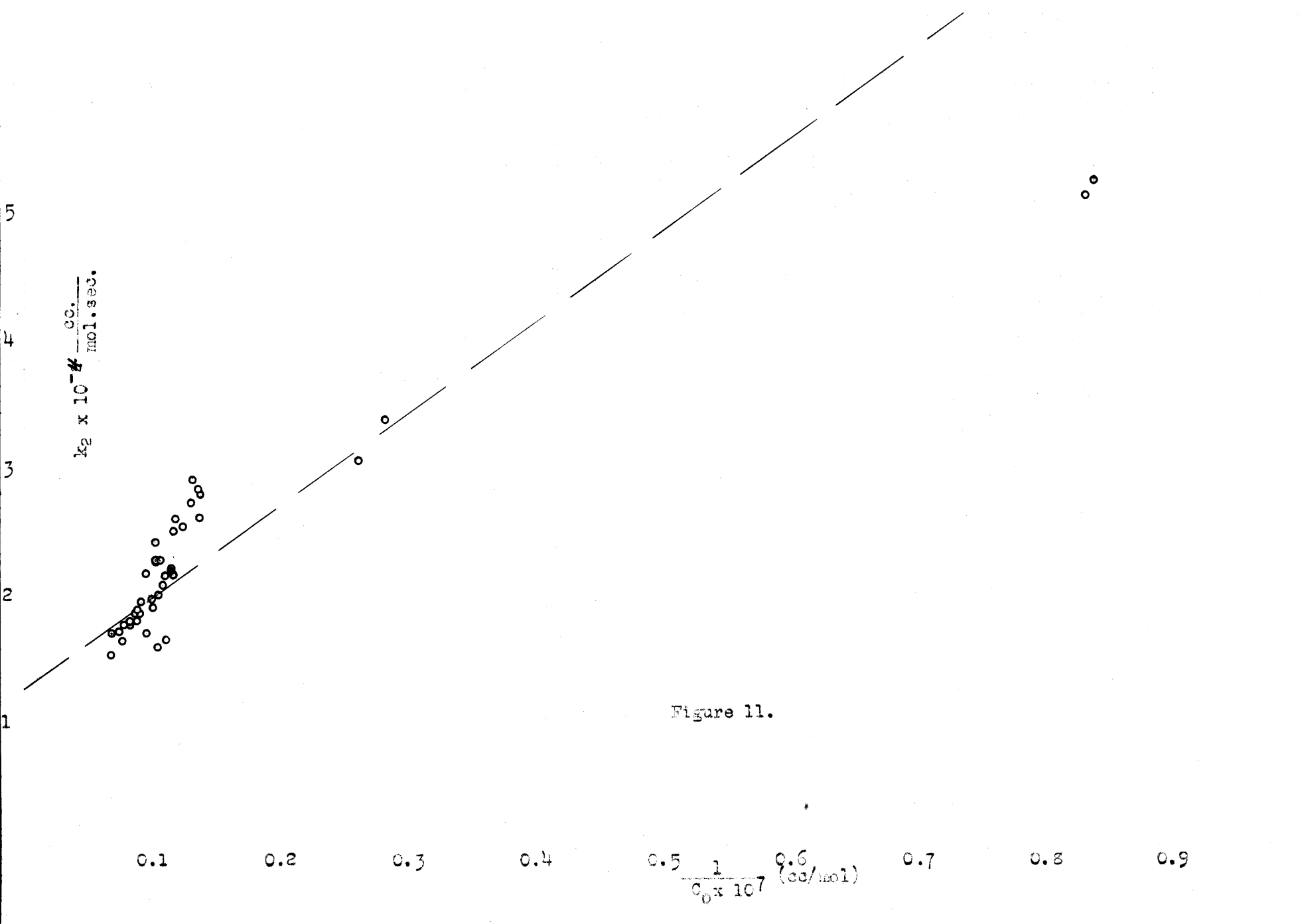
5
4
3
2
1
$k_2 \times 10^{-4}$ cc./mol.sec.
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
$\frac{1}{C_0 \times 10^7}$ (cc/mol)

Figure 11.

way, since they indicate at least the general direction of the curve. This is all that is required. The dotted curve is drawn in not as the correct one through these points, but to emphasize that with any reasonable weighting of the data the curve so drawn will indicate an intercept somewhere between 1.5×10^2 and 1.0×10^2 cc/mol. sec.

With this conclusion drawn from the experiments made with "caustic" ozone, we will pass to the experiments of a similar nature in which "acid"(electrolytic) ozone was used.

Seven series comprising a total of thirty five determinations of the drop in concentration over known time intervals were made at the same temperature and with the same apparatus as in the preceding measurements. It became at once apparent that the electrolytic ozone exhibited far less variation in character than that made by the silent discharge acting on the oxygen from the electrolysis of sodium hydroxide solution.

The results are summarized in Table XIII, the columns being designated in the same way as in Table XII. The great constancy of the rate in these experiments is immediately seen, as well as the lower average value of the constant. The concentration range due to the characteristics of the electrolytic ozonizer is moreover somewhat lower than in the preceding experiments, being approximately $3\text{-}9 \times 10^{-2}$ mol/cc.

Table XIII

Date	Reaction time (sec.)	$C_o \times 10^7$ (mol/cc.)	$C \times 10^7$ (mol/cc.)	$k_2 \times 10^{-4}$ (cc/mol sec.)
1926				
Feb. 27	50.5	5.52	3.64	1.85
	"	5.45	3.64	1.81
	67.3	5.27	3.19	1.84
	"	5.32	3.03	2.11
Mar. 1	50.5	7.06	4.69	1.42
	67.3	6.18	3.70	1.61
	"	6.14	3.80	1.49
	50.5	3.77	2.80	1.82
	"	3.55	2.59	2.07
	67.3	3.27	2.29	1.94
	"	3.10	2.23	1.87
Mar. 2	50.5	7.78	4.90	1.50
	"	7.34	4.76	1.46
	67.3	6.50	3.93	1.49
	"	6.32	3.85	1.51
	101.0	5.50	2.97	1.55
	"	5.58	2.97	1.57
Mar. 6	50.5	8.04	4.88	1.59
	"	7.65	4.88	1.47
	101.0	5.72	3.06	1.50
	"	5.60	3.13	1.39
	50.5	7.05	4.57	1.52
	50.5	6.92	4.57	1.47

Table XIII (Cont.)

Date	Reaction time (sec.)	$C_o \times 10^7$ (mol/cc.)	$C \times 10^7$ (mol/cc.)	$k_2 \times 10^{-4}$ (cc/mol sec.)
Mar. 10	50.5	3.96	2.95	1.71
	"	3.79	2.80	1.84
	"	3.25	2.47	1.92
	"	3.08	2.39	1.85
	101.0	2.79	1.81	1.92
	"	2.71	1.84	1.73
Mar. 11	50.5	8.82	5.32	1.48
	"	8.60	5.17	1.53
	101.0	6.45	3.23	1.53
	"	6.37	3.25	1.49
	50.5	4.38	3.27	1.53
	"	4.08	2.87	2.04

The graph of these results plotted on the same scale as the data of Table XII are given in Figure 12. While here, too, the variation in the constant for the same initial concentration is considerable, it is much less than in the former case. The dotted curve in Figure 12 is drawn in, therefore, with much more assurance. It intercepts the axis of ordinates close to a value of $k_2 = 1.15 \times 10^2$ cc/mol. sec. - a value in agreement with that obtained from the measurements on "caustic" ozone, within the limits of error in that extrapolation.

Furthermore, the second-order character of the decomposition is shown by the data of Table XIII. In particular the measurements of Maf. 2 are suitable for this comparison. Over three different time intervals, each with two determinations of the constant, the rate remains constant. This is to be found throughout the table with very few exceptions. From day to day, however, the rate shows small but definite variations.

On the contrary the higher values of the constant found in the measurements on the ozone made by the silent discharge show a tendency to increase with time, as evidenced by the measurements of Jan. 1.

These two series of measurements confirmed the earlier observations that the rate of decomposition could undergo a variation of an average value without greatly losing its second-order character. They gave a clear value for the specific second-order rate for the "acid" ozone at this temperature, and for the "caustic" ozone a value, which although less certain than that for the "acid" ozone, agreed with the latter within the limits of error of extrapolation.

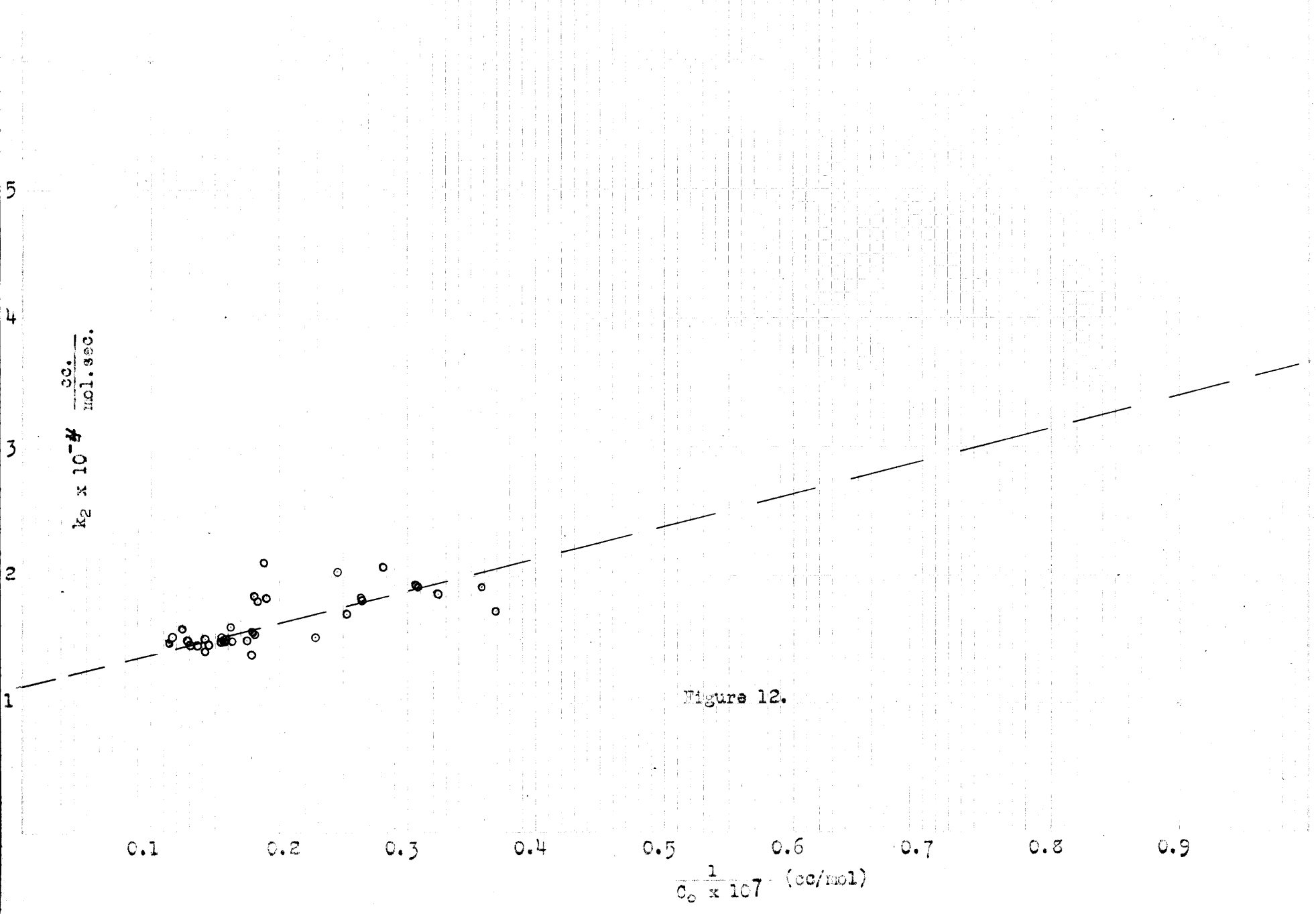
5
4
3
2
1
$k_2 \times 10^{-7}$ $\frac{cc.}{mol.sec.}$
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
$\frac{1}{C_o \times 10^7}$ (cc/mol)

Figure 12.

Dilution Experiments

At this point a brief survey of the work accomplished showed clearly that, with the interpretation of past results becoming clear, there was one point which stood out as crucial, awaiting experimental verification. This was the influence of oxygen on the decomposition. The experiments of Chapman and Jones*on the effect of added oxygen and our own recorded in Part III, in which only a small retardation by oxygen was observed, had been explained by assuming (with considerable justification) the presence of a positive catalyst in the added oxygen. Only the few experiments on the dilution with air performed by Jahn† had given satisfactorily the effect of oxygen predicted by the mechanism now taken as describing the decomposition. And in these the presence of nitrogen as well as the smallness of the effect itself introduced some uncertainty as to their interpretation.

These considerations left no doubt that the most important prediction of the decomposition hypothesis remaining to be verified experimentally was the retardation inversely as the oxygen pressure. Two methods of attack were available. First, the partial pressure of oxygen could be changed and the rate compared with that before. As we have seen, the static method is most readily adapted to this; indeed, three experiments in which this was done are recorded in Part III. Also, with a different technique than the present, the dynamic method could be used at pressures other than one atmosphere, and so it was possible to perform this experiment by the dynamic method. Jahn had already used the method at a pressure a little less than half an atmosphere.

*See Part I, page 6.

†See Part I, page 7.

However, a second way of verifying the prediction presented itself. Dilution could be carried out satisfactorily using the dynamic method at one atmosphere; that is, with our present technique. The decomposition hypothesis definitely predicts the effect of dilution with oxygen, as contrasted with any inert diluents. While the latter should increase the second-order rate in proportion to the dilution, oxygen should leave it unaltered, since the partial pressure of oxygen on dilution with oxygen remains practially unaltered.

The apparatus was changed slightly to permit dilution. Two small cylindrical bulbs, connected in series with small tubing and at right angles to one another, were interposed at a short distance before the reaction chamber. The delivery tubes from the electrolytic ozone train and the silent discharge ozone train entered the first cylindrical bulb at opposite sides of the upper end. These conditions were such as to insure mixing before entering the reaction chamber. The two delivery tubes were of small tubing such that with either generator setting idle the gas in that delivery tube could be considered as stagnant, and diffusion through it could be neglected. Thus either one of the two sets could be run alone as before, or both could be run, one gas diluting the other in the mixing bulbs.

Four series of experiments were made during which there resulted eight determinations of the rate of decomposition of "acid" ozone diluted with its own volume of "caustic" ozone, eight determinations of the rate of decomposition of "acid" ozone diluted by its own volume of "caustic" oxygen, and ten determinations of the rate of decomposition of "acid" ozone undiluted. The results of these determinations are collected in the following table.

Table XIV

Date	Reaction time (sec.)	$k_2 \times 10^{-4}$ (cc/mol.sec.) "Acid" ozone	"Acid" ozone and "caustic" oxygen	"Acid" ozone and "caustic" ozone
Mar. 16	50.5	1.55	2.17	
	"	1.65	2.01	
	101.0	1.57		
	"	1.50		
Mar. 20	50.5		2.39	1.88
	"		2.08	1.80
	"			1.77
	"			1.74
	101.0	1.55		
		1.69		
Mar. 21	50.5		1.97	1.56
	"		2.12	1.65
	101.0	1.83		
	"	1.69		
Mar. 23	101.0	1.36		
	"	6.75		
	50.5		1.82	1.53
	"		2.05	1.78
	Mean	1.60	2.08	1.71

If the effect of total pressure were not in reality the effect of the oxygen pressure, then upon dilution of ozone with its own volume of the inert diluent oxygen a two-fold increase in rate should be expected; or, considering the fact that there may be some positive catalyst in the oxygen diluent, it would be fairer to predict an increase at least two fold. On the contrary, if the rate is inversely proportional to the partial pressure of oxygen, the dilution should cause no effect on the rate, since it produces no change in the oxygen pressure; or better, a small increase depending on the amount of positive catalyst in the oxygen. But, as was done, dilution of ozone may also be done with ozone. Here again if the rate is inversely proportional to the oxygen pressure, it should remain unaffected. And since from almost all points of view the action of a silent discharge ozonizer on oxygen would tend if anything to remove any positive catalyst, the dilution of ozone with ozone made from the oxygen used in the previous dilution experiments should probably show more satisfactorily the absence of any effect on the rate.

Table IV shows the support which these experiments lend to the point of view that the rate is inversely proportional to the oxygen pressure. The mean values* show an increase in the rate of decomposition of "acid" ozone of 30% when diluted with "caustic" oxygen. It falls to 7% when this oxygen diluent is first ozonized by the silent discharge. Thus, except for the effect due to positive catalyst occurring in the "caustic" oxygen which has evidenced itself in other ways heretofore, these results are in accord with the above view-point.

*In calculating the means the value 6.75 on March 23rd which, due to an unknown cause is obviously in error, has been neglected.

In considering the evidence for this mechanism of the decomposition other possibilities have not been neglected; in fact all other apparent possibilities have been studied in detail. The most important of these is the presence of an unknown negative catalyst. However, the evidence at present appears to support the retarding effect of oxygen, and the mechanism first given by Jahn. Resting upon the above work, combined with the results of other investigators, it is advanced again still with some reserve.

Following the experiments recorded in Table XIV, two sets of measurements have been made, the first on the order of the decomposition of the "acid" ozone, and the second on the order of the decomposition of the "caustic" ozone. Experimental conditions were the same as in the preceding measurements, and the results are given in the following tables.

Table XV

"Acid" ozone

Reaction time (sec.)	C x 10^7 (mol/cc.)	C x 10^7 (mol/cc.)	k_2 x 10^{-4} (cc/mol.sec.)
40.4	8.53	5.70	1.44
"	8.18	5.38	1.58
50.5	8.09	4.90	1.59
"	7.83	4.85	1.55
67.3	7.50	4.29	1.48
"	7.63	4.54	1.33
101.0	6.35	3.20	1.54
"	6.49	3.03	1.74
		Mean	1.53

Table XVI

"Caustic" Ozone

Reaction time (sec.)	$C_o \times 10^7$ (mol/cc.)	$C \times 10^7$ (mol/cc.)	$k_2 \times 10^{-4}$ (cc/mol.sec.)
40.4	8.28	4.61	2.38
"	7.39	4.23	2.50
50.5	9.09	4.70	2.04
"	8.54	4.49	2.09
67.3	7.44	3.45	2.31
"	7.45	3.40	2.37
95.3	6.57	2.72	2.26
"	6.68	2.64	2.40
		Mean	2.29

The agreement of each with the second-order is evident. Here, long after the earlier work of Part II was carried out, the observations again recall the variations in the specific rate of decomposition of ozones that occur without appreciable alteration of the second-order character. Here at this higher temperature the same second-order decomposition evidences the same peculiarities which it showed in the many experiments carried out at 100°.

At present the experimental work is concentrated upon obtaining oxygen of sufficient purity to give clear cut results in dilution experiments, and then in oxygen addition experiments. For this point is crucial and alone remains insufficiently well demonstrated; namely, that the specific second-order rate of ozone decomposition varies inversely as the partial pressure of the oxygen.

Summary of Part IV

The "dynamic" method of measuring rate of reaction has been used to determine the order and the specific rate at approximately 140° of the decomposition of ozone obtained from two different sources.

The decomposition is a change of the second-order, and its specific rate approximately 1.2×10^4 cc/mol. sec. at this temperature.

Dilution of ozone with oxygen at constant pressure leaves the specific rate of decomposition unchanged, except for a small acceleration which is shown to be probably due to the presence of a positive catalyst.

The results indicate that the probable mechanism of ozone decomposition is that given earlier by Jahn, and described by the equations

$$O_3 \rightleftharpoons O_2 + O \quad \text{(fast; equilibrium far to left)}$$

$$O_3 + O \longrightarrow 2O_2 \quad \text{(measurably slow; to completion)}$$

An electrolytic oxygen generator using alkaline electrolyte, suitable for laboratory use with high currents, has been devised.

An electrolytic ozone generator with a simple lead anode has been devised, suitable for laboratory use with high currents.

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EVIDENCE FOR THE EXISTENCE OF ACTIVATED MOLECULES IN A CHEMICAL REACTION

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It is known that when ozone decomposes rapidly radiation is emitted, part of which at least lies in the visible and ultra-violet. Stuchtey[1] has photographed the spectrum of the radiation using a quartz spectrograph. The radiation is scattered across the visible and extends well out into the ultra-violet. In particular, the well known bands of ozone in the vicinity of 2450 Ångstrom units come in definitely in the spectrum of the luminescence of the decomposition; there is also radiation of still higher frequency extending to approximately 2200Å which seems to have been the limit of observation of Stuchtey's work.[2] It is the purpose of this article to give the probable explanation of the emission of this remarkably short wave-length radiation, which, as will be shown, requires for its excitation energy quantities much larger than can be afforded by the ordinary heat of reaction.

The heat of decomposition of ozone is well known, the best value being that given by Jahn,[3] who found 34,500 calories per mol. The decomposition can under no circumstances be in entirety a simple monomolecular process, for we cannot obtain an even number of oxygen atoms from one of ozone. The interaction of three molecules is impossible as the complete mechanism; for this also does not yield an even number of oxygen atoms. The interaction of four molecules, while leading to possible mechanisms, is so improbable that we shall not consider it here.

We hence conclude that the process leading to the decomposition of ozone involves the interaction of two molecules and thus would make available not more than the energy of decomposition of two molecules. This does not mean that the mechanism which determines the rate of

decomposition is bimolecular, and indeed from our knowledge of the kinetics of this decomposition it may be said with considerable certainty that such is not the case. It does mean, however, that the energy available as a result of a single complete decomposition process will not exceed the energy of decomposition of two molecules of ozone.

The individual process in the case of the decomposition of two molecules of ozone would only liberate $2 \times 34{,}500/6.06 \times 10^{23}$ calories. Expressing this in terms of the frequency of a light quantum of the same energy, or better still in terms of the corresponding wave-length, we have 4120 Å. Hence, if the decomposition results from the interaction of two ozone molecules of normal energy content, and if the energy liberated in decomposition were in certain of the elementary processes liberated as light, the shortest wave-length that could possibly be emitted would be in the blue at 4120 Å.

Actually wave-lengths corresponding to an energy of practically two times this value are observed to be emitted. Now, the spectrum of the emitted light agrees closely with the emission spectrum of ozone molecules. We must accordingly conclude that ozone molecules have been raised from the normal state to states of excitation of much greater energy, the reversion of which again to the normal state being the process of the emission of the observed radiation. Our interest lies in discovering the source of this energy. If we reject the highly improbable possibility of this excitation occurring in steps, then it is a consequence[4] of the experimental facts that at least a part of the *decomposing* ozone molecules be in an activated[5] state, a state of energy-content higher than the normal state, so that the total energy available as the result of the decomposition is the energy represented by *the reversion of two normal ozone molecules to oxygen plus the energy of activation of the reacting molecules.* That is, at least a part of the ozone molecules do not revert to oxygen directly from their normal state; instead these molecules first become activated to states of higher energy content. These molecules may then revert to oxygen, the total energy liberated, a quantity greater than that corresponding to the transformation of two normal ozone molecules into oxygen being available for the excitation of ozone molecules. These excited ozone molecules then constitute the source of the radiation that is observed.

This seems to be a first case where in a homogeneous chemical reaction, there is direct evidence of the formation of activated molecules prior to reaction.

It should be noted that there is still uncertainty as to whether perfectly pure ozone emits radiation when it decomposes.[6] This might be thought to seriously limit the conclusions drawn above, since in a reaction between ozone and impurity there might be sufficient energy liberated to account for the very short radiation that is observed to be emitted. It is possible

that ozone could react with a compound of carbon (for example, acetylene) where the heat of reaction would be sufficient to account for the observed radiation. But it does not appear at all probable that such a possible reaction could occur in a single step. Moreover, the phenomenon has been observed by several investigators under conditions of gas purity which must have varied widely. It appears very probable that the influence of the impurity is a catalytic one, accounting in this way for the bringing out of the luminescence at lower temperatures than those at which it appears in purer ozone. For with increased rate of decomposition the luminescence would be expected to become visible at a lower temperature than that at which it appears in the uncatalyzed reaction. Stuchtey finds no change in the spectrum when it is excited by purely thermal means, or when excited partially by the introduction of an oxidizable impurity, the luminescence spectrum in all cases showing far-reaching agreement with the emission spectrum of ozone. No bands are observed that would have to be ascribed to the impurity. The existence of activated reactants is of course just as necessary a consequence of the catalyzed decomposition as of the normal decomposition, since no more energy is available in the individual process in the former case than in the latter. Therefore the ideas expressed in this paper seem to rest upon grounds of sufficient certainty to allow of the conclusion that in ozone decomposition we have experimental evidence that at least some of the ozone molecules suffer activation before they revert to oxygen.[7]

Summary.—It is shown in this article that the radiation emitted when ozone decomposes into oxygen, considered in relation to the quantum theory, makes it necessary to assume that ozone gas, under conditions favorable for its decomposition, contains ozone molecules in activated states of much higher energy content than that of the normal molecule. The existence of molecules as well as atoms in states of energy content higher than that of the state in which they are normally found, has of course been common experience in the study of the physical processes of the absorption and emission of radiation. But such molecules have hitherto in no case been identified with the activated molecules postulated by Arrhenius to explain the temperature coefficient of chemical reactions. This article is believed to give the first direct evidence which has been offered of the existence of these activated molecules.

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[1] Stuchtey, *Zs. wiss. Photogr.*, **19**, 161 (1920).

[2] The important question as to whether the oxygen bands in the vicinity of 1900 Å which are active in converting oxygen to ozone also are present in the luminescence spectrum remains as yet unanswered.

[3] Jahn, *Zs. anorg. Chem.*, **60**, 337 (1908). Kailan and John, *Zs. anorg. Chem.*, **68**, 243 (1910).

[4] It must be pointed out that this is a consequence only if we also reject chain reactions in which consecutively normal ozone molecules are decomposed for the activation of some molecule in successive steps, which, after a sufficient number of such steps, may clearly be made to possess enough energy to account for the observed excitation energies. Chain mechanisms of this type, and of such a design as to actually account for the observed radiation appear, from energy considerations and our knowledge of the kinetics of ozone decomposition, to be highly improbable.

[5] By this activation there is understood any passage of the ozone molecule to a form of higher energy. Thus a possible form of activation would be $O_3 \longrightarrow O_2 + O$.

[6] Trautz and Seidel, *Ann. Physik*, **67**, 527 (1922).

[7] In regard to the possibility of reaction between ozone and impurity affording sufficient energy to account for the luminescence observed without any activation of these reactants, it may be pointed out that if it be assumed, in view of the work of Trautz and Seidel referred to above, that it is the reaction between ozone and carbon monoxide which yields the energy that excites the luminescence, the conclusions of this paper remain substantially unchanged. For, while this reaction affords more energy than the reaction of two normal ozone molecules, it does not give a sufficient amount to account for the short wave-length radiation that is observed. Thus from thermochemical data it may readily be computed that the reaction $O_3 + CO = CO_2 + O_2$ is attended by an energy liberation of 102,500 calories. This might account for radiation of wave-lengths as short as 2780Å, but not shorter. As has been said above, Stuchtey finds an important part of the total radiation to be of considerably shorter wave-length than this, namely that lying in the vicinity of 2540Å, and radiation extending even farther in the direction of shorter wave-length than this latter is also observed. Therefore the conclusions of this paper can be applied equally as well to the reaction between ozone and carbon monoxide, if this reaction be thought responsible for the luminescence.

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Possible Limits for the Heat of Dissociation of Oxygen.—The ionization of oxygen to form singly charged oxygen molecules has been found to occur at about 16 v. by Lockrow and Duffendack[1] and by Smyth.[2] In their study of the low-voltage arc in oxygen, Lockrow and Duffendack find a marked strengthening of lines and the appearance of new lines at 19.5 v.,[3] and they ascribe this to dissociation and simultaneous ionization of one atom.[1] Smyth, working at low pressures and using his method of positive-ray analysis, did not find oxygen atom ions below 23.0 v.

For the similar process in hydrogen Smyth showed that the appearance of atom ions depended on a secondary process involving collisions, since by changing the pressure in the impact region, the voltage at which atom ions appeared could be greatly altered, this voltage decreasing as the pressure increased, until atom ions appeared at the same point as molecule ions.

Returning to the case of oxygen, in view of the fact that at very low pressure, oxygen atom ions do not appear until a considerably higher voltage is reached than that at which they appear at the relatively large pressures used in the low-voltage arc, it would seem probable that excited oxygen molecule ion can dissociate into oxygen atom and oxygen atom ion upon collision with some neutral particle, provided that its energy is greater than, or equal to, the energy change represented in such a process of dissociation. Now, atom ions are not found to occur at 16 v. and, therefore, unless the state of the molecule ion corresponding to 16 v. is metastable, for some special reason not being able to dissociate upon collision, the 16 v. molecule ion does not possess the energy necessary for the dissociation. The molecule must possess more energy than that represented by 16 v. to be able to dissociate upon collision. It appears that at 19.5 v. the excited molecule ion has sufficient energy to undergo this change upon collision. It may well be, however, that the energy increase represented in the dissociation is less than that corresponding to 19.5 v., but that under 19.5 v.

[1] Lockrow and Duffendack, *Phys. Rev.*, **25**, 110 (1925).

[2] Smyth, *Proc. Roy. Soc.* (London) **105A**, 116 (1924).

[3] Communicated by Dr. Duffendack in a letter to the author.

there is no state of the molecule ion the energy of which is greater than that corresponding to the dissociation. Again, there may be such a state, but it may be metastable, one which upon collision will not undergo dissociation. Considering, then, that this value may be somewhat greater than that strictly required in the change alone, a maximum value can be calculated for the heat of dissociation of oxygen; and a minimum value can be determined, since no atom ions occur at 16 v.

These calculations can be made in the familiar way from the following simple thermochemical considerations. The reactions in question can be represented by the following equations.

$$O_2 = O + O^+ + E^- \quad (1)$$
$$O = O^+ + E^- \quad (2)$$

Subtracting (2) from (1) there results

$$O_2 = 2O \quad (3)$$

The heat of ionization corresponding to Equation 2 can be found from the ionization potential of the atom, which has been determined spectroscopically by Hopfield[4] to be 13.56 v. This corresponds to a heat of ionization of 312,600 cal. per mole. The heat of dissociation and simultaneous ionization of one atom corresponding to Equation 1 is not greater than the energy corresponding to 19.5 v. which is 450,000 cal. per mole, and not less than that corresponding to 16.0 v. which is 369,000 cal. per mole, for the reasons given above. The difference in the first case is 137,400 cal. and in the second 56,400 cal. Therefore, the heat of dissociation of molecular oxygen into atomic oxygen is not less than 56,400 cal. per mole and not greater than 137,400 cal. per mole. While these limits are wide, it is believed that they are narrower than could be given heretofore.

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[4] Hopfield, *Nature*, **112**, 437 (1923).