TABLE II

Sample	Analysis	Wt. of $ScCl_3$ in vac., g.	Wt. of Ag in vac., g.	Nephelometric test Ag, g.	Wt. of Ag in vac. g. (corr.)	Ratio $ScCl_3$:3Ag	At. wt. of Sc
I	1	0.59311	1.26725	−0.00036	1.26689	0.46815	45.142
I	2	1.13724	2.43079	− .00289	2.42790	.46838	45.225
I	3	2.14857	4.59452	− .00528	4.58924	.46817	45.149
I	4	1.10970	2.36999	− .00054	2.36945	.46832	45.202
II	5	1.02956	2.19887	+ .00047	2.19934	.46811	45.132
II	6	1.50457	3.21502	− .00016	3.21486	.46801	45.094
II	7	0.90557	1.93452	− .00043	1.93409	.46822	45.161
II	8	1.79432	3.83723	− .00466	3.83257	.46817	45.151
II	9	1.71420	3.66193	− .00110	3.66083	.46826	45.174
				Av. for Sample I			45.179
				Av. for Sample II			45.142
				Av. of all			45.160

The author desires to express his sincere thanks to Dr. Hiram S. Lukens, under whose direction and kindly encouragement this work was carried out.

Summary

1. Anhydrous scandium chloride was prepared by the action of pure anhydrous carbon tetrachloride on scandium oxide.
2. A new type of bottling apparatus is described for filling the weighing bottle with scandium chloride in the presence of dry air.
3. The ratio of pure scandium chloride to pure silver was determined and the average of nine analyses gave 45.160 as the atomic weight of scandium.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 137]

THE THERMAL DECOMPOSITION OF OZONE. III. THE TEMPERATURE COEFFICIENT OF REACTION RATE

BY OLIVER R. WULF[1] AND RICHARD C. TOLMAN

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1. Introduction

In two earlier papers,[2] the authors have presented the results of investigations on the thermal rate of ozone decomposition, which to a considerable extent explain the lack of agreement among the earlier researches in this field. The resulting clarification of the problem, as well as our discovery of certain improvements in technique, including in particular the discovery of a relatively reproducible source of ozone, have led us also to carry out a new investigation of the temperature coefficient of the rate of this decomposition.

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[1] National Research Fellow in Chemistry.

[2] Wulf and Tolman, THIS JOURNAL, **49,** (a) 1183, (b) 1202 (1927).

As will be shown in the latter part of this paper, a knowledge of the temperature coefficient for this reaction is of particular interest, since it appears to afford definite evidence against the mechanism of ozone decomposition suggested by Jahn, which has heretofore seemed the most plausible proposal for this reaction.

2. Previous Researches on Temperature Coefficient

Before proceeding to our own experiments, we must first briefly review the results of earlier determinations of temperature coefficient, and to do this it will be most convenient to give the values obtained from previous work for the energy of activation ΔE as calculated from the Arrhenius equation in the original form

$$\mathrm{d}\log k_2/\mathrm{d}T = \Delta E/RT^2 \tag{1}$$

where k_2 is the specific second-order rate for the decomposition. As will be shown later, the use of an equation of precisely this form is probably not theoretically justifiable for calculating the energy of activation for this reaction, and indeed the choice of the exactly correct form would involve assumptions as to the mechanism of ozone decomposition which cannot now be made with any degree of certainty. Nevertheless, this is the form used by previous investigators in the field and will be satisfactory for the purpose of comparing results. Furthermore, we shall see later that different forms of the equation lead to values for the energy of activation which do not differ greatly.

The first calculation of temperature coefficient was made by Warburg[3] from his measurements of the specific second-order rate at 100° and a total pressure of 91.5 cm. and at 126.9° and a total pressure of 98.1 cm., the difference in pressures arising from the use of oxygen at the same concentrations at the two different temperatures. He thus obtained a result which is equivalent to an energy of activation of 26,700 cal.

The next calculations were made by Clement,[4] who measured the specific rate by the dynamic method at eight different temperatures in the range 100 to 250° and at a total pressure of 72.9 cm. These measurements would furnish an excellent determination of temperature coefficient were it not for the fact that at 100 and 127°, where from other researches we know the specific rate fairly well, Clement's values are much too high. The reason for this disagreement is not clear, but the disagreement leaves some doubt as to whether any conclusions may be drawn from these measurements as to the temperature coefficient of the normal decomposition. As already pointed out in the first of these articles,[5] the assumptions made regarding the type of gas flow could hardly have been satisfied

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

[4] Clement, *ibid.*, **14**, 341 (1904).

[5] See Ref. 2 a, where a discussion will be found of the conditions of flow necessary for the dynamic method.

in a reaction vessel of the shape Clement used, but it does not appear that this would cause high calculated values for the specific rate. If the explanation lies in the presence of positive catalyst in the ozone, the temperature coefficient of the normal decomposition might indeed be somewhat different. The value of the energy of activation calculated from Clement's measurements is 26,100 cal.

Perman and Greaves,[6] in their study of ozone decomposition, observed the reaction at five temperatures over the range 40–120°, always at approximately 1 atm. total pressure; however, their results in general are rather discordant. The decomposition did not appear to proceed in agreement with the second order, and the change with temperature of the average values of the specific rate between temperatures of 100 and 120° was quite different than over the other three intervals. They expressed the specific rates in the units, per minute per millimeter pressure of sulfuric acid. Specific rates are, however, usually expressed in units of concentration, and since at constant concentration the pressure is a function of temperature, the specific rates calculated by them will vary with the temperature in a different way than those expressed in units of concentration. We have converted the average values of their specific rates into the units per second per mole per cubic centimeter, although the use of an average value in such cases is questionable. The values they find for the specific rate for the interval 100–120° then lead to an energy of activation of 38,300 cal. But for the intervals 80–100°, 60–80° and 40–60° the results are 25,900 cal., 26,400 cal. and 26,600 cal., respectively. It does not appear, therefore, that one may conclude much from these measurements. We are chiefly interested in the measurements at 100° and above, for in this region it seems to be easier to carry out the second-order homogeneous decomposition free from disturbing influences. However, their results over the interval 100–120° are so far removed from those over the other three lower intervals that little weight can be given to them.

Belton, Griffith and McKeown[7] have recently measured the decomposition at 78.1 and 100° and at three different pressures. They give apparently one determination at each pressure of the specific rate at 78.1 and 100°, thus permitting three calculations of the energy of activation. The average of the three values obtained is 27,770 cal. One regrets that the complete data of a typical run are not given, in order to illustrate the extent to which each decomposition adhered to the second order. In earlier work in their Laboratory[8] it was invariably observed that the decomposition was not of the second order, but that the calculated second-

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

[7] Belton, Griffith and McKeown, *J. Chem. Soc.*, **129**, 3153 (1926).

[8] Griffith and McKeown, *ibid.*, **127**, 2086 (1925).

order specific rate increased somewhat over each separate decomposition. It is concluded from what they say that the deviation from second order over each of these decompositions is similar to that observed earlier.

So far as the authors are aware, there are no further measurements in the literature which permit a calculation of the temperature coefficient of this reaction rate. The most reliable previous value of the energy of activation is presumably that of Warburg, of 26,700 cal.; our own value, calculated by a method which corresponds to his, has the value of 30,000 cal.

3. Experimental Procedure

In the present work the specific rate of ozone decomposition was measured at five different temperatures, using the dynamic method. The ozone used was the so-called "acid" ozone of our earlier work, which was shown in the second article of this series[2b] to have very reproducible properties.

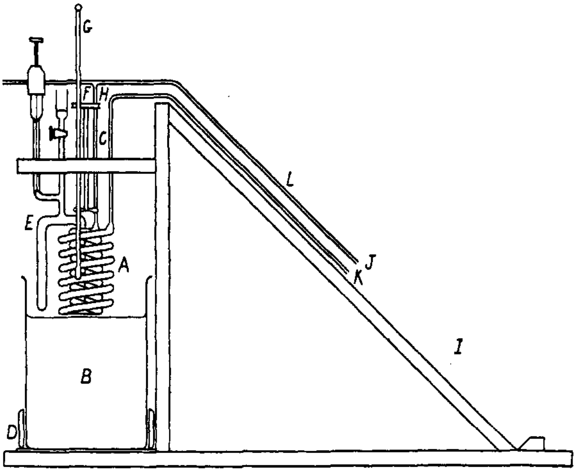

Fig. 1.—Decomposition apparatus.

The ozone was obtained by the electrolysis of sulfuric acid solution at high anode current density and the entire generating apparatus, including the drying train, was the same as that used in our earlier work, with the single exception of a new anode.[9] The old one had been rendered useless by corrosion eating through the copper cooling pipe within the glass-tube shield. The new unit was identical with the old, except that the glass tube was filled with paraffin up to and around the lead plug anode, thus preventing the electrolyte from entering the glass tube. This protected the copper cooling tube from corrosion.

The decomposition apparatus was new, and the attempt was made to reduce as far as practicable the errors inherent in the dynamic method. The apparatus is illustrated in Fig. 1. The reaction tube A consists of a double concentric helix. This was constructed of Pyrex tubing, approximately 2 meters in length and 5 mm. in bore.

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[9] For a description of the generating apparatus, see an article by Wulf, to appear soon elsewhere.

The measured volume of this helical reaction chamber was 44.73 cc. The connecting tubes C were of small bore. The helix was suspended in a bath B of paraffin, which was contained in a 3-liter Pyrex beaker and was heated from the outside near its base by a collar heater D. The temperature of the bath was maintained constant by a two-arm mercury regulator E, which controlled through a relay the current in the collar heater. One arm of the regulator was inside the inside coil of the helix and the other arm just outside the outside coil. A motor-driven stirrer F directed the paraffin downward through the helical coils. The thermometer G was placed so that its bulb was close to the outside helical coil and about half way down its depth. All this apparatus was mounted as a unit, independent of the 3-liter beaker, on a cover of hard wood separately supported.

The bath could be raised and lowered, the paraffin never being allowed to solidify over the decomposition apparatus because of the danger of the paraffin crushing the apparatus due to its high coefficient of expansion.

The small-bore connecting tubes of the helical reaction chamber passed upward through the cover. One of these made a T connection at H with the tube line from the ozone-generating set, this line continuing parallel to the other leading-in tube which made a right-angle bend at H, both tubes passing down an inclined surface on which the analytical absorption tubes could be raised or lowered in tracks provided for them.

The apparatus permitted the collection of a sample of gas either at J of the original oxygen-ozone mixture, or at K, this gas having suffered decomposition at the temperature of the bath for the length of time t required to pass through the helical tube. Thus a value of the initial concentration C_0 and of the concentration C after a time t were obtained. These are sufficient data to calculate the specific rate according to the expression

$$k_2 = (1/t)[(1/C) - (1/C_0)] \qquad (2)$$

the order being known to be second from our earlier work. A determination of the order was, however, also made at two different temperatures in the present work.

Fig. 2.—Absorption tube.

The samples for analysis were collected in absorption tubes especially constructed for the purpose, the method of collection, however, being the same as that previously employed. Fig. 2 shows an absorption tube and the relative amount of potassium iodide solution used. Such a tube in place at I was raised quickly in the trackway over the respective delivery tube to the position L. The orifice of the delivery tube then was roughly 2 cm. above the surface of the absorbing liquid. The volume of gas collected, determined by the rate of flow and the time t_a used in collecting the sample, was considerably smaller than the volume of the tube over the liquid. The sample was thus collected by the upward displacement of the air. After the desired time t_a of collection of the absorption sample, the tube was immediately lowered to the position I, the glass stopper inserted and the tube shaken and set aside, where the absorption was allowed to continue for about an hour. The absorbed sample was analyzed by acidification and titration with standard sodium thiosulfate solution. During the collection of a sample, the orifice of the other delivery tube was closed by a little distilled water which held itself in place by surface tension. The use of this method of analysis has been described in more detail in the second paper of this series.

4. Experimental Data

There are three quantities necessary for the calculations of the specific rate at a given temperature, namely: a value of the concentration of the ozone at the reaction temperature and pressure as it enters the reaction tube; a similar value as it leaves the reaction tube; and the time required for the molecules to make the transit of the reaction tube.

To obtain these it is necessary to measure the following quantities: the temperature T, the atmospheric pressure P, which is substantially that in the reaction chamber, the current I in the electrolytic ozone generator, the time t_a used for the absorption of analysis samples, and the titer value of each sample against standard sodium thiosulfate.

As an illustration, the complete data for a run made on October 7th are given in Table I. C_0 values, with a few exceptions, were taken one minute after the corresponding C value, many minutes elapsing before the taking of the next C value, since sufficient time must be allowed to set up again the steady-state condition in the helical reaction tube.

Table I

Data of the Run of October 7th

Pressure, 0.966 atm.; t_a, 60 seconds

I, amp.	T, °K.	Titer, cc. of thiosulfate C	C_0
10.05	452.2	0.88	3.69
10.00	452.2	.82	3.66
9.95	441.7	1.42	3.49
10.00	441.7	1.43	3.55
10.00	431.3	2.14	3.48
10.00	431.3	2.10	3.41
9.90	420.9	2.59	3.27
10.00	420.9	2.58[a]	3.30

[a] I = 9.85 amp.

5. Treatment of the Data

The number of moles of total gas collected in the sample for analysis is given by

$$N = t_a \frac{I}{4 \times 96{,}500}\left(1 - \frac{1}{3}\alpha\right) \tag{3}$$

where α is the fraction of the total oxygen in the form of ozone. This will be different for the initial and final concentrations. In this work the initial fraction of the total oxygen in the form of ozone was always of the order of 0.018. The correction term $^1/_3\,\alpha$ is thus so small that the error involved in assigning a rough average value to α is negligible. The value α = 0.009 will be used in these calculations. Combining the numerical factors, we obtain

$$N = 2.583 \times 10^{-6}\, t_a I \tag{4}$$

The volume of this quantity of gas at reaction temperature T is

$$V = NRT/P = 2.583 \times 10^{-6}\, t_a IRT/P;\ V = 2.120 \times 10^{-4}\, t_a IT/P \tag{5}$$

The number of moles of ozone collected in this sample is evidently

$$N_{O_3} = \mathbf{N} \times \text{titer (in cc.)}/2000 \tag{6}$$

where **N** is the normality of the thiosulfate. Hence, the concentration of the ozone initially and finally at reaction temperature and pressure may be computed by dividing Equation 6 by 5, giving us the expression

$$C_{O_3} = 2.359\ (\mathbf{N}P/t_aT)\ (\text{titer}/I) \tag{7}$$

The volume of the helical tube, as previously stated, was 44.73 cc. The small-bore connecting tubes were immersed for a distance roughly 2.5 cm. in the bath. The volume of the length immersed was small and the rate of passage of the gas through this volume was high. This tended to raise the entering ozone rapidly to temperature, and similarly the gas leaving was cooled rapidly as it passed quickly out through the long length of small-bore tubing. In using the dynamic method it is assumed that the ozone is raised immediately to reaction temperature as it enters the reaction helix, remains so as it passes through the helix, and is cooled immediately upon leaving it. The assumption is justified here, since the time of heating and cooling is small compared to the time of passage.

The time of passage through the reaction chamber may be assumed equal to the volume of the chamber divided by the volume rate of flow. The conditions necessary for the justification of this assumption are rather complicated, and as they have been treated in the second paper of this series, a discussion of them will not be repeated here. It is, however, well to repeat again that this assumption is not one which at first sight appears justifiable, and is dependent on such factors as shape of vessel and rate of flow. The present apparatus was designed in such a way that the assumption is justifiable.

The volume rate of flow in the reaction chamber is given by

$$r = (I/4 \times 96{,}500) \times (82.07T/P)(1 - {}^1/_3\alpha) \tag{8}$$

in cubic centimeters per second, where α is the average fraction of the total oxygen in the form of ozone in the reaction tube. The initial fraction varies but is of the order of 0.018 in this work. The extent of decomposition varies widely over the runs. However, the correction ${}^1/_3\alpha$ is less than 1% in any case. Hence it is sufficiently accurate to use as a constant value of the parenthesis 0.997, corresponding to $\alpha = 0.009$ as the average value in the helical tube.

The time of passage through the reaction chamber is then given by

$$t = \frac{44.73}{\dfrac{I}{4 \times 96{,}500}\ 82.07\ \dfrac{T}{P}\ 0.997} = 2.110 \times 10^5\ \frac{P}{IT} \text{ seconds} \tag{9}$$

Since ozone decomposition is a change which proceeds homogeneously at a rate proportional to the square of the ozone concentration under the conditions of our experiments, the specific rate may now be calculated. By substituting into the expression

$$k_2 = (1/t_1)[(1/C_1) - (1/C_0)] \tag{10}$$

where C_0 is the concentration of ozone initially at time $t = 0$ and C_1 is this concentration after the time t_1, we obtain

$$k_2 = \frac{I_1T}{2.110 \times 10^5\ P}\left(\frac{t_aI_1T}{2.359\ \mathbf{N}P \times \text{titer}_1} - \frac{t_aI_0T}{2.359\ \mathbf{N}P \times \text{titer}_0}\right) = \frac{2.009 \times 10^{-6}\ I_1T^2t_a}{\mathbf{N}P^2}\left(\frac{I_1}{\text{titer}_1} - \frac{I_0}{\text{titer}_0}\right) \tag{11}$$

6. Results

Using this expression, the specific rate was calculated for the data of five runs comprising 42 sets of initial and final titer values taken at five different temperatures. The results are given in Table II in the column under the absolute temperature at which they were obtained.

TABLE II

VALUES OF k_2 (CC./MOLE SEC.) × 10^{-4}

Date	452.2°	441.7°	431.3°	426.1°	420.9°
Oct. 7	21.98	9.93	4.12	..	1.70
	23.80	10.00	4.18	..	1.70
Oct. 21	21.79	10.13	4.57	..	..
	21.63	10.30	4.32	..	..
Oct. 26	...	11.01	4.10	..	1.68
	...	10.16	4.38	..	1.86
	...	...	..	..	1.63
	...	...	..	..	1.67
Oct. 27	23.75	9.99	4.43	..	1.76
	23.00	9.95	4.59	..	1.77
Oct. 28	23.05	10.03	4.57	..	1.82
	22.52	10.03	4.35	..	1.94
Oct. 29	...	...	..	2.75	..
	...	...	..	2.96	..
	...	...	..	2.69	..
	...	...	..	2.82	..
Av.	22.69	10.15	4.36	2.81	1.75
Av. deviation, %	3.1	2.0	3.4	3.0	4.4

The second-order character of the decomposition in the vicinity of these temperatures, as has been said above, was known from our previous work. Even though this was practically the same ozone as we had earlier found satisfactory, it seemed well to test the order in this case also, particularly because of the new decomposition vessel, in view of the possibility that the conditions of flow in the vessel used in the earlier work might not be the same as in this investigation.

In using the dynamic method the order of a reaction may be determined

TABLE III

RESULTS SHOWING SECOND-ORDER CHARACTER OF THE REACTION

T, °K.	t_1, seconds	Titer$_0$	Titer$_1$	$k_2 \times 10^{-4}$, cc./mole sec.
		(cc. of thiosulfate)		
420.9	49.1	3.36	2.66	1.68
	48.9	3.39	2.64	1.86
	98.7	3.07	2.08	1.63
	98.7	3.19	2.10	1.67
426.1	48.5	3.90	2.61	2.75
	48.3	3.84	2.53	2.96
	96.6	3.05	1.74	2.69
	96.6	3.16	1.74	2.82

by changing either the initial concentration or the rate of flow or both. Here the rate of flow was changed, but the initial concentration also varied considerably. The results are contained in Table II, but are retabulated here with the times and titer value observed.

The agreement with the second order is evident.

7. The Temperature Coefficient and the Energy of Activation

Although the thermal decomposition of properly prepared ozone is very closely of the second order, the mechanism cannot necessarily be assumed to be bimolecular with respect to ozone because of the known inhibiting effect of oxygen, and at the present time the correct mechanism of the reaction must be regarded as unknown. This introduces difficulties into the determination of the energy of activation, since the precisely correct method of calculation would have to be determined from a knowledge of the mechanism.

For this reason we have calculated the energy of activation ΔE from each of the four following equations and obtained the results shown below,

$$k_2 = k\, e^{-\frac{\Delta E}{RT}} \quad ; \quad \Delta E = 30{,}900 \text{ cal.} \quad \text{(A)}$$

$$k_2 = \frac{k}{C_{O_2}}\, e^{-\frac{\Delta E}{RT}} \quad ; \quad \Delta E = 30{,}000 \text{ cal.} \quad \text{(B)}$$

$$k_2 = kT^{\frac{1}{2}}\, e^{-\frac{\Delta E}{RT}} \quad ; \quad \Delta E = 30{,}400 \text{ cal.} \quad \text{(C)}$$

$$k_2 = \frac{k}{C_{O_2}}\, T^{\frac{1}{2}}\, e^{-\frac{\Delta E}{RT}}; \quad \Delta E = 29{,}600 \text{ cal.} \quad \text{(D)}$$

k being, of course, a different constant in the four expressions. The different values of ΔE differ from each other by an amount which is somewhat greater than that corresponding to the limit of accuracy in the data.

Each of the above equations would correspond to a different set of assumptions as to the nature of the mechanism responsible for ozone decomposition, although these assumptions would not necessarily be very plausible ones.

Case A is chiefly of interest as giving the simplest empirical expression for the rate of decomposition of dilute ozonized oxygen at 1 atm. total pressure and different temperatures. In order for it to correspond to an actual mechanism we should have to assume that the temperature coefficient of the rate was determined by some unimolecular process with an energy of activation ΔE, and either to neglect the inhibiting effect of oxygen or to assume this inhibiting effect to be determined solely by the total pressure, since this was not varied in our experiments. The mechanism would also have to include steps, perhaps of a chain-like nature, to make the total reaction second order with respect to ozone.

Case B differs from the above in assuming that the rate is to be taken as inversely proportional to the concentration of oxygen, C_{O_2}. Its interest lies in the fact that Warburg's experiments were made at constant concentration of oxygen, and hence Case B furnishes the most natural value of ΔE to compare with that obtained by Warburg.

Case C would correspond to a mechanism in which the rate-determining step was bimolecular, and the overall rate determined by the total pressure.

Case D corresponds to a mechanism in which the rate-determining step is bimolecular and the overall rate is inversely proportional to the concentration of oxygen, C_{O_2}. This is a particularly interesting case since, as we shall see, the definite mechanism proposed by Jahn fulfils these conditions.

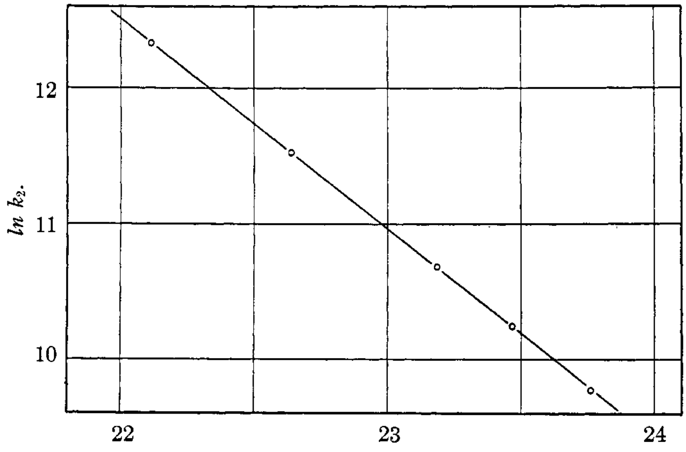

Fig. 3.

These four cases by no means exhaust the possible assumptions as to mechanism. Thus, for example, the inhibiting effect of oxygen might be taken proportional to the number of collisions made between oxygen molecules and some molecular form present during the decomposition rather than to the pressure or concentration. Nevertheless, the four cases show that different assumptions probably will not lead to greatly different values for ΔE.

Let us now turn to a more specific consideration of Case A which gives a simple empirical formula for the rates found, and Case D which corresponds to the Jahn mechanism.

8. Empirical Equation for Rate of Decomposition of Ozone at 1 Atm. Total Pressure

The values of ΔE and k in Expression A were actually obtained by plotting log k_2 against $1/T$ and determining the slope and intercept of the line. The plot of the data given in Table II is shown in Fig. 3. It will be noticed that the points do fall practically on a straight line, indicating that ΔE may be taken as a constant over the range of temperatures employed.

As a result of the plot we obtain as an expression for the specific second-order rate of decomposition of dilute ozonized oxygen at approximately one atmosphere pressure

$$k_2 = 2.04 \times 10^{20}\, e^{-30{,}900/RT} \qquad (12)$$

This may be regarded as a simple empirical expression for the rate of decomposition of ozone at 1 atm. pressure. At 100° it gives a value of the specific rate of 1.55×10^2 cc. moles^{-1} sec.$^{-1}$. This falls well within the range of values given in the first article of this series for ozone at 100°.

9. The Jahn Mechanism

To explain the inhibiting effect of oxygen and the second-order character of ozone decomposition, Jahn[10] assumed the following intermediate reactions as expressing the mechanism of the overall change.

$$O_3 \rightleftharpoons O_2 + O \qquad \text{(To equilibrium)} \qquad (E)$$
$$O_3 + O \longrightarrow 2O_2 \qquad \text{(Rate determining)} \qquad (F)$$

In accordance with the first of these reactions, we should have for the concentration of monatomic oxygen

$$C_O = K\, C_{O_3}/C_{O_2} \qquad (13)$$

where K is the equilibrium constant for the reaction, and hence, in accordance with the second reaction, we could write for the overall rate

$$-\mathrm{d}C_{O_3}/\mathrm{d}t = k'T^{\frac{1}{2}}\, C_{O_3}\, K\, C_{O_3}/C_{O_2} = k'KT^{\frac{1}{2}}\, C_{O_3}^2/C_{O_2} \qquad (14)$$

where k' is a constant independent of temperature, and the number of collisions between ozone molecules and oxygen atoms is taken proportional to the square root of the absolute temperature. The mechanism evidently accounts both for the inhibiting effect of oxygen and the second-order character with respect to ozone.

To obtain the effect of temperature on the overall rate, we may now use the van't Hoff expression for the change in equilibrium constant K with the temperature

$$\mathrm{d}\log K/\mathrm{d}T = \Delta E/RT^2 \qquad (15)$$

and by integrating on the assumption that ΔE is constant, and substituting in Equation 14 obtain the result

$$-\mathrm{d}C_{O_3}/\mathrm{d}t = kT^{\frac{1}{2}}\, e^{-\Delta E/RT}\, C_{O_3}^2/C_{O_2}$$

or

$$k_2 = (k/C_{O_2})\, T^{\frac{1}{2}}\, e^{-\Delta E/RT} \qquad (16)$$

where k is a new constant independent of the temperature and ΔE is evidently the heat absorbed when Reaction E takes place at constant volume.

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[10] Jahn, *Z. anorg. Chem.*, **48**, 260 (1905).

It will be noted that Equation 16 agrees with Case D considered above. To determine the values of the constants occurring in Equation 16, we have plotted in Fig. 4 the value of ($\log k - \frac{1}{2}\log T + \log C_{O_2}$) against $1/T$ and thus obtained the numerical equation

$$k_2 = (5.89 \times 10^{13}/C_{O_2})\, T^{\frac{1}{2}}\, e^{-29,600/RT} \qquad (17)$$

As will be seen from Fig. 4, the experimental values fall well on a straight line, and in passing it may be remarked that this was also true for the plots corresponding to Cases B and C, which it did not seem worth while to reproduce here. It should also be remarked that if we regard Equation 17 as an empirical expression of the rate of ozone decomposition, it would presumably take reasonable care of the inhibiting effect of oxygen, which is not done by Equation 12.

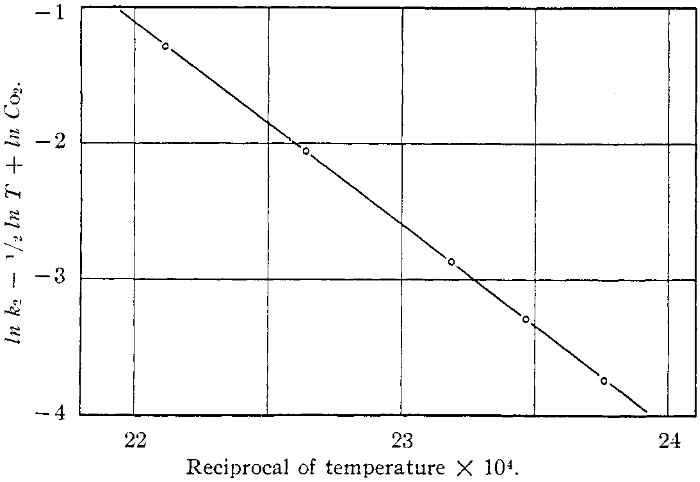

Fig. 4.

10. Energy of Activation on Basis of Jahn Mechanism

Since the Jahn mechanism furnishes us with a definite interpretation of the numerical quantities occurring in Equation 17, we now have the possibility of testing this mechanism by investigating the reasonableness of these quantities.

On the basis of the Jahn mechanism the energy of activation, 29,600 cal., should be the heat absorbed at constant volume by the reaction $O_3 = O_2 + O$, giving us the thermochemical equation $O_3 = O_2 + O - 29,600$ cal. Neglecting the small effect of temperature on heats of reaction we may now combine this with the known heat of decomposition of ozone[11] at constant volume and room temperature as given by the equation $2O_3 = 3O_2 + 69,000$ cal., and obtain for the heat of dissociation of

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[11] See the critical analysis of Moeller, "Das Ozon," Vieweg, Braunschweig, **1921**, p. 34.

oxygen at constant volume, $O_2 = 2O - 128{,}200$ cal., which falls within the probable limits for this reaction.[12]

Hence we must conclude that the Jahn mechanism gives a reasonable value for the heat of dissociation of ozone into diatomic and monatomic oxygen and may use the value 29,600 cal. for our further interpretation.

11. Number of Collisions on Basis of Jahn Mechanism

Turning now to the other numerical factor, namely, 5.89×10^{13}, occurring in Equation 17, it is evident on the basis of the Jahn mechanism that this must be related to the number of collisions between ozone molecules and oxygen atoms. Indeed, as a necessary requirement, it is evident that we could calculate the maximum possible value of this constant by assuming reaction at every collision between an ozone molecule and an oxygen atom. We must now investigate this point.

To do so we shall content ourselves with a comparison of the number of collisions and number of reactions occurring in 5% ozonized oxygen at one atmosphere and 100°. To make this comparison we shall first have to calculate by thermodynamic methods the amount of monatomic oxygen which would be present in 5% ozone at 100°, and then use kinetic theory methods to calculate the number of collisions between monatomic oxygen and ozone.

a. **Thermodynamic Calculation of Partial Pressure of Monatomic Oxygen.**—To calculate the partial pressure of monatomic oxygen in equilibrium with ozone and molecular oxygen, we must know the heat change ΔH and entropy change ΔS accompanying the reaction $O_3 = O_2 + O$. On the basis of the Jahn mechanism, as we saw above, the energy change accompanying this reaction would be 29,600 cal., and hence the heat change at constant pressure and 100° would be

$$\Delta H_{373} = \Delta E + RT = 29{,}600 + RT = 30{,}300 \text{ cal.} \qquad (18)$$

To calculate the entropy change accompanying the reaction is more involved. We have, however, at room temperature for the reaction $O_3 = {}^3/_2O_2$, the well substantiated value, $\Delta H_{298} = -34{,}200$ cal., and taking the specific heats of ozone and oxygen as given by the equations[13]

$$O_3,\ C_p = 7.0 + 0.0071\ T - 0.00000186\ T^2 \qquad (19)$$

and

$$O_2,\ C_p = 6.50 + 0.0010\ T \qquad (20)$$

obtain at 0° to the nearest hundred calories the same value

$$\Delta H_{273} = -34{,}200 \text{ cal.} \qquad (21)$$

For the free-energy change at 0°, however, we have the value obtained by Jahn,[14]

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[12] See Wulf, THIS JOURNAL, **47**, 1944 (1925); *Lockrow, Astrophys. J.*, **43**, 205 (1926). See also, however, Hogness and Lunn, *Phys. Rev.*, **27**, 732 (1926). Birge and Sponer, *ibid.*, **28**, 259 (1926).

[13] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, pp. 80, 475.

[14] Jahn, *Z. anorg. Chem.*, **60**, 332 (1908). See also Ref. 11, p. 57, which also takes this value.

$$\Delta F_{273} = -30{,}000 \text{ cal.} \qquad (22)$$

which Jahn considers to be correct within an error that cannot be greater than 2000 cal., and may be considerably less.

Combining Equations 21 and 22 we obtain for the entropy change at 0° the value

$$\Delta S_{273} = (\Delta H - \Delta F)/T = -15.39 \text{ cal. deg.}^{-1} \qquad (23)$$

and by integrating from 0 to 100° we obtain, with the help of Equations 19 and 20 for the entropy change at 100°, the value

$$\begin{aligned}\Delta S_{373} &= \Delta S_{273} + \int_{273}^{373} \left[\frac{3}{2}\, C_p\,(O_2) - C_p\,(O_3)\right] \frac{dT}{T} \qquad (24)\\ &= -15.03 \text{ cal. deg.}^{-1}\end{aligned}$$

for the reaction $O_3 = {}^3/_2O_2$.

Furthermore, for the reaction $\frac{1}{2}O_2 = O$, we have at 25° the entropy change[15] $\Delta S_{298} = 9.97$, and taking the specific heat of monatomic oxygen as 5.0, we obtain for this reaction at 100°, by an integration similar to that in Equation 24, $\Delta S_{373} = +10.33$ cal. deg.$^{-1}$.

We may now add the values of the entropy changes at 100° for the reactions $O_3 = {}^3/_2O_2$ and ${}^1/_2O_2 = O$, and obtain for the reaction $O_3 = O_2 + O$, the value $\Delta S_{373} = -4.70$ cal. deg.$^{-1}$.

Referring back to Equation 18 we may then write for the free-energy change and equilibrium constant for this reaction at 100°

$$-RT \log K_p = \Delta F_{373} = \Delta H_{373} - T\Delta S_{373} = 32{,}100 \text{ cal.} \qquad (25)$$

Solving for the equilibrium constant we obtain

$$K_p = p_{O_2}\, p_O/p_{O_3} = 1.5 \times 10^{-19} \qquad (26)$$

where the partial pressures are in atmospheres. For 5% ozone we obtain for the partial pressure of monatomic oxygen at 100° and 1 atm. total pressure

$$p_O = (0.05/0.95)\, K_p = 7.9 \times 10^{-21} \text{ atm.} \qquad (27)$$

This partial pressure corresponds to a very small concentration of monatomic oxygen, of the order, indeed, of considerably less than a molecule per cubic centimeter. Nevertheless, we need have no hesitation on this score in taking the figure as giving the true time average corresponding to the monatomic oxygen present, and using it for calculating the number of collisions between monatomic oxygen and ozone.

b. **Calculation of Number of Collisions between Monatomic Oxygen and Ozone.**—The number of collisions between ozone molecules and oxygen atoms per cubic centimeter per second may now be calculated from the kinetic theory expression

$$Z = 1.679 \times 10^{52}\, C_1C_2\sigma_{12}^2T^{\frac{1}{2}}\sqrt{(M_1 + M_2)/M_1M_2} \qquad (28)$$

where σ_{12} is the sum of the radii of the two different kinds of molecules, and C_1 and C_2 are their concentrations in moles per cubic centimeter. For σ_{12}, which is the sum of the radii of an ozone molecule and an oxygen atom, we shall use the value 3×10^{-8} cm., which is practically the same as Chapman's[16] value 2.93×10^{-8} for the sum of the radii of two oxygen molecules.

Substituting in Equation 28 we obtain

$$\begin{aligned}Z &= 1.679 \times 10^{52}\,\frac{0.05}{82.07 \times 373}\,\frac{7.9 \times 10^{-21}}{82.07 \times 373}\,(3 \times 10^{-8})^2(373)^{\frac{1}{2}}\sqrt{\frac{48 + 16}{48 \times 16}}\\ &= 3.6 \times 10^7 \text{ collisions per cc. per sec.} \qquad (29)\end{aligned}$$

c. **Comparison of Number of Collisions and Number of Reactions.**—We may now

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[15] Ref. 13, p. 464.

[16] Chapman, *Phil. Trans. Roy. Soc.*, **216A,** 347 (1916).

compare this figure with the number of reactions occurring under the same conditions between ozone molecules and oxygen atoms which will be given by the expression

$$Z_{\text{React.}} = \tfrac{1}{2}k_2 C_{O_3}{}^2 \, N \tag{30}$$

where k_2 is the specific second-order rate at 100°, N is Avogadro's number, and the factor $^1/_2$ enters because in all, two molecules of ozone are used for each such reaction. Taking the specific rate k_2 at 100° as having the value 1.5×10^2 cc. moles^{-1} sec.$^{-1}$ and substituting in Equation 30 we then obtain

$$\begin{aligned} Z_{\text{React.}} &= \tfrac{1}{2} \times 1.5 \times 10^2 \times (0.05/82.07 \times 373)^2 \times 6.06 \times 10^{23} \\ &= 1.2 \times 10^{14} \text{ reactions per cc. per sec.} \end{aligned} \tag{31}$$

Comparing Equations 29 and 31, we thus see that the number of collisions would be too small by a factor of more than 10^6 to permit us to account for the decomposition of ozone on the basis of the Jahn mechanism.

To obtain a large enough number of collisions to make the Jahn mechanism possible we should have to assume that reaction between ozone and monatomic oxygen could be induced by an approach of the two molecules to a distance of 5.5×10^{-5} cm., or to assume that the free-energy value in Equation 25 is in error by +11,100 cal.

12. Summary

The temperature coefficient of the thermal decomposition of ozonized oxygen has been measured at one atmosphere's pressure using five temperatures in the range 148 to 179°.

The rate of decomposition may be expressed as a function of the temperature at *one atmosphere* pressure by the empirical equation $-dC/dt = 2.04 \times 10^{20} \, e^{-30,900/RT} \, C^2$.

The rate under the same conditions may also be expressed by the equation $-dC/dt = (5.89 \times 10^{13}/C_{O_2}) T^{\frac{1}{2}} \, e^{-29,600/RT} \, C^2$, and this equation will also give reasonable values at total pressures other than one atmosphere.

It has been shown by calculation that the Jahn mechanism of ozone decomposition would require more collisions between ozone molecules and oxygen atoms than could actually occur and hence cannot be regarded as tenable, at least in its original simple form.

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