as for the unknown. An amount of mercuric sulfate, free from mercurous ion, approximately equal to that in the unknown should be added to the blank before heating. Mercuric ion in considerable amount tends to cause a slight decomposition of ceric sulfate in hot solution.

The experiments in Table I show that mercurous ion is quantitatively oxidized to mercuric ion provided that a large excess of ceric salt is used, that the acidity of the solution is not too great and that the oxidizing agent is allowed to act in hot solution for thirty to sixty minutes. A moderate amount of perchloric acid causes no interference but nitric acid produces a slight effect. A large amount of mercuric ion does not interfere if a blank correction is made for its slight action on ceric sulfate in hot solution.

Summary

An accurate method has been developed for mercurous mercury, based upon its oxidation in hot sulfuric acid solution by excess ceric sulfate and titration of the excess electrometrically with standard ferrous sulfate. Mercuric ion in large amount does not interfere.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. XI. THE QUANTUM EFFICIENCY OF OZONE FORMATION IN THE FLUORITE REGION

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The photochemistry of the range of wave lengths below those transmitted by quartz has received scant attention. The difficulty of obtaining monochromatic radiation of sufficient intensity to produce measurable chemical effects in this region of the spectrum is great. In a recent article the photochemical decomposition of ammonia was studied in the fluorite region.[1] By a comparison of the rate of ozone formation with the rate of decomposition of ammonia under the influence of those wave lengths transmitted by fluorite but not by quartz, it was possible to calculate the quantum efficiency of the latter reaction by making the following assumptions: (1) that the photochemical decomposition of ammonia is represented by the equation $2NH_3 = N_2 + 3H_2$; (2) that the absorption of ammonia is identical with that of oxygen in this range of wave lengths; (3) that two molecules of ozone are formed per quantum of radiation absorbed by oxygen. With these assumptions it was possible to show that the average quantum efficiency of ammonia decomposition is about 0.7 for the approximate spectral region 150mμ to 190mμ.

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[1] Kassel and Noyes, THIS JOURNAL, **49**, 2495 (1927).

Since the publication of this work, additional confirmation has been received for the validity of the second assumption.[2] The validity of the first assumption is not so certain,[3] since some of the decomposition products may not appear in the gas phase. The possible formation of hydrazine as an intermediate product hardly offers a satisfactory explanation of the discrepancy.[1,4] The quantum efficiency would, therefore, be slightly higher than 0.7.

The present research was undertaken with the object of investigating the validity of the third assumption, namely, that two molecules of ozone are formed from oxygen per quantum absorbed. The work has been carried out at atmospheric pressure. Since oxygen has a region of continuous absorption below 175mμ,[5] this reaction is a convenient one for measuring light intensities in the range of wave lengths transmitted by fluorite but not by quartz. This investigation, it is hoped, will establish the quantum efficiency of this reaction so that it may be used in the future.

I. Experimental Procedure

The first requisite for the determination of the quantum efficiency of ozone formation is an accurate method of analysis. After a review of the literature and an investigation of the various methods for the quantitative determination of small amounts of ozone,[6] it was decided that the most reliable method was by absorption of the ozone in a solution of potassium iodide. The solutions were acidified and to each one was added a definite quantity of starch freshly prepared each few days. All of the calculations are based on the equation

$$2H^+ + O_3 + 2I^- = O_2 + I_2 + H_2O \qquad (1)$$

Some uncertainty exists as to the exactness of this equation, but it undoubtedly represents the main course of the reaction. In basic solution there may be some simultaneous reaction of the type $I^- + O_3 = IO_3^-$.

The source of radiation was a condensed discharge through hydrogen at a pressure of about 0.1 mm. Current was supplied from the secondary of a 1-kw. transformer with a peak voltage of 30,000. The dimensions of the discharge tube are given in Fig. 1. The electrodes (A) were made of iron. The windows (B) and (C) were of fluorite. The ends of the discharge tube were carefully ground, so that there was little contact between the hydrogen and the picein wax used. A continuous flow of hydrogen was maintained through the discharge tube. Hydrogen was prepared in an ordinary electrolytic gen-

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[2] Bonhoeffer and Farkas, *Z. physik. Chem.*, **134**, 337 (1928).

[3] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926); Mitchell and Dickinson, This Journal, **49**, 1478 (1927); Taylor and Bates, *Proc. Nat. Acad. Sci.*, **12**, 714 (1926); Bates and Taylor, This Journal, **49**, 2438 (1927).

[4] Elgin and Taylor, *ibid.*, **51**, 2059 (1929).

[5] See "Molecular Spectra in Gases," by Kemble, Birge, Colby, Loomis and Page, *Bull. Nat. Research Council*, 11, Part 3, 244 (1926).

[6] Allen, M. S. "Dissertation," University of Chicago, **1929**; *Ind. Eng. Chem., Analytical Edition*, **2**, 55 (1930).

erator and passed continuously over heated platinized asbestos, sodium hydroxide sticks and phosphorus pentoxide before being admitted to the discharge tube through the capillary (D). (F) was attached to a mercury diffusion pump backed by an oil pump. The pressure of hydrogen in the tube remained quite constant.

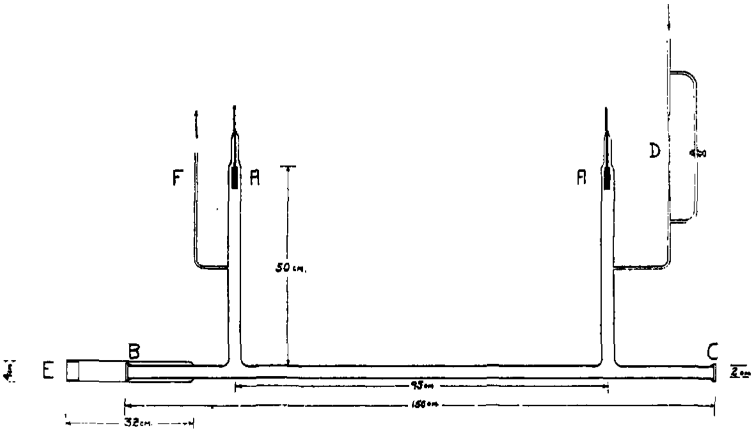

Fig. 1.

The radiation given out by the discharge tube formed a slightly diverging beam. The intensities were measured by means of two different thermopiles, both calibrated by a radiation standard furnished by the Bureau of Standards.

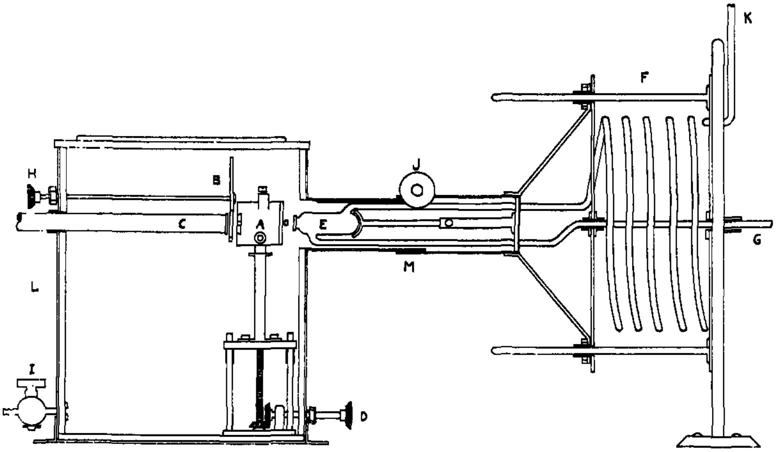

Fig. 2.

One end of the discharge tube (C) projected into the box shown in Fig. 2. This box was constructed of brass and no oil was used on any of the bearings. The box was not, of course, vacuum tight, but it was kept under slight positive pressure of gas transparent to the region of the spectrum under consideration. At first helium was tried, but it was found impossible to purify commercial helium satisfactorily at the rate of flow necessary. Consequently, attempts were made to use hydrogen and nitrogen. After many measurements of absorption in the fluorite region it was found that it was easier to obtain nitrogen of reproducible purity and this gas was used to fill the box in all of the final measurements.

The nitrogen was obtained from a cylinder. It was water-pumped and of 99.7% purity. It was passed first over heated copper turnings, then partially dried by sodium hydroxide sticks and finally passed through a charcoal trap immersed either in liquid air or in carbon dioxide snow and ether. The distance traversed by the radiation through the nitrogen was about 1.4 cm.

The thermopile (A) was fitted with a fluorite window and was arranged so that it could be lowered and raised by turning the handle (D). The reaction vessel (E) was 7.4 cm. in length and 2 cm. in internal diameter. It was arranged so that when the thermopile was lowered it could be moved forward to such a point that the window was the same distance from the discharge tube as the elements of the thermopile. The glass spiral (F) was of such length and flexibility that the reaction vessel could be moved without introducing any rubber tubing into the apparatus. The shutter (B) had three openings. On one was placed a piece of crystal quartz 3 mm. in thickness with the optical axis such that there was no polarization of the radiation traversing it. On the second opening was cemented a piece of optically plane pyrex 3 mm. in thickness. The third opening was left vacant.

The oxygen was streamed through the reaction vessel at various rates. It had already been shown[1] that the amount of ozone formed was independent over quite wide limits of the amount of oxygen passing through the reaction vessel in unit time. This is in agreement with tests made during the present experiments.

The oxygen was passed first over heated platinized asbestos, partially dried by passing over sodium hydroxide sticks and finally passed through a trap immersed in carbon dioxide snow and ether. It entered the reaction vessel through the spiral (F). The tube (G) was attached to two Fischer wash bottles containing either 0.01 or 0.001 *M* potassium iodide and 0.0013 *M* sodium hydroxide.

The first runs (shown in Table I) were made in the following manner: the thermopile (A) was raised to the position shown in Fig. 2 and the intensity of the radiation measured. The discharge tube had been allowed to run until the current through the transformer became constant. The intensity of the radiation transmitted by 1.4 cm. of nitrogen without filter through quartz and through pyrex was determined before each run. The thermopile was then lowered and the reaction vessel (E) moved forward. The oxygen was allowed to pass through the reaction vessel for a definite length of time, the rate of flow being determined by a flowmeter (not shown). Following the run the intensity of the radiation was determined. Good agreement between the initial and final intensity readings was found in nearly every case. The rate of flow of oxygen was varied by a factor of about forty without causing a definite trend in the amount of ozone found.

A definite fraction (50 cc. out of 152 cc.) of the potassium iodide solution from the first wash bottle was acidified with 5 cc. of 0.05 *M* sulfuric acid and 2 cc. of a clear starch solution was added. The mixture was well shaken and allowed to stand for about ten hours. A sample from the second wash bottle was treated in exactly the same manner. In a few cases a third wash bottle was also used. In no case did the solution in the third wash bottle give any test for iodine liberated and usually the amount in the second wash bottle was small.

The intensity of coloration was compared in Nessler tubes with standards made in exactly the same manner except that a carefully measured (by pipet) amount of 2.48×10^{-5} *M* solution of iodine dissolved in potassium iodide was added. These standards were allowed to stand for the same length of time as the unknown.

The fraction of the total radiation absorbed by the oxygen was determined in two different manners. In one the other end of the discharge tube (B) (Fig. 1) was used. The tube at (E) was attached to an iron cylinder by wax. A thermopile was placed in the iron cylinder. The cylinder was evacuated to a pressure of about 10^{-5} mm. by mercury diffusion pumps. Mercury vapor was excluded by a trap immersed in liquid air. The absorptions of nitrogen and of oxygen were determined for a 19-cm. path. In this manner it was found that 3.3% of the radiation was absorbed by oxygen that was not absorbed by nitrogen. The absolute measurement of the amount of radiation seemed to have little significance.

The second method was to replace the reaction vessel by a tube of exactly the same length fitted with fluorite windows at both ends. A thermopile without fluorite windows was placed directly in back of the absorption tube. The tube was evacuated and the deflection measured. The deflection was measured again when the tube was filled with oxygen. When the fluorite window used on the reaction vessel was interposed, three determinations gave 3.0, 3.5 and 3.1 as the percentage decrease in the deflection when the tube was filled with oxygen.

The calculation of the fraction of the incident radiation absorbed can only be made by an indirect method. Let us consider a perfectly parallel beam of radiation. Then we may make the following comparisons, where I represents intensity.

Through oxygen

I_1 Fluorite window I_2 oxygen I_3 Fluorite window I_4

With cell evacuated

I_1 Fluorite window I_2 vacuum I_2 Fluorite window I_5

The fraction $(I_5 - I_4)/I_5$ is measured directly in the experiments. Put $I_1/I_2 = a$, $I_3/I_4 = b$ and $I_2/I_5 = c$. The fraction of the incident radiation absorbed by the oxygen is $(I_2 - I_3)/I_1 = X$. Put $(I_5 - I_4)/I_5 = Y$. We now find that

$$X = [c-(1-Y)b]/ac \qquad (2)$$

The measurement of the quantities a, b and c was accomplished by removing the windows from the absorption cell and determining the absorption of the fluorite when the radiation had traversed nitrogen and the proper length of column of oxygen. In this way it was found that $a = 1.160$, $b = 1.134$ and $c = 1.137$, each value being the average of a large number of readings. Hence

$$X = (1.137 - 0.968 \cdot 1.134)/1.160 \cdot 1.137 = 0.030$$

Table I gives a summary of the data obtained in preliminary runs made by the method described above.

Another series of measurements was made in which the cell used previously to determine the absorption was used as a reaction vessel. Since this cell could not be moved, the light intensity back of the cell (through oxygen) was measured during the run. The procedure for the determination of ozone was the same as that used previously, except that in half of the runs an acid solution of potassium iodide was used in place of a basic solution.

TABLE I

PRELIMINARY DETERMINATION OF QUANTUM EFFICIENCY

Iodine solution, 0.0000248 M. Thermopile, 14.3 ergs/mm.^{2}/sec./cm. Area of window, 154 mm.^{2} Wave length (av.), 175mμ. Fraction absorbed, 0.03

Run	Total cc. of I_2	Length of run, hrs.	Av. defl., cm.	Molecules of O_3	No. of quanta	M/N
1	9.4	3	1.09	1.41×10^{17}	6.92×10^{16}	2.0
2	9.9	3	1.08	1.49×10^{17}	6.85×10^{16}	2.2
3	13.6	4	1.13	2.04×10^{17}	9.57×10^{16}	2.1
4	12.2	3	1.19	1.83×10^{17}	7.56×10^{16}	2.4
5	8.5	3	0.96	1.28×10^{17}	6.03×10^{16}	2.1
						Av. 2.2

Since a different fluorite window was used at the front of the reaction vessel in these experiments, it was necessary to redetermine the absorption. Table II gives the data obtained in making these determinations.

TABLE II

ABSORPTION OF OXYGEN

Defl. av. vacuum, cm.	No. of readings	Defl. av. oxygen, cm.	No. of readings	Fraction $(I_5 - I_4)/I_5$ av.
1.70 (0)	14	1.62 (2)	12	
1.70 (1)	12	1.61 (5)	10	
1.69 (3)	14	1.63 (1)	11	
1.70 (0)	10	1.60 (3)	11	
1.69 (6)	10	1.61 (4)	10	0.048 ± 0.006

By the use of Equation 2 it is found that the fraction of the incident radiation absorbed by the oxygen is 0.044.

Since the radiation intensity is measured back of the cell through oxygen, it is necessary to find the factor by which it must be multiplied to obtain the incident intensity. Since the beam was not perfectly parallel, but diverged somewhat, this factor could not be calculated directly. However, this factor was obtained by removing the reaction vessel and obtaining the ratio of the deflection at 1.4 cm. from the discharge tube to the deflection at 8.8 cm. Eight determinations gave 4.9 as the average ratio. The observed intensity must be multiplied, therefore, by $4.9 \cdot 1.137 \cdot 1.134/0.952$ or 6.64. Direct measurement of this factor gave 6.6.

Table III gives the data obtained in this manner. Absorption of the ozone was carried out in acid (with hydrochloric acid) solution of potassium iodide in the last three runs. It has been shown previously[7] that ozone has an apparently higher oxidizing power in acid solution than in neutral or basic solution. This fact was studied[6] and it was found that within the experimental error 1.25 times as much iodine was liberated when ozone was absorbed in acid solution as when it was absorbed in neutral or basic

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[7] Mellor, "Comprehensive Treatise," Longmans, Green and Co., London, **1922**. Vol. I, p. 905.

solution and then acidified. The number of molecules of ozone obtained by direct calculation in the last three runs in Table III is multiplied by 0.8.

TABLE III

QUANTUM EFFICIENCY OF OZONE FORMATION

Iodine solution, 0.00005 *M*. Thermopile, 2.8 ergs/mm.²/sec./cm. Area of window, 73 mm.² Wave length (av.), 175mμ. Fraction absorbed, 6.64·0.044

Run	Total cc. of I_2	Length of run, min.	Av. defl., cm.	Molecules of O_3	No. of quanta	M/N
6	18.0	395	2.28	5.45×10^{17}	2.88×10^{17}	1.9
7	8.8	272	2.39	2.64×10^{17}	2.07×10^{17}	1.3
8	18.2	385	2.41	5.52×10^{17}	2.96×10^{17}	1.9
9	22.8	355	2.46	5.53×10^{17}	2.78×10^{17}	2.0
10	19.8	325	2.48	4.80×10^{17}	2.57×10^{17}	1.9
11	19.8	300	2.38	4.80×10^{17}	2.28×10^{17}	2.1
						Av. 1.85
					(Omitting second)	Av. 2.0

It is difficult to form a very precise idea of the probable accuracy of the values obtained for the quantum efficiency. The determination of the number of molecules of iodine liberated is undoubtedly the main cause for variation among the various results. On the average these values should be good to better than 10%. The error in the calibration of the thermopile is undoubtedly small compared to other errors. The determination of Y in Equation 2 is somewhat uncertain, but the values used should be accurate to somewhat better than 10%. The quantities a, b and c in Equation 2 are of importance; a and c are each known with a probable error not exceeding 1%, but small errors in c and b would produce a relatively large error in X. These values were carefully determined and when all the factors entering into Equation 2 are considered, it is probable that the value of X is accurate to within 15%.

It seems safe to state that the quantum efficiency of ozone formation for radiation transmitted by fluorite is 2.0 ± 0.3.

It should be pointed out that the error in choice of the average wave length of the active radiation is certainly small compared to other errors. It is recognized that the quantum efficiency is not obtained for monochromatic radiation. A discussion of the possible effect of change of wave length will be given in the next section. However, since no lenses were used errors due to such factors as chromatic abberration are negligible.

Using a different type of discharge, Kassel and Noyes[1] showed that approximately 3.5 times as much ozone is formed when fluorite windows are used as with quartz. One attempt was made in these experiments to determine the amount of ozone formed by radiation transmitted by quartz, but the inaccuracies in the determination of the ozone and in the measurement of the light absorption were so great that the matter was not pursued further. Since absorption would not be complete (about

15%[8] for the shortest wave length transmitted by quartz) whereas no greatly increased absorption was observed for a 19-cm. path, it seems probable that a very large fraction of the radiation absorbed in these experiments lies below the limit of transmission of quartz. Except for certain isolated bands, nitrogen is quite transparent to the region of the spectrum under consideration. There are several bands near 170mμ and stronger bands at 145mμ.[9] The limit of transmission of the nitrogen is probably determined by the impurities it contains. The fluorite used transmitted to about 140mμ. The probable limits of the spectrum involved in the above experiments are from about 190mμ to somewhat less than 170mμ.

II. Theoretical Discussion

It has been shown that the oxygen molecule is normally in a $^3\Sigma$ level and that this is the ground level for both the atmospheric absorption bands and the Schumann–Runge bands.[10] The interpretation of the atmospheric absorption bands is now quite satisfactory[11] and is found to involve a $^3\Sigma - {}^1\Sigma$ transition. The $^1\Sigma$ level lies only 1.62 volts above the normal level and combines with it exceedingly weakly. To all intents and purposes oxygen at ordinary pressures and thicknesses is practically completely transparent to radiation of wave lengths found in the atmospheric absorption bands.

The Schumann bands are found to involve in all probability a $^3\Sigma - {}^3\Sigma$ transition.[12] They involve, in absorption, a transition from the normal to a 6.09-volt electronic level. The convergence limit of this series of bands occurs at 175.1mμ, or a little over 7 volts. Dissociation of the molecule should, therefore, be brought about by radiation of wave length shorter than this value. The products of dissociation should be one normal and one excited atom. The exact state in which this excited atom will leave the molecule is uncertain[13] but it may lie between 1.5 and 2.0 volts above the normal level.[14] Due to the fact that no exact determination of the heat of dissociation of oxygen by calorimetric methods has been made, this level cannot be calculated indirectly.

[8] See "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. V, p. 269.

[9] Hopfield, *Phys. Rev.*, **31**, 1131 (1928).

[10] Ossenbrüggen, *Z. Physik*, **49**, 167 (1928).

[11] Mulliken, *Phys. Rev.*, **32**, 880 (1928); Giauque and Johnston, THIS JOURNAL, **51**, 1436, 3528 (1929).

[12] See Mulliken, *Phys. Rev.*, **32**, 213 (1928).

[13] The earlier idea that the atom was in an energy level differing by only a few hundredths of a volt from that of the normal atom has since been shown to be very doubtful. *Cf.* "Molecular Spectra in Gases," Kemble, Birge, Colby, Loomis and Page, *Bull. Nat. Res. Council*, Vol. XI, Part 3, No. 57 (1926).

[14] See Kaplan, *Phys. Rev.*, **31**, 1126 (1928); Herzberg, *Z. physik. Chem.*, **4B**, 223 (1929).

In the range of wave lengths longer than the convergence limit, excited molecules in a $^3\Sigma$ state are produced by absorption of radiation. Ozone is, however, produced in this region of the spectrum. Warburg[15] has studied the quantum efficiency of ozone formation at relatively high pressures at 207mμ and 253mμ and finds values of about 2 at about 47 atmospheres, becoming lower at higher pressures. The quantum efficiency is lower at the longer wave length.

In view of the present knowledge of band spectra the primary process in the region of the Schumann bands at wave length greater than 175mμ is the production of an excited molecule and this may be followed by some such reaction as

$$O_2' + O_2 = O_3 + O \qquad (3)$$

A second molecule could be produced by the reaction

$$O_2 + O = O_3 \qquad (4)$$

However, this latter reaction, in accord with well recognized principles, can only take place as the result of triple collisions or on the walls, since otherwise the molecule would still possess energy adequate to produce redissociation. Similarly, the reaction

$$O + O = O_2 \qquad (5)$$

could only take place in this fashion. Enough is not known to permit an adequate calculation of the relative probabilities of Reactions 4 and 5, but unless the light intensity were exceedingly great the chance of Reaction 5 would be small. Also, the formation of ozone by Reaction 4 would be less exothermic than Reaction 5, so that the probability of its occurrence would be greater. Hence it would not be surprising if two molecules of ozone were produced by wave lengths longer than the convergence limit.

In the region of continuous absorption below the convergence limit, two oxygen atoms, one of which is excited, are produced. There are now several possibilities. The normal atom may undergo Reaction 4 by triple collision. The excited atom may lose its energy by radiation and subsequently undergo Reaction 4. In this event the quantum efficiency would be two in this region of the spectrum. If the energy of the excited atom is sufficiently large, it might lose its energy to an oxygen molecule by a collision of the second kind, thereby raising the latter to some higher vibration state of either the normal or the 1.62 electron level. In either event the excited molecule produced could not undergo Reaction 3. As a result of a triple collision with molecules in higher vibration states it might undergo the reaction

$$O_2'' + 2O_2 = 2O_3 \qquad (6)$$

Since the production of two molecules of ozone from three molecules of oxygen involves the absorption of energy corresponding to about 2.5 volts,

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[15] Warburg, *Z. Elektrochem.*, **27**, 133 (1921). See Wulf, THIS JOURNAL, **50**, 2596 (1928), for a discussion of the possible relationship of this work to the existence of O_4.

the two oxygen molecules in the normal state must possess an energy of 2.5 − E_1 volts, where E_1 represents the energy of the molecule O_2'' above the normal. Since E_1 is not known, it is impossible to make any definite statement in this connection. Reaction 6 must not be considered as impossible, however.

Still one other possibility may be mentioned. Since Reaction 4 is exothermic and can occur only as the result of triple collisions, the third molecule involved may be raised to a higher vibration or electronic level. However, since the energy available by Reaction 4 only slightly exceeds 1 volt, this possibility would seem to be of small importance.

As a result of these considerations we see that the quantum efficiency of ozone formation to be expected from theoretical consideration agrees with experiment well within the experimental error. A value slightly greater than two would not be impossible.

Eucken[16] has studied the formation of ozone by short wave length radiation and finds a negative temperature coefficient. This effect is particularly noticeable at low oxygen pressures. Eucken attempts to explain this phenomenon by assuming that the mean life of activated molecules in high rotation states is shorter than when the rotational quantum number is less. Another effect may also be of importance. The oxygen atoms produced by Reaction 3 may have time to diffuse to the walls and be removed before undergoing the triple collision necessary for Reaction 4. This effect would be particularly noticeable at low pressures. Since third order reactions have, in general, negative temperature coefficients, the necessary triple collisions might occur more often at low temperatures. In the region of continuous absorption the temperature coefficient should be unity unless the effect of the walls in removing the oxygen atoms is of importance. Since this removal process may be more important at low than at high temperatures, this effect cannot be neglected.

Summary

1. Approximately two molecules of ozone are formed per quantum absorbed by oxygen in the fluorite region.

2. A short theoretical discussion is given. The value found is in agreement with theory, although a slightly higher value would not be impossible.

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[16] Eucken, *Z. physik. Chem.*, **107**, 436 (1923).