[3] Mortimer, *J. Amer. Chem. Soc.*, **44**, 1416 (1922); **45**, 633 (1923).

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[5] Dorfman, M., and Hildebrand, J. H., *Ibid.*, **49**, 729 (1927).

[6] Cf. Hildebrand, J. H., and Glasscock, B. L., *Ibid.*, **31**, 26 (1909).

[7] Porter, A. W., *Trans. Faraday Soc.*, **16**, 336 (1921).

[8] Cf. Ref. 2, p. 48.

[9] Taylor, N. W., *J. Amer. Chem. Soc.*, **45**, 2865 (1923).

[10] Hildebrand, J. H., and Eastman, E. D., *Ibid.*, **37**, 2459 (1915); cf. also Ref. 2, pp. 64–65.

[11] Biron, E., *J. Russ. Phys. Chem. Soc.*, **44**, 1264 (1912).

[12] See, for example, Ref. 2, pp. 146, 161, 194.

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THE THERMAL DECOMPOSITION OF OZONE

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The kinetics of ozone decomposition possess considerable importance and interest, and much experimental work has been done both on the thermal and the photochemical change. The thermal decomposition has, however, proved bothersome to control experimentally. The authors have been engaged for some time in an investigation of this reaction, and the results of the work are embodied in three articles soon to appear elsewhere. The purpose of this paper is to give a résumé of the work, stating the results and mentioning briefly the most important characteristics of this reaction.

Remarkable discrepancies existed in the results of the seven or more earlier researches. A substantial part of the present task was, therefore, to survey critically this work, and the conclusions finally arrived at come from a consideration of both our own experimental results and the results of earlier investigators.

The thermal decomposition can be made to take place homogeneously at 100° and above in pyrex and in certain other glasses. This appears to be established by the work of Warburg[1] and in particular of Clarke and Chapman[2] as well as from our own results in reaction vessels of different surface to volume ratio. Under certain conditions, reaction at the walls of the container may take place to a considerable extent, as seems probable from the work of Perman and Greaves[3] and of Griffith and McKeown.[4]

The homogeneous decomposition can be carried out so as to be very

closely of the second order with respect to ozone. The earlier careful researches of Warburg and of Jahn[5] showed this. The work of Clarke and Chapman and of Chapman and Jones[6] is in agreement with it. In contrast, however, are the results of Perman and Greaves and also of Griffith and McKeown, who found that the calculated second-order coefficient increased as the reaction progressed. In neither of these cases does it seem certain, however, that the cause was reaction at the walls. In our own work, in eleven experiments made under the most favorable conditions of gas purity, the second-order character is closely adhered to. In other of our experiments, under less favorable conditions, cases were found in which the calculated second-order coefficient varied markedly as the reaction progressed.

The specific rate for different samples of the gas, all of which decompose in accordance with the second order may, nevertheless, vary quite markedly. Thus, in the results of six of our experiments made with the same kind of ozone, the mean deviation from the mean of the specific rate was about 12% of the mean value. Similarly in the results of eight runs recorded by Warburg deviations of approximately the same order were observed. These deviations are apparently greater than could be caused by the errors in the experimental measurements. It appears, in general, that ozone decomposition is very susceptible to the accelerative influence of small amounts of catalytic impurities, although if the cause of the deviations here mentioned is the presence of catalytic impurities, it is rather remarkable that the order remains so nearly the second over the larger portion of the complete decomposition. From the many results in which the reaction has been observed to proceed according to the second order an idea of the numerical value of the specific rate may be obtained. If there is a true second-order rate for pure ozonized oxygen, it has at 100°C. and 1 atmosphere total pressure a specific rate as low as 1.5–1.7×10^2 cc./(mol. sec.).

During the decomposition of the ozone in the common ozonized oxygen of low per cent ozone the total pressure increases only slightly, and is for most purposes practically constant. When, however, the total pressure is materially altered, in other ways, the specific second-order rate is found to change. For ozonized oxygen, which decomposes in accordance with the second order, the specific rate is closely inversely proportional to the total pressure. This was originally demonstrated by Jahn and this influence of total pressure has been observed by others including ourselves.

For this rather surprising fact two possible explanations present themselves. (1) The decomposition of ozone is inhibited by oxygen, the specific second-order rate being inversely proportional to the concentration of oxygen. This hypothesis was believed by Jahn to be true, and was the fact used by him to support the particular mechanism which he proposed

for ozone decomposition.   This mechanism attributed ozone decomposition to the reaction of molecular ozone with atomic oxygen, the latter, with molecular oxygen, being in thermodynamic equilibrium with molecular ozone.   (2) The decomposition of ozone is inhibited by some unknown negative catalyst present in ozonized oxygen and the specific second-order rate is inversely proportional to the concentration of this negative catalyst, so that the specific rate is inversely proportional to total pressure.

Experiments on the effect of total pressure are clearly not sufficient to differentiate between these two hypotheses.   Jahn and Chapman and Jones had each made some measurements that were sufficient in principle to distinguish.   The results, however, were contradictory; those of Jahn indicating an inhibiting effect due to oxygen closely proportional to its concentration, while those of Chapman and Jones showed oxygen to possess at the most only a small inhibiting effect.   The question as to which of these two hypotheses was in reality correct was thus left unanswered. During the present investigations experiments have been made attempting particularly to answer this question, and the results have led to the conclusion that the decrease in the specific second-order decomposition rate which accompanies increase in the total pressure of oxygen-ozone mixtures is due to the inhibiting effect of oxygen on the decomposition.

In general, oxygen is liable to contain positive catalyst for the decomposition.   Different samples of oxygen show different degrees of ozonizability in an electric discharge ozonizer, and there is a tendency for high ozonizability to be correlated with low specific second-order decomposition rate. By electrolysis under suitable conditions from sulphuric acid, oxygen and ozone can be prepared which contain either no catalyst for ozone decomposition or at least a nearly constant amount.

Finally, in the present investigations, the temperature coefficient[7] of the rate of this decomposition has been measured at one atmosphere total pressure, using five temperatures in the range 148–179°C.   The rate of decomposition may be expressed as a function of the temperature at *one atmosphere* pressure by the equation

$$-\frac{dC}{dt} = 2.04 \times 10^{20} \, e^{-\frac{30,900}{RT}} \, C^2.$$

The rate under the same conditions may also be expressed by the equation

$$-\frac{dC}{dt} = \frac{5.89 \times 10^{13}}{C_{O_2}} \, T^{\frac{1}{2}} \, e^{-\frac{29,600}{RT}} \, C^2$$

and this equation will also give reasonable values at total pressures other than one atmosphere.

These equations are to be regarded as purely empirical expressions. If, however, it be assumed that the decomposition actually occurs in ac-

cordance with the mechanism proposed by Jahn, the temperature coefficient leads to a value for the heat of dissociation of ozone into molecular oxygen and atomic oxygen. Calculating by thermodynamic methods the concentration of monatomic oxygen at $100°$ and 1 atmosphere pressure in 5% ozone, and by kinetic theory methods the number of collisions between molecular ozone and atomic oxygen, it has been shown that these collisions are many times too small in number to account for the observed rate and hence that the Jahn mechanism cannot be regarded as tenable, at least in its original simple form.

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

[3] Perman and Greaves, *Proc. Roy. Soc.*, A80, 353 (1908).

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

[5] Jahn, *Zeit. anorg. Chemie*, 48, 260 (1905).

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

[7] Earlier observations of the influence of temperature on the specific rate had been made by Warburg (loc. cit.); Clement, *Ann. Physik*, 14, 341 (1904); and Perman and Greaves (loc. cit.); and recently by Belton, Griffith and McKeown, *J. Chem. Soc.*, 129, 3153 (1926).

CONCERNING POINTS OF A CONTINUOUS CURVE THAT ARE NOT ACCESSIBLE FROM EACH OTHER

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The purpose of this paper is to establish the following theorem:

THEOREM. *If A and B are two distinct points of a continuous curve M and every simple continuous arc from A to B contains at least one point of M distinct from A and from B then there exists a simple closed curve which is a subset of M and which separates A from B.*

Proof. By a theorem due to Schoenflies,[1] A and B do not both belong to the boundary of the same complementary domain of M. Suppose that A does not belong to the boundary of the unbounded complementary domain of M. Let C denote a circle with center at A and not containing or enclosing B. Since M is regular there exists a circle C_1 with center at A and such that any point of M within C_1 can be joined to A by an arc of M lying within C. There are not[1] more than a finite number of complementary domains of M having A on their boundaries and containing points without C_1. If there be any, let $D_1, D_2, D_3, \ldots, D_n$ denote them, let $T_1, T_2, T_3, \ldots, T_n$ denote their respective boundaries and let H denote