In 1916 A. L. Caulkins and the writer began an investigation of the dual rôle of hydrogen peroxide as an oxidizing agent and as a reducing agent. The reactions considered were the oxidation of iodine to iodic acid, and the reduction of iodic acid to iodine, viz.:

\[ 5\text{H}_2\text{O}_2 + \text{I}_2 = 2\text{HIO}_3 + 4\text{H}_2\text{O} \quad (1) \]

and

\[ 5\text{H}_2\text{O}_2 + 2\text{HIO}_3 = 5\text{O}_2 + \text{I}_2 + 6\text{H}_2\text{O}, \quad (2) \]

both of which, it is to be noted, involve the iodic acid-iodine oxidation-reduction "couple." This couple was chosen because we expected that, under suitable conditions, it would catalyze the decomposition of hydrogen peroxide:

\[ \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \frac{1}{2}\text{O}_2. \quad (3)^1 \]

In other words, we hoped to find in this case an intimate relationship between the dual rôle of hydrogen peroxide as oxidizing and reducing agent and the catalytic decomposition of the hydrogen peroxide. These expectations were based upon free energy calculations for the above reactions; by means of the free energy data of Lewis and Randall\(^2\) we calculated that the decreases in free energy for Reactions 1 and 2 are large and approximately equal, and that the free energy decrease per mol of \(\text{H}_2\text{O}_2\) consumed in each of these reactions is therefore approximately equal to that in Reaction 3. Accordingly all three reactions have a marked tendency to take place; and our experimental problem was to determine what actually happens under a variety of experimental conditions. Detailed experimental results will not be presented in the present paper, since its purpose is merely to describe an interesting phenomenon which was first observed in the summer of 1917 just before the close of Caulkins' work.

We had at that time found: that Reaction 1\(^3\) is markedly autocatalytic and proceeds rapidly in solutions which contain iodate and a moderately high concentration of acid; that, on the other hand, Reaction 2 proceeds relatively slowly even under the most favorable conditions.

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1 The sum of Equations 1 and 2 is ten times Equation 3.
2 Lewis and Randall, This Journal, 36, 1912, 2268 (1914). \(F_{\text{o}2\text{ss}}\) values are: \(\text{H}_2\text{O}(l)\) —56,620 cal.; \(\text{H}_2\text{O}(aq)\) —30,970 cal.; \(\text{IO}_3^-\) —32,270 cal. \(\Delta F_{\text{o}2\text{ss}}\) values were calculated: Reaction 1, —136,170 cal.; Reaction 2, —120,330 cal.; Reaction 3, —25,650 cal.
3 Credit for the discovery of Reactions 1 and 2 belongs to Auger, Compt. rend., 152, 712–3 (1911); 153, 1005–7 (1911).
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(very low hydrogen-ion concentration); and that in all cases more hydrogen peroxide disappears than would correspond to Equation 1 or 2. From the last result we concluded that these reactions were accompanied by catalytic decomposition of hydrogen peroxide, Reaction 3.

Catalytic decomposition alone occurs when iodate is present with the hydrogen peroxide, and the hydrogen-ion concentration is moderately high. At 60° after a short induction period this reaction takes place rapidly and smoothly; its rate is proportional to the concentration of hydrogen peroxide and of iodate ion, and is but little affected by the concentration of hydrogen ion above about 0.2 N. Curve IV, Fig. 1, represents a typical experiment, and shows after about 7 minutes (the induction period) a steady increase in the volume of the oxygen with the time. A faint but permanent coloration due to iodine was observed. In this experiment the initial concentrations were $\text{H}_2\text{O}_2$, 0.190 $M$; $\text{KIO}_3$, 0.094 $M$; $\text{H}_2\text{SO}_4$, 0.055 $N$; II, 0.078 $N$; III, 0.0916 $N$; IV, 0.110 $N$; temp. 60°.

![Graph](image-url)
and $\text{H}_2\text{SO}_4$, 0.110 $N$; the volume of the solution used was 46 cc., and the theoretical volume of moist oxygen, measured at 25°, was 110 cc. Super-saturation of oxygen was prevented by the usual precaution of rapid shaking. The reaction mixture was exposed to the diffused light of the laboratory.

Curve I represents the result obtained in a similar experiment at a low concentration of hydrogen ion: 0.055 $N$ $\text{H}_2\text{SO}_4$ instead of 0.110 $N$. The rate of evolution of oxygen is very low, and after 60 minutes is not as high as in the preceding experiment at the end of 7 minutes. It would seem that the state of affairs is similar to that in the induction period in the catalysis experiment. Iodine formation was noted in this experiment (No. 1) and the depth of color of the solution slowly increased with time. In experiments at considerably lower concentrations of hydrogen ion the rate of formation of oxygen was also very low, but the rate of formation of iodine (Reaction 2) was greater; solid iodine ultimately formed. When we recall the small concentration of iodine present in the catalytic reaction it becomes extremely probable that its slow formation is one of the determining factors in the induction period phenomenon.

Curves II and III represent the results obtained in two experiments exactly similar to the preceding, but with intermediate concentrations of acid, 0.073 and 0.0916 $N$ $\text{H}_2\text{SO}_4$. While initially the rate of formation of oxygen is small and the same as the two preceding experiments, and the lengths of the induction period, approximately 18 and 12 minutes, respectively, show the expected decrease with increasing acid concentration, the remaining portions of the curves present a new phenomenon—periodicity. Although the smooth curves through the experimental points are drawn necessarily in a somewhat arbitrary manner, their actual shape cannot differ materially from that shown. It is certain that the evolution of oxygen is a periodic phenomenon. Each period is represented by (1) a relatively flat portion of the curve followed by (2) a nearly vertical portion. The first corresponds to a slow evolution of oxygen, and in this region the iodine color was observed to deepen slowly with time; the analogy with the induction period is obvious. The second portion corresponds to a very rapid evolution of oxygen, and this was observed to be practically coincident with a rapid fading of the iodine color. The regularity of the periods is evident; Curve III shows 7, the length of each being between 3 and 3.5 minutes, while Curve II shows 4 with the length of each increasing gradually from 10 to 13 minutes.

The only factor varied in the four experiments (Curves I to IV) is the concentration of sulfuric acid, and the total change in this concentration is only 2-fold. There is a gradual increase in the average rate of formation of oxygen, but the most striking feature of the transition is in
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the nature of the periodicity: at 0.055 N acid no periodicity is encountered within 60 minutes, at 0.070 N acid there are periods 10 to 13 minutes in length, at 0.0916 N acid periods 3 to 3.5 minutes in length, and at 0.110 N acid there is pure catalysis and no detectable periodicity. In the last case, however, the nature of the transition forces the conclusion that Curve IV (after the short induction period) really consists of a large number of very short periods, and that the apparently smooth catalysis by the iodic acid–iodine couple consists in the simultaneous oxidation and reduction of the hydrogen peroxide. There is then a stationary state or dynamic equilibrium, involving iodic acid and iodine, at any instant in the catalytic decomposition of the hydrogen peroxide. The phenomenon of periodicity demonstrated by Curves II and III is of course an exceptional feature, characteristic of this particular case, but the gradual transition to a typical example of catalysis in homogeneous solution furnishes striking evidence in favor of the intermediate reaction theory of catalysis,—which has long been accepted, at least for homogeneous reactions, by all investigators working in this field. It may be well to add, since confusion frequently arises with regard to the interpretation of experimental evidence in this field, that Reactions 1 and 2 undoubtedly take place in steps, and that these two reactions alone cannot therefore constitute the mechanism of the catalytic decomposition of hydrogen peroxide in this case.

While several examples of heterogeneous periodic reactions are known, and one example of periodic gas evolution due to supersaturation at regular intervals, the writer believes the present example to be the first instance of a periodic reaction in homogeneous solution. The possibility of such periodicity had, however, been appreciated. Lotka and Hirniak independently examined the problem; each assumed a definite mechanism for a hypothetical reaction, set up differential equations for the various intermediate reactions, and by a mathematical analysis set up conditions sufficient to account for periodicity. In Lotka's example the autocatalytic character of the second of a series of three successive

1 Cf., for example, Bray, Z. physik. Chem., 54, 463 (1906); Abel, Z. Elektrochem., 19, 933 (1913).

Another interesting example of evidence in favor of the intermediate reaction theory is furnished by Abel's work on the iodide-iodine catalysis of hydrogen peroxide, Z. Elektrochem., 14, 598 (1908).

2 Cf., for example, Bredig and Weinmayr, Z. physik. Chem., 42, 601 (1903); Bredig and Antropoff, Z. Elektrochem., 12, 585 (1906).


reactions is an essential feature of the assumed mechanism, and it seems possible that an explanation of the present case might be found along these lines. Reaction 1 is strikingly autocatalytic, as has already been mentioned; and it will be shown below that Reaction 2 is autocatalytic in some degree. However, until further experimental evidence has been presented, the writer prefers not to discuss possible mechanisms.

In the preceding the assumption has been made that we are dealing with a homogeneous reaction, in spite of the fact that oxygen gas is being evolved. This assumption was considered justifiable because no evidence has ever been obtained that oxygen gas influences the rate of decomposition of hydrogen peroxide.1

However, in order to obtain evidence on this point, Dr. H. E. Miller and the writer have continued the investigation at a lower temperature 25°, and under conditions in which in general the oxygen is evolved so slowly that it diffuses out of the solution without the formation of bubbles. The concentration of iodine in the solution was determined by a colorimetric method; and, except in the first experiments, we have also determined the concentration of hydrogen peroxide. The iodine color can easily be seen to deepen and fade in a solution free from gas bubbles, and any doubt about the occurrence of periodicity in homogeneous solution is thus removed.

A sample run is shown in Fig. 2, in which the concentration of iodine in mols × 10⁴ per liter is plotted against time in days. The initial concentrations were H₂O₂, 0.0327 M; and HIO₃, 0.0090 M; in this preliminary experiment a commercial sample of 3% hydrogen peroxide was used, which contained an unknown preservative, some sulfuric acid and an appreciable amount of hydrochloric acid; the reaction mixture was at rest in a thermostat at 25° but was exposed to the diffused light

1 Spear, This Journal 30, 195 (1908).
of the laboratory. Later work has shown the marked influence of the following factors which previously had not been considered: a trace of chloride, light, and the presence of a suspended solid; and our present experiments are being conducted in the dark, without agitation, with pure materials and in solutions free from turbidity. Evidence of periodicity has been obtained under these conditions for suitable concentrations of iodate and acid, although the curves obtained differ in appearance from that shown in Fig. 2. Accordingly Fig. 2 is presented merely as a demonstration of periodicity.

The gradual formation of iodine in the first 8 days corresponds to the induction periods in the experiments shown in Fig. 1; the curvature towards the ordinate axis proves that this reaction (No. 2) is somewhat autocatalytic. The remaining portions of the curve show 6 periods, the lengths of which decrease gradually from 4 to 2 days. The rate of formation of oxygen is most rapid in the region of maximum concentration of iodine and during the rapid decrease in the iodine concentration.

That the decomposition of hydrogen peroxide, Reaction 3, is an important phase of the phenomenon, was shown by determining the concentration of hydrogen peroxide at the end of the run. After 29 days the concentration of hydrogen peroxide was found to have decreased from 0.0327 M to 0.0022 M, i.e., the decrease was 0.0305 mols per liter, or about 93%. From Fig. 2, by summing the increases and decreases in iodine concentration and assuming that 5 mols of hydrogen peroxide disappeared for each mol of iodine, it was found that the total decrease in the concentration of hydrogen peroxide corresponding to Reactions 2 and 1 was only 0.0104 mols per liter, or approximately \( \frac{1}{3} \) of the total decrease. The rate of decomposition of hydrogen peroxide in a 0.009 N acid solution at 25° is relatively slow, and therefore much of the remaining decrease, 0.0201 mols per liter, must be due to decomposition accompanying Reactions 1 and 2. In other words, these reactions may be said to catalyze this decomposition.

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