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Kinetics of the uncatalyzed, alkaline decomposition of hydrogen peroxide

Trice Walter Haas
Iowa State University

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KINETICS OF THE UNCATALYZED, ALKALINE DECOMPOSITION
OF HYDROGEN PEROXIDE

by

Trice Walter Haas

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1960

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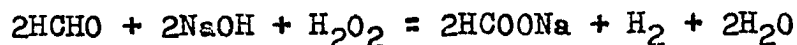
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I. INTRODUCTION

The chemistry of hydrogen peroxide has been the subject of many studies. A good summary of the work done up to the year 1955 can be found in the book by Schumb, et al. (24). Because of the large number of available references that are related to the present work no attempt at completeness will be made. A summary of the most closely related work follows.

One of the earliest measurements of the rate of any reaction was the investigation by Thenard into the rate of the decomposition of hydrogen peroxide in the presence of alkalis carried out around the year 1818 (17, p. 1). Little attempt was made to interpret the data obtained.

Burki and Schaaf (5) investigated the influence of the different components on each other in the analysis of HCHO according to the reaction:



Their experiments on the influence of alkalis on the decomposition of H_2O_2 led them to believe that the decomposition is first order with respect to H_2O_2 . The velocity also increased with increasing alkali concentration but not linearly. KOH was found to catalyze the reaction more than NaOH. The rate of the decomposition was found to increase with temperature. No wide varying of the (OH^-) appears to have been carried out.

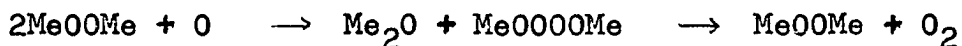
C. Pana (19) has also studied the base catalyzed decomposition of hydrogen peroxide. His work was carried out in glass, silica and wax lined glass vessels. He ascribes any decomposition in the wax vessels to dust. The range of hydroxide ion concentrations studied was rather low. The work was done at two temperatures, 40 and 50°C, the rate being greater at 50°C. No order of peroxide or rate equation was given. He stresses the extreme sensitivity of the reaction to catalysis by trace impurities.

In his study of this reaction Dorfelt (8) has found a maximum in the rate of the decomposition with increasing concentration of NaOH. At 25°C this maximum comes with 0.6 g/l of NaOH and 1.5 g/l of H₂O₂. With increasing temperature the maximum shifts to lower alkali concentrations. He finds a constant molar ratio between NaOH and H₂O₂ at the maximum decomposition velocity. Dorfelt also finds that sodium silicate is far superior to sodium pyrophosphate as a stabilizer for this reaction. No explanation of the maximum in rate was discussed.

V. W. Slater (26) has also given some data on the effect of pyrophosphate on the rate of this decomposition at room temperature. His data go only as high as a pH of 9. He finds changes in the decomposition rate between pH 5 and 6 and again between 8 and 9. He has also stressed the importance of using very pure reagents to study this reaction.

P. Pierron (20) appears to have carried out a fairly

extensive study of this reaction. No discussion of the experimental methods employed was given, therefore it is not known whether the reaction studied was heterogeneous or not and what precautions against catalysis by trace impurities were taken. The reaction was carried out in the presence of the following bases: NH_4OH , $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, KOH , NaOH , and LiOH . He found that the rate for equivalent amounts of these bases was faster in the order $\text{LiOH} < \text{NaOH} < \text{KOH} < \text{Ca}(\text{OH})_2 < \text{Ba}(\text{OH})_2 < \text{NH}_4\text{OH}$. On the basis of his experimental data he suggests the following mechanism for the base catalyzed decomposition of hydrogen peroxide:

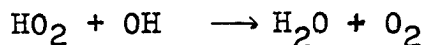
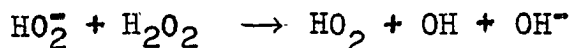
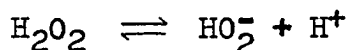


where Me is the cation of the base added. Thus he attributes the differences in the rate observed as the cation of the base is changed as due to fragility of the intermediate $\text{Me OOOO}^-\text{Me}$. He explains the period of induction observed as due to the need to build up the concentration of nascent oxygen needed in the initial reaction. It should be pointed out that the initial step appears to be a termolecular reaction, between two unionized metal peroxide molecules and one nascent oxygen.

Pierron also finds a diminishing of the rate when silk, wool or cellulose is added. He feels this inhibition is due to adsorption of the nascent oxygen by these bodies.

E. Abel (1) has suggested the following mechanism for the

base catalyzed decomposition of hydrogen peroxide:



The second reaction would be the rate determining step.

Although Abel has done no experimental work on this reaction himself, he does cite the data obtained by Bredig in 1890 and uses this to obtain a rate constant for this reaction. The rate constant obtained by Abel is:

$$k \sim 10^{-1} \quad (\text{mole (l)}^{-1} \text{ min; } 25^\circ\text{C})$$

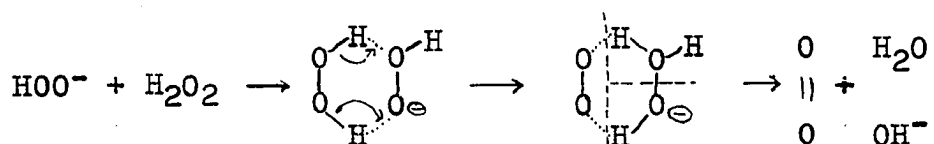
Bredig found the reaction to go through a maximum at a pH = 12. Abel then measured the decomposition as catalyzed by metal colloids. He found a maximum in the rate at a pH = 12 and suggested that both reactions proceed with the same mechanism.

L. Erdey (10) has also discussed this decomposition in conjunction with his study of lucigenin -H₂O₂ as an indicator for acid-base titrations.

Later Erdey and Inczedy (11) conducted a rather thorough study of this decomposition in basic solutions. Their work was done in glass vessels and the decomposition was found to be heterogeneous. The rate was found to go through a maximum at a pH = 12. They found the rate to be of the second order at this pH, whereas at other pH values it is of a fractional order. The decomposition rate is directly proportional to

the surface area of the glass exposed to the solution below a pH of 12 and is proportional to the square root of this area above a pH of 12. At all pH values they find that the rate extrapolated to zero wall area becomes zero. This is interpreted to mean that the reaction is completely heterogeneous. A period of induction was found in all cases. The activation energy obtained at pH = 12 was 20 kcal/mole. The pH was adjusted by using buffers of Na_3PO_4 and NaBO_2 .

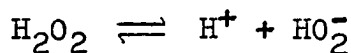
Erdey and Inczedy on the basis of this information postulate the following mechanism:



They postulate that the transition ion decomposes exclusively on the vessel walls. The rate equation which they derive is:

$$\frac{d(\text{O}_2)}{dt} = k \frac{K (\text{H}_2\text{O}_2)_0^2 \cdot (\text{H}^+)}{[K + (\text{H}^+)]^2}$$

where K is the equilibrium constant for the reaction:



Doyle (9) has also observed the decomposition of 5 weight % H_2O_2 at 70°C over the pH range 5.3 to 9.3. His rate expression was first order with respect to H_2O_2 over the

entire pH range studied. Due to a change in the rate constant at a pH 8.7 he suggested that below this pH the reaction is heterogeneous and above pH 8.7 the reaction is homogeneous.

An even larger number of references to the catalysis of this reaction by various ions is available. For a summary and list of references see Chapters 8 and 9 in Schumb, et al. (24) or the excellent review by Baxendale (3).

Despite the large amount of work done on this reaction Schumb, et al. (24, p. 476) are led to say that

"No completely acceptable mechanistic explanation of the acid or alkali induced decomposition is available, chiefly because of the lack of reliable kinetic data".

There appear to be two main reasons why the kinetics for the homogeneous base catalyzed decomposition of hydrogen peroxide have not previously been solved. The first is the importance of assuring that adventitious impurities are absent or that they are not interfering with the reaction being studied. The other important factor which must be considered is assuring that the vessels used have an inert surface for this decomposition.

A knowledge of the kinetics of this homogeneous base-catalyzed decomposition would be essential to any studies of catalytic decompositions of hydrogen peroxide in basic solution. For example the catalysis of the decomposition of H_2O_2 by the halides has been studied extensively in acid and neutral solution (3). The uncatalyzed decomposition in acid

or neutral solutions is very small in comparison to the catalyzed rate hence these studies are comparatively easy. In basic solutions one must account for the base-catalyzed decomposition as this might be of equal magnitude as the catalytic rate being studied. Hence the results of this work should allow some very interesting studies of catalytic decompositions of hydrogen peroxides in basic solution to be carried out.

II. EXPERIMENTAL

A. Apparatus

Most of the decompositions were run in 8 oz polyethylene bottles. The caps were left on the bottles during the course of the reaction so that dust, etc. could not get into the solution. The caps were left loose, however, so that the oxygen given off did not build up pressure inside the bottle. These bottles were then submerged in a constant temperature bath.

The constant temperature water bath was held to $\pm 0.05^{\circ}\text{C}$. The temperature of this bath was regulated by means of a Fisher Scientific Micro-Set Thermoregulator connected through a Precision Scientific Electronic Relay to a 500 watt knife heater. For those runs made below room temperature the cooling of the bath was accomplished by means of cold tap water running through a copper tubing coil submerged in the bath.

It was found that the temperature of the solution in the polyethylene bottles varied by $\pm 0.5^{\circ}\text{C}$. The temperature increased by 0.5 degrees during the rapid part of a reaction due to the heat liberated by this decomposition.

In several runs the solutions were stirred. This was accomplished by cutting small holes in the tops of the bottles and extending the shaft of a stirring rod through

this hole. The stirring rod was constructed of a short length of glass rod around which was fitted a length of stiff polyethylene tubing. A small piece of polyethylene was fitted at the bottom of this tubing to act as a propellor in the stirring. The stirring was mechanically powered by a small variable speed electric motor. Stirring accomplished in this manner was very efficient.

The burettes used in the cerium titration described later were of the Kimble Exax automatic leveling, gravity filling type.

B. Quenching Technique

The rate of decomposition of hydrogen peroxide in acidic solution is relatively slow. The pipettes measuring the 10 ml samples periodically taken were drained into dilute H_2SO_4 . The samples were then ready for titration.

In order to test the effectiveness of the quenching technique several samples were taken from one solution and quenched in acid. These were then titrated after various times of standing. No change was noted up to about 8 hours, hence the quenching technique was effective.

In the experiments on the iodide catalysis, when the pipette was drained into the acid, a dark brown color due to the iodine appeared. Thus it was necessary to extract these solutions with CCl_4 before titration as the end point was

obscured by this color. This undoubtedly introduced some error due to the time delay as I_2 also catalyzes this reaction in acid solution. It is felt that this error is rather small.

C. Analytical Techniques

The alkalinity of the solutions was determined by titration with a standard HCl solution using a methyl orange indicator.

The hydrogen peroxide concentration was determined in two ways. The first method employed was the use of a standard solution of $KMnO_4$. The slight pink color of excess $KMnO_4$ was used as the end point. The difficulty with this method however is that $KMnO_4$ is not stable and must be frequently standardized. Also MnO_2 tends to form and makes the use of automatic burettes impossible; many solutions were titrated and the use of automatic burettes seemed quite practical. For this reason cerium (IV) sulfate was used in most of the titrations. Cerium (IV) sulfate solutions have the advantage of being stable over long periods of time and can be very conveniently used with an automatic burette. It can also act as its own indicator, the yellow color of a slight excess being easily discernable. In most cases, however, ferroin was used as the indicator as this gives better warning for proximity of the end point. Duplicate

titrations were found to agree within 0.05 mls. Greater precision than this is obtainable but is not needed. For the more concentrated peroxide solutions the Ce (IV) concentration was about 0.5 M, while for the more dilute peroxides solution a 0.1 M solution was used.

The Ce (IV) was standardized in several ways. One method was the use of primary standard arsenious oxide according to the procedure outlined in Diehl and Smith (7, p. 274). Ethylenediammineiron (II) sulfate was also used but some question as to its being a primary standard arose and this method was abandoned. Most of the standardizations were done by preparing by weight an exactly 0.1 M solution of cerium (IV) sulfate from primary standard ammonium hexanitratocerate (IV). This solution was then used to standardize a solution of H_2O_2 which was in turn used to standardize the unknown Ce (IV) solution. This method worked well and had the added advantage that any end point error was taken care of.

The determination of the iron content of the reagents used was a very important one. This was accomplished by three methods. The first method employed was the use of O-phenanthroline described in Diehl and Smith (7, p. 366). This method was not suitable however for the KOH. Trusell and Diehl (27) have worked out a method for determining iron in solutions as alkaline as saturated NaOH. The method consists essentially of forming a complex of iron (II) with phenyl-2-

pyridyl ketoxime and extracting this purple colored complex into isoamyl alcohol. The iron is all reduced to iron (II) by adding sodium hydrosulfite. The optical density of the organic layer was measured on a Coleman Junior Spectrophotometer. Plots of the optical density versus iron concentration gave straight lines. By means of using a small volume of isoamyl alcohol compared with the volume of this KOH solution it was possible to estimate iron concentration as low as 10^{-7} molar.

Iron content of the water and the KNO_3 solution was determined by the method of Collins and Diehl (6) using 2,4,6-tripyridyl-s-triazine as the complexing agent and extraction into nitrobenzene. This method was also useful down to concentrations of iron as low as 10^{-7} molar.

No method was found in the literature for the determination of copper in very basic solutions. A method is described on page 444 of Sandell (23) using sodium diethyldithiocarbamate as the complexing agent in slightly basic solution. The copper complex is extracted into carbon tetrachloride or chloroform. This same method was found to work in 5 M potassium hydroxide if the extraction is made into isoamyl alcohol. Chloroform and carbon tetrachloride both react with strong alkali hence their use was impossible. Two extractions with isoamyl alcohol were required. Good reproducibility was obtained and a plot of optical density versus concentration gave a straight line. By using a

smaller volume of isoamyl alcohol than potassium hydroxide it was possible to estimate copper to 10^{-7} molar. No work on finding interfering elements was done as the purpose of this work was only to find a way to estimate small amounts of copper in strongly basic solution.

The diethyldithiocarbamate method was also used to determine copper in the water, potassium nitrate and other solutions in the manner described by Sandell (23, p. 444).

Chloride ion concentration was determined in two ways. The first method was the usual gravimetric method consisting of precipitation of silver chloride and weighing.

The other method for chloride involved titration with standard silver nitrate using an adsorption indicator. The method is described on page 335 of Diehl and Smith (7).

D. Purification Methods

The water used to make up the stock solutions was the distilled water available in this laboratory which was then redistilled from an alkaline potassium permanganate or an alkaline hydrogen peroxide solution. The distilling apparatus was of Pyrex brand glass that was scrupulously cleaned with concentrated nitric acid and distilled water prior to use. Some sodium ions may have been leached from the glass during the distillation but this was not considered harmful. Impurity concentrations were below detectable limits in this water.

The hydrogen peroxide used in the solutions studied was from several sources. The first work was done with Fisher Scientific 30% unstabilized hydrogen peroxide. It was found that 90% hydrogen peroxide was usually much more pure than the 30%. This is to be expected as the only safe way to keep 90% hydrogen peroxide is to have it quite pure. The 90% hydrogen peroxide was obtained through the courtesy of The Columbia-Southern Chemical Corporation and also from the Becco Chemical Division of Food Machinery and Chemical Corporation.

In some of the work it was decided to get an even purer hydrogen peroxide as it was known that some iron and possibly trace amounts of copper were in the hydrogen peroxide. The best way to purify hydrogen peroxide is by distillation. This can, however, be quite hazardous. Data is given in Schumb, et al. (24, p. 182) from which one can calculate what combinations of pressure, temperature, and hydrogen peroxide concentration are safe for this distillation. It was found that if the distillation was carried out under the vacuum produced by a water aspirator, about 10-20 mm of mercury, and if the solution was below 70% hydrogen peroxide that the distillation was quite safe. The distillate produced under these conditions was quite dilute hence a concentration of the product by evaporation was required. This procedure was slow but comparatively safe.

The starting product in the hydrogen peroxide

distillation was 90% hydrogen peroxide that had been diluted to about 30% with redistilled water. The distilling apparatus was made of Pyrex glass that had been scrupulously cleaned with concentrated HNO_3 , distilled water, and steamed several days.

The potassium nitrate was "Baker Analyzed" reagent grade material that was recrystallized two times from redistilled water. Impurity concentrations were below detection.

This recrystallized nitrate was used to make a stock 2.0 molar solution. This solution was made by weight. It was found that this method was sufficiently accurate for this purpose. Some solutions were analyzed by passing the potassium nitrate solution through a cation exchange column in the hydrogen cycle and titrating the effluent acid with standard base. There was good agreement between the value calculated by this procedure and that obtained by knowing the weight of potassium nitrate used.

The purification of the potassium hydroxide was the most difficult of the purification procedures. No references were found in the literature for an entirely satisfactory method of preparing sodium or potassium hydroxide in very pure form.

Recrystallization of either sodium or potassium hydroxide proved to be quite unsatisfactory. Redistilling sodium or potassium metal and reacting this with water was also considered unsatisfactory as the principal impurity in

these metals is probably mercury and this would be too volatile compared with these metals for any satisfactory separation by distillation to be accomplished.

An ion exchange method consisting of passing recrystallized potassium nitrate over an anion exchange resin was tried. This was found to be unsatisfactory because for the amounts of potassium hydroxide needed the capacity of a reasonably sized bed was found to be too small. Furthermore, some materials were picked up from the bed which had an adverse effect on the reaction.

Electrolytic plating of the heavy metal impurities was also tried using various combinations of electrodes. No successful procedure was found.

A procedure using adsorption of the heavy metal ion impurities on activated charcoal was found to work. Three disadvantages were found with this method. First the charcoal as might be expected, contained a certain amount of chloride which was leached out during the adsorption process. Secondly small amounts of finely divided charcoal were left suspended in the solution even after repeated filtration; charcoal would catalyze the decomposition. It should be also mentioned that all filtrations made on these strong potassium hydroxide solutions were done with a special paper made to withstand strong alkalis. This paper was Whatman No. 50. The third difficulty in this adsorption procedure was that the complete removal of the heavy metals was uncertain,

depending upon such factors as temperature, time of adsorption, manner of stirring and so on.

The first difficulty was not considered serious. The possibility of removing the chloride by passing the potassium hydroxide through an anion exchange column in the hydroxide cycle was considered but not attempted.

The second difficulty could be overcome by shaking the hydroxide with isoamyl alcohol; the finely divided bits of charcoal were found to congregate at the aqueous-alcohol interface.

The third difficulty was overcome by adding complexing agents prior to adsorption. It was found for example that the phenyl-2-pyridyl ketoxime complex of iron (II) was very strongly adsorbed in very short periods of time. The EDTA complexes of several metals, such as iron, copper, and lead were also strongly adsorbed. Under these conditions removal of these trace impurities was rapid and sure. The whole procedure was rather involved, however, and a simpler procedure was sought.

Since adsorption with charcoal worked it was felt that other adsorbing agents might also work. It was found that small amounts of copper could be removed by adding ferric nitrate as a coprecipitating agent. Small amounts of the colloidal hydroxide passed through the filter paper and hence another coprecipitating agent, magnesium nitrate, was added. This removed all but the very smallest traces of iron. These

last traces of iron were removed by extraction of the phenyl-2-pyridyl ketoxime complex of iron (II) into isoamyl alcohol. This procedure was found to work very well and was adopted for most of the work.

As a check on the purity of the reagents used, samples were sent to the spectrographic laboratory for qualitative analysis. A sample of the recrystallized KNO_3 was sent. The potassium hydroxide was first neutralized with redistilled nitric acid and the potassium nitrate thus formed was dried and homogenized so as to get a representative sample. A solution whose decomposition had been studied was also neutralized with the redistilled nitric acid and a sample of this potassium nitrate sent out. The results of this analysis indicated that no unsuspected impurities were present in any detrimental amounts. The sample of the decomposed solution did show some iron in trace to very weak quantities. Since iron did not show up in the potassium hydroxide or potassium nitrate it must have come from the hydrogen peroxide used in making up this solution. This confirmed earlier evidence gotten by colorimetric analysis.

The potassium chloride used in studying the chloride ion catalysis was recrystallized one time. The potassium iodide used in the iodide catalysis studies was a "Bakers Analyzed" reagent. The copper nitrate, lead (II) nitrate and iron (III) nitrate used in catalysis studies were all reagent grade materials.

The zirconium used in the zirconium catalysis studies was ZrOCl_2 that was recrystallized from concentrated hydrochloric acid. The arsenic used in the arsenic catalysis studies was primary standard arsenious oxide.

III. RESULTS AND DISCUSSION

A. The Homogeneous, Uncatalyzed Decomposition

1. General

Any attempt to determine the kinetics for the homogeneous uncatalyzed decomposition of hydrogen peroxide must include some study of the various factors which may affect the rate of the decomposition of hydrogen peroxide. Some of the possibilities which must be examined are surface effects, impurity catalysis and effect of light. The rate due to these effects must be zero or negligible with respect to the rate due to the homogeneous, uncatalyzed decomposition.

2. Impurity effects

In the early experiments no special attempts to purify the reagents used were made. In order to account for catalysis by impurities in the analytical grade reagents used, some disodium ethylenediaminetetraacetate (EDTA) was added. Several people have reported that various heavy metal ion-organic amine complexes are inert to catalyzing this decomposition (21). This work showed subsequently that the EDTA complexes are less active than the uncomplexed ions but that they were not totally inactive. It was, however, found that the rate was independent of the amount of EDTA added, above a certain minimum amount. Thus, the use of complexing agents to mask the impurities in the reagents used did not

appear to be a satisfactory way to overcome possible unwanted catalysis of the decomposition. Purification methods were then tried.

The two main impurities in the solutions which would catalyze the rate extensively are copper and iron. A fairly large lowering in some cases in the rate of decomposition was found when the reagents used were further purified as described in the experimental section of this paper. The major portions of the impurities, mainly iron, were found to come from the KOH used. The commercial 90% H_2O_2 used was known to contain only very small amounts of copper and iron. Much of the early work on the homogeneous, uncatalyzed decomposition was done with purified KOH, KNO_3 , and H_2O and commercial 90% H_2O_2 . It was felt necessary to remove the last traces of impurities found in the solutions whose decompositions were being followed. It was found that these were due mainly to the H_2O_2 and hence redistilled H_2O_2 was tried. Copper and iron were then found to be below detection (i.e., about 10^{-7} molar) in the solutions made up with redistilled H_2O_2 ; before using redistilled H_2O_2 copper was below 10^{-7} m and iron was about 3×10^{-6} m. This last lowering of impurity concentrations had, however, essentially no effect on the rate, except in those solutions decomposing at very slow rates. This would indicate that the level of impurities was already low enough in most cases so as to no longer be important.

Undoubtedly some catalysis due to trace impurities must always be present, as to reduce impurity concentrations to zero would be impossible. In all the work done on specific heavy metal ion catalysis, however, it was found EDTA has a considerable damping effect. In the last work addition of EDTA had only a very slight effect. This together with the evidence cited in the previous paragraph would indicate that although there certainly must be some catalysis by those heavy metal ions, the magnitude of that term in the kinetic expression in all but the slowest rates would be small in comparison to the terms representing the homogeneous uncatalyzed mechanism.

Of the anions suspected of being catalysts only chloride ion was present in amounts large enough to be detected (about 10^{-5} m). As discussed later chloride ions were found to have no effect on the rate.

It has also been postulated that a certain level of impurities is necessary to initiate the reaction. Since, as stated earlier, it would be impossible to reduce foreign ions to zero concentration it is impossible to unequivocally refute this postulate. However, it must be said that the mechanism proposed fits the experimental data and no level of impurities is necessary for initiation of this mechanism.

3. Surface effects

In order to study the homogeneous decomposition it is essential that the surface of the vessel be inert. That is,

if there is any reaction of the peroxide molecules adsorbed on the vessel walls then this reaction must be entirely negligible compared to the homogeneous rate. It was felt that the reaction in polyethylene might be homogeneous.

The rate of a surface reaction is often quite dependent on what prior treatment is given to the surface. In order to test for any such effects in using polyethylene vessels various methods were used to prepare the polyethylene bottles prior to use. In one instance the bottle was soaked with warm concentrated nitric acid prior to its use as a reaction vessel. In another case the bottle was rinsed first with warm concentrated, then with warm dilute nitric acid. Another treatment given was to soak the bottles with hot concentrated potassium hydroxide prior to use. Soaking for several days with dilute potassium hydroxide and EDTA was also tried. Various combinations of these treatments were also employed. In none of these cases, however, was any effect due to prior treatment of the surface of the reaction vessel found.

The best test of potential surface activity is to vary the surface area available to the solution and note the effect this produces on the reaction rate (17, p. 35). The first work along these lines was done by taking a polyethylene film and cutting this into thin strips and putting this into the reacting solution. The area was increased by a factor of from 2 to 3. No effect was noted.

It was felt however that a greater increase in the surface area should be made before any final conclusions were made. Furthermore it was known that there are several methods of producing polyethylene and hence the type of polyethylene found in the film used in the first test might differ from the kind actually used in making the polyethylene vessels. It is conceivable that polyethylene produced by one company might have an active surface for this decomposition whereas that produced by another might be inert because of less frozen impurities or a different degree of crystallinity. These objections were overcome by taking several of the bottles actually used in these studies, freezing them in a dry ice cabinet and then filing on them with a wood file to produce fine roughened particles. They were then cleaned in various ways to remove dirt, etc.

The minimum area of the polyethylene particles was determined in the following manner. Numerous representative particles were taken and measured roughly considering them as cubes. The weights of a definite number of "average sized" particles were taken and then the total weight for all the particles. From this a rough minimum area was calculated. These particles had very roughened surfaces so that the area obtained was certainly an underestimate. The results of this work indicate that the surface area available to the solution was increased by at least a factor of 50 and probably more like 100.

Comparative solutions, one with this added polyethylene and one without this added polyethylene, were made and their decompositions followed. This type of experiment was carried out under many various conditions. The temperature was varied, runs being carried out at 25° and 35°C. The reason for carrying this out at two temperatures is that at one temperature the term representing a heterogeneous decomposition in the rate equation might not show up but could at a different temperature due to differences in the activation energies. No essential difference beyond experimental error was found between the solutions with and without the added polyethylene.

Other variables were also tested in connection with the surface area. For example, no effect was found when the initial (H_2O_2) was varied in the presence of the added polyethylene. No effect was also found when the (OH^-) was varied for the two solutions.

Oxygen is one of the products of this decomposition. It was observed that this oxygen occasionally had a tendency to form air pockets and push up the polyethylene out of the solution. This was overcome by using a polyethylene stirrer connected to a small motor and stirring both solutions. This gave very good contact between the solution and the added polyethylene. No effect of the stirring on either solution was noted.

It was mentioned above that the surface area was

increased by a factor of about 50. Assuming the order in surface area to be something between 0.5 and 2, as one would expect, then one can see that the rate of decomposition should have increased by a factor of from 7 to 2500 times if the reaction being studied was heterogeneous. Nothing even approaching these figures was found. It is felt that any differences found were within experimental error. Hence, it is concluded that polyethylene vessels of the type being used have inert surfaces for this decomposition.

One side effect of the added polyethylene was that it acted like boiling chips in the solution and supersaturation by the oxygen given off in the reaction did not take place. This was evidenced by the lack of foaming that took place when samples were drawn up into the pipettes; without this added polyethylene considerable foaming took place. This would suggest that oxygen content in the solution has no effect on the rate.

This reaction was also studied in vessels other than polyethylene. In glass it was found that the reaction proceeded at a faster rate than it did in polyethylene in agreement with the work reported by Erdey and Inczedy, suggesting that the reaction in glass was heterogeneous. For this work a new erlenmeyer flask was cleaned by soaking it overnight with warm concentrated nitric acid prior to its use as a reaction vessel.

A little work was done also in paraffin lined glass

vessels. In this case the reaction tended to proceed rapidly at first followed by an abrupt slowing down. After this the rate proceeded roughly the same as would a comparable solution in polyethylene. The paraffin used to line the glass vessels was of C. P. grade with no further purification, however, it is quite possible that easily oxidizable organic impurities on the surface of the wax reacted with the peroxide. After this reaction was complete the rate then was comparable to that of the homogeneous decomposition. If this is presumed to be the case then one would conclude that paraffin is also inert toward this decomposition. No further work was carried out in paraffin vessels as polyethylene vessels were already known to be satisfactory and were readily available.

No work was done in quartz vessels although quartz has been used in studies of this reaction. Robertson (22) has reported that the reaction in quartz vessels is homogeneous. On the other hand Pana (19) has reported that quartz vessels have even more active surfaces than Pyrex vessels.

4. Effect of light

The possibility that the reaction being studied was catalyzed by light was also investigated. For this purpose a special polyethylene bottle was prepared. First this bottle was painted with black paint. On this was then placed a layer of aluminum foil. No light leaks were found. Two identical solutions were prepared, one in an ordinary

bottle and one in this bottle. These were then placed in a constant temperature bath near a large window in the laboratory. No effect due to light was found in this experiment.

This experiment was also repeated at various temperatures and in solutions of various initial hydrogen peroxide and hydroxide ion concentrations.

The experiment was also carried out in conjunction with work on surface effects, the extra polyethylene being added to the darkened bottle.

In none of the above runs was any effect due to light found and hence it is concluded that varying amounts of light did not materially effect the results under the conditions with which this work was carried out.

5. Inert ions

The ionic strength in all cases was adjusted by adding the proper amount of potassium nitrate. It was felt that some indication as to whether or not the nitrate ion was entering into the reaction should be obtained. To this end in several runs the ionic strength was adjusted with sodium sulfate instead of potassium nitrate. No effect was noted hence it was concluded that the nitrate ions were not entering into the reaction.

There is another interesting sidelight to this work. Since sodium sulfate was used instead of potassium sulfate some information about sodium and potassium ions was also

obtained. As mentioned above no effect was noted. Since KOH, NaOH, Na_2SO_4 , and KNO_3 are very nearly 100% ionized the effect of using Na_2SO_4 in place of KNO_3 should be essentially the same as using NaOH in place of KOH in these solutions. Pierron as mentioned earlier found an inhibiting effect when using NaOH as opposed to KOH in his work on this reaction. He has ascribed this to the greater fragility of the salts NaOONa or NaOOH over KOOK or KOOH . The results of this work are not in agreement with his conclusions.

6. Experimental results and discussion

There are five things which might be suspected of having an effect on the rate of the homogeneous uncatalyzed decomposition of hydrogen peroxide. These are the temperature at which the reaction is carried out; the pressure, since a gas is one of the products; the (OH^-) , the (H_2O_2) and the ionic strength.

No study of pressure effects was done in this work, all runs being carried out at atmospheric pressure. Shanley and Greenspan however have stated (25) that the rate of decomposition of H_2O_2 is independent of pressure at any ordinary pressures. They do not state at what pH this work was done, but presumably it was done in near neutral solutions.

One run was done varying only the ionic strength. The ionic strength was varied from 2.0 to 1.0. Only a very small effect was noted. All other runs were made at a constant

ionic strength of 2.0.

The initial (H_2O_2) was also varied while keeping the (OH^-) constant. The results of this work indicated that the rate equation did not contain a term in the initial (H_2O_2). The reason for this conclusion is that a curve representing the change of (H_2O_2) with time for an initial (H_2O_2) of say 0.5 M would if only displaced along the time axis fit along an equivalent curve representing an initial (H_2O_2) of 1.0 M from the time the latter had decomposed to 0.5 M on. One would not expect this type of behaviour if the initial (H_2O_2) were in the rate equation.

A more interesting observation was made when the dependence of the rate on (OH^-) was studied. It was found that the rate as the (OH^-) was varied from 0.1 M to 2.0 M appeared to go through some kind of maximum. This maximum in rate appeared to come at a value of the hydroxide ion concentration equal to about 0.5 M. Since the ionic strength was kept constant in these experiments the main effect that varying the (OH^-) would have would be in the ionization of the H_2O_2 . Work done on determining the ionization constant of H_2O_2 has shown the existence of a doubly ionized H_2O_2 to be very doubtful (12). Hence one should consider only the species HO_2^- and H_2O_2 . One would not expect termolecular reactions and also one would not expect a reaction between like charged ions, such as between two HO_2^- ions. These

considerations lead one to the possibility of the initial and rate controlling step being one between a singly ionized and a unionized H_2O_2 . The rate equation would then be of the form:

$$\frac{-d(\text{H}_2\text{O}_2)_t}{dt} = k_1 (\text{H}_2\text{O}_2) (\text{HO}_2^-) \quad (1)$$

where

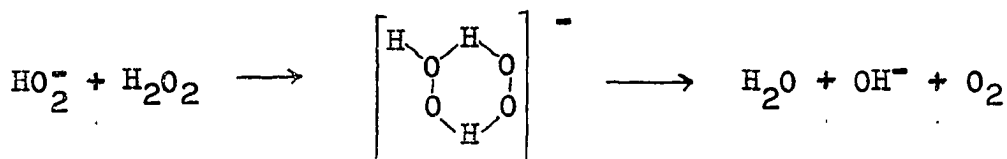
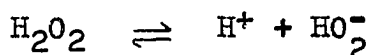
$(\text{H}_2\text{O}_2)_t$ is the total hydrogen peroxide concentration as determined by the titration with the cerium (IV) solution,

(H_2O_2) is the concentration of the unionized H_2O_2 molecules,

(HO_2^-) is the concentration of the singly ionized H_2O_2 molecules,

t is the time.

The mechanism would then perhaps be:



The second reaction would be the rate controlling step.

One can readily see that when the hydrogen peroxide is 50% ionized, i.e., $(\text{HO}_2^-) = (\text{H}_2\text{O}_2)$, the rate will be a maximum for a particular $(\text{H}_2\text{O}_2)_t$.

The form of the rate equation in equation 1 is not very useful. One can know only the quantities $(\text{OH}^-)_t$, that is the total hydroxide ion added—the (KOH) assuming 100% ionization—and the $(\text{H}_2\text{O}_2)_t$. In order to use equation 1 one must be able to calculate the (HO_2^-) and (H_2O_2) from these quantities. Thermodynamic data are available to aid this calculation. Thus, consider the reactions:



Adding reactions I and II gives:



The equilibrium constant for reaction III is:

$$K_{\text{III}} = \frac{a_{\text{HO}_2^-}}{a_{\text{H}_2\text{O}_2} \times a_{\text{OH}^-}} = \frac{\gamma_{\text{HO}_2^-}}{\gamma_{\text{H}_2\text{O}_2} \gamma_{\text{OH}^-}} \frac{(\text{HO}_2^-)}{(\text{H}_2\text{O}_2) (\text{OH}^-)} \quad (2)$$

where

K_{III} is the thermodynamic equilibrium constant for reaction III,

$a_{\text{HO}_2^-}$ is the activity of the HO_2^- ions

$a_{\text{H}_2\text{O}_2}$ is the activity of the H_2O_2 molecules,

a_{OH^-} is the activity of the hydroxide ions,

γ_{OH^-} is the activity coefficient for the hydrogen ions,
 $\gamma_{\text{HO}_2^-}$ is the activity coefficient for the HO_2^- ions,
 $\gamma_{\text{H}_2\text{O}_2}$ is the activity coefficient for the H_2O_2 molecules.

The free energy change for reaction III is given by:

$$\Delta F_{\text{III}} = \Delta F_{\text{I}} + \Delta F_{\text{II}} \quad (3)$$

where

ΔF_{I} is the free energy change for reaction I,
 ΔF_{II} is the free energy change for reaction II,
 ΔF_{III} is the free energy change for reaction III.

The values of ΔF_{I} and ΔF_{II} at various temperatures are known. Thus since:

$$\Delta F_{\text{III}} = -RT \ln K_{\text{III}} \quad (4)$$

one can calculate K_{III} at various temperatures (29).

The equilibrium constant contains the terms $\gamma_{\text{HO}_2^-}$, $\gamma_{\text{H}_2\text{O}_2}$, and γ_{OH^-} , the activity coefficients for the species present in this system. No data are available for the system which was studied hence only two alternatives were possible, either determine these activity coefficients, or assume them to be constant at unity. There are several methods available for determining activity coefficients, none of which are suited in any way for this system (29). Hence in all

following calculations these activity coefficients will be assumed to unity. Thus:

$$K_{III} = \frac{(HO_2^-)}{(H_2O_2) (OH^-)} \quad (5)$$

The next problem encountered was to get the quantities (HO_2^-) , (H_2O_2) , and (OH^-) in terms of the only two known quantities, the $(H_2O_2)_t$ and the $(OH^-)_t$.

From reaction III it can readily be seen that:

$$(H_2O_2)_t = (HO_2^-) + (H_2O_2) \quad (6)$$

and that:

$$(OH^-)_t = (OH^-) + (HO_2^-) \quad (7)$$

If one substitutes these into the expression for the equilibrium constant one can obtain:

$$K_{III} = \frac{(HO_2^-)}{[(H_2O_2)_t - (HO_2^-)] [(OH^-)_t - (HO_2^-)]} \quad (8)$$

The only unknown in equation 8 is the (HO_2^-) . Solving for this term by means of the quadratic formula one arrives at:

$$(HO_2^-) = \frac{(H_2O_2)_t + (OH^-)_t + \frac{1}{K_{III}}}{2} \quad (9)$$

$$+ \frac{\sqrt{[(H_2O_2)_t + (OH^-)_t + \frac{1}{K_{III}}]^2 - 4(OH^-)_t (H_2O_2)_t}}{2}$$

The negative value in this equation is always used as it is found that the positive factor leads to a $(\text{HO}_2^-) > (\text{H}_2\text{O}_2)_t$, which is clearly impossible.

Since:

$$(\text{H}_2\text{O}_2) = (\text{H}_2\text{O}_2)_t + (\text{HO}_2^-)$$

one can now write equation 1 in terms of known or measurable quantities. The result is:

$$-\frac{d(\text{H}_2\text{O}_2)_t}{dt} = k \left\{ \frac{X - \sqrt{X^2 - 4(\text{OH}^-)_t (\text{H}_2\text{O}_2)_t}}{2} \right\} \left\{ (\text{H}_2\text{O}_2)_t - \frac{X - \sqrt{X^2 - 4(\text{OH}^-)_t (\text{H}_2\text{O}_2)_t}}{2} \right\} \quad (10)$$

where

$$X = (\text{H}_2\text{O}_2)_t + (\text{OH}^-)_t + \frac{1}{K_{\text{III}}}$$

Much of this work was done at a temperature of 35°C. Values for K_{I} as a function of temperature as given by Evans and Uri (12) are only over the temperature range 15 to 30°C. The value at 35°C was estimated by making a plot of $\log K_{\text{I}}$ versus $\frac{1}{T^\circ K}$ (29). The value obtained in this manner was 4.28×10^{-12} . The value at 15°C as reported by Evans and Uri is 1.39×10^{-12} and at 25°C is 2.24×10^{-12} . Values of K_{II} versus temperature available from the results of various workers as listed by Harned and Owen (14, p. 485) at 15°, 25°, and 35°C are 0.4505×10^{-14} , 1.008×10^{-14} and 2.089×10^{-14} respectively.

With the use of this data one can calculate K_{III} for various temperatures. These values at 15°, 25°, and 35°C are 205, 222, and 309 respectively.

Using these values for K_{III} one is able to calculate the value of the $(HO_2^-)_t$ and the $(H_2O_2)_t$ for a given $(OH^-)_t$ and $(H_2O_2)_t$ at 15°, 25° or 35°C. Some selected values of this product are given in Table 1 for 35°C. Values for 15°C are given in Table 2.

In order to test a given rate expression there are several methods available (17, p. 13). For this equation only two methods seem plausible, integration of the rate equation and subsequent plot of the integrated function of the concentration of reaction versus time, or to actually determine slopes,

$$- \frac{d(H_2O_2)_t}{dt}$$

from the $(H_2O_2)_t$ versus time plot, and plot these values versus $(H_2O_2) (HO_2^-)$. The former method was not used as integration of equation 10 proved too difficult. Therefore the second method must be used.

The differentiation of a curve is easily done by the method discussed by Latshaw (18). It consists of using a plane mirror fixed at right angles to the plane of the graph. One then follows the curve into its reflection in the mirror and when and only when the mirror is at right angles to the

Table 1. Values of (H_2O_2) (HO_2^-) and $-\frac{d(\text{H}_2\text{O}_2)}{dt}$ for various values $(\text{OH}^-)_t$ and $(\text{H}_2\text{O}_2)_t$ at 35°C

$(\text{OH}^-)_t = 0.1 \text{ m}$			$(\text{OH}^-)_t = 0.5 \text{ m}$		$(\text{OH}^-)_t = 1.0$	
$(\text{H}_2\text{O}_2)_t$	$(\text{HO}_2^-)(\text{H}_2\text{O}_2)$	$-\frac{d(\text{H}_2\text{O}_2)}{dt}$	$(\text{H}_2\text{O}_2)(\text{HO}_2^-)$	$-\frac{d(\text{H}_2\text{O}_2)}{dt}$	$(\text{HO}_2^-)(\text{H}_2\text{O}_2)$	$-\frac{d(\text{H}_2\text{O}_2)}{dt}$
1.1	0.1000	0.290	0.2999	0.600	0.1141	0.260
1.0	0.0900	0.235	0.2500	0.490	0.0412	0.218
0.9	0.0800	0.232	0.2002	0.400	0.0141	0.0120
0.8	0.0700	0.201	0.1506	0.280	0.00551	0.0090
0.7	0.0600	0.175	0.1035	0.250	-	0.0075
0.6	0.0500	0.161	0.0576	0.190	-	0.0045
0.5	0.0400	0.125	0.0145	0.110	-	0.0035
0.4	0.0300	0.077	0.00314	0.050	-	0.0030
0.3	0.0197	0.056	0.000596	0.030	-	-
0.2	0.0100	0.034	0.000199	0.015	-	-
0.1	0.0011	0.012	-	0.001	-	-

tangent does the curve appear to go smoothly into itself.

This method was used in determining

$$- \frac{d(\text{H}_2\text{O}_2)_t}{dt}$$

for a particular value of the $(\text{H}_2\text{O}_2)_t$. Some typical values are listed in Tables 1 and 2.

Table 2. Values of $(\text{HO}_2^-)(\text{H}_2\text{O}_2)$ and $-\frac{d(\text{H}_2\text{O}_2)_t}{dt}$ for various values of the $(\text{OH}^-)_t$ and the $(\text{H}_2\text{O}_2)_t$ at 15°C

$(\text{OH}^-)_t = 0.1$			$(\text{OH}^-)_t = 0.5$	
$(\text{H}_2\text{O}_2)_t$	$(\text{HO}_2^-)(\text{H}_2\text{O}_2)$	$-\frac{d(\text{H}_2\text{O}_2)_t}{dt}$	$(\text{HO}_2^-)(\text{H}_2\text{O}_2)$	$-\frac{d(\text{H}_2\text{O}_2)_t}{dt}$
0.9	0.0793	0.085	0.2007	0.240
0.8	0.0694	0.075	0.1521	0.200
0.7	0.0595	0.072	0.1045	0.140
0.6	0.0496	0.068	0.0594	0.115
0.5	0.0397	0.061	0.0245	0.070
0.4	0.0296	0.045	0.00832	0.040
0.3	0.0197	0.037	0.00262	0.015
0.2	0.0100	0.025	0.00008	0.005
0.1	0.00148	0.010	0.00005	-

The values of

$$- \frac{d(\text{H}_2\text{O}_2)_t}{dt}$$

having been obtained one can now proceed to the plotting of this quantity versus various functions of (H_2O_2) and (HO_2^-) . The only function tested which gives any resemblance to a straight line is the product $(\text{HO}_2^-) (\text{H}_2\text{O}_2)$. Typical results are shown in Figures 1 and 2 for various values of the $(\text{OH}^-)_t$ and temperatures.

It was stated above that the rate appeared to go through some sort of maximum value at around a $(\text{OH}^-)_t = 0.5$ molar and $(\text{H}_2\text{O}_2)_t = 1.0$ molar. One can find the value of the independent variable which gives the maximum or minimum or point of reflection to a function, if one exists, by taking its derivative and setting this function equal to zero (4, p. 139). If one takes the derivative of equation 10 with respect to the $(\text{OH}^-)_t$ while keeping the $(\text{H}_2\text{O}_2)_t$ constant and sets this equal to zero one obtains equation 11:

$$\left\{ \frac{\partial \left[- \frac{d(\text{H}_2\text{O}_2)_t}{dt} \right]}{\partial (\text{OH}^-)_t} \right\} (\text{H}_2\text{O}_2)_t = \frac{k}{4}$$

$$\left\{ \frac{\partial \left[X - \sqrt{X^2 - 4(\text{OH}^-)_t (\text{H}_2\text{O}_2)_t} \right] \left[(\text{H}_2\text{O}_2)_t - X + \sqrt{X^2 - 4(\text{OH}^-)_t (\text{H}_2\text{O}_2)_t} \right]}{\partial (\text{OH}^-)_t} \right\} (\text{H}_2\text{O}_2)_t$$

$$= 0 = \left\{ X - \sqrt{X^2 - 4(\text{OH}^-)_t (\text{H}_2\text{O}_2)_t} \right\} \left\{ -1 + \frac{1}{2} \left[X^2 - 4(\text{OH}^-)_t (\text{H}_2\text{O}_2)_t \right]^{-\frac{1}{2}} \right.$$

$$\left. \left[2X - 4(\text{H}_2\text{O}_2)_t \right] \right\} + \left\{ (\text{H}_2\text{O}_2)_t - X + \sqrt{X^2 - 4(\text{OH}^-)_t (\text{H}_2\text{O}_2)_t} \right\}$$

$$\left\{ +1 - \frac{1}{2} \left[X^2 - 4(\text{OH}^-)_t (\text{H}_2\text{O}_2)_t \right]^{-\frac{1}{2}} \left[2X - 4(\text{H}_2\text{O}_2)_t \right] \right\} \quad (11)$$

Figure 1. Plot of $-\frac{d(\text{H}_2\text{O}_2)_t}{dt}$ versus (H_2O_2) (HO_2^-) for $(\text{OH}^-)_t$
= 0.1

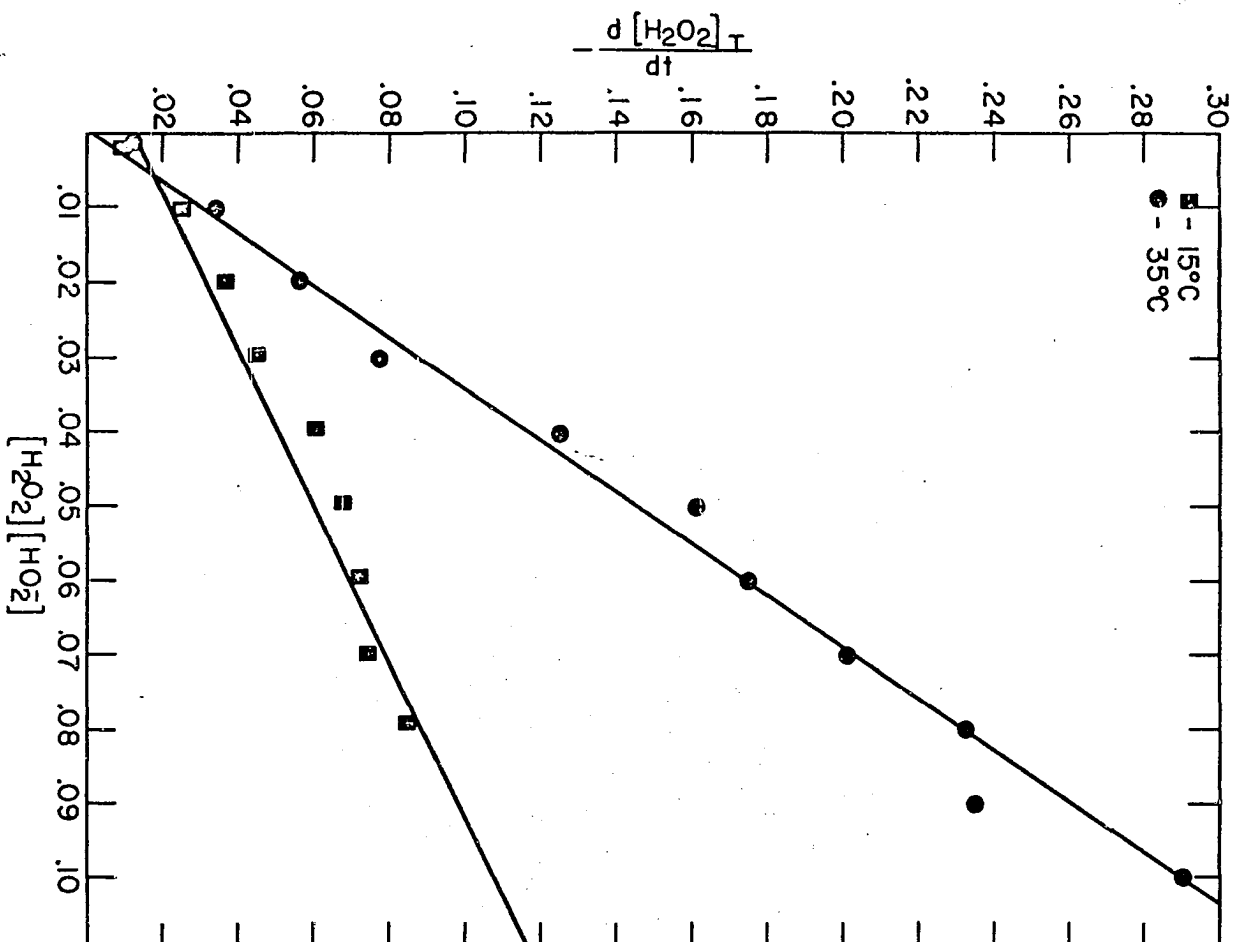
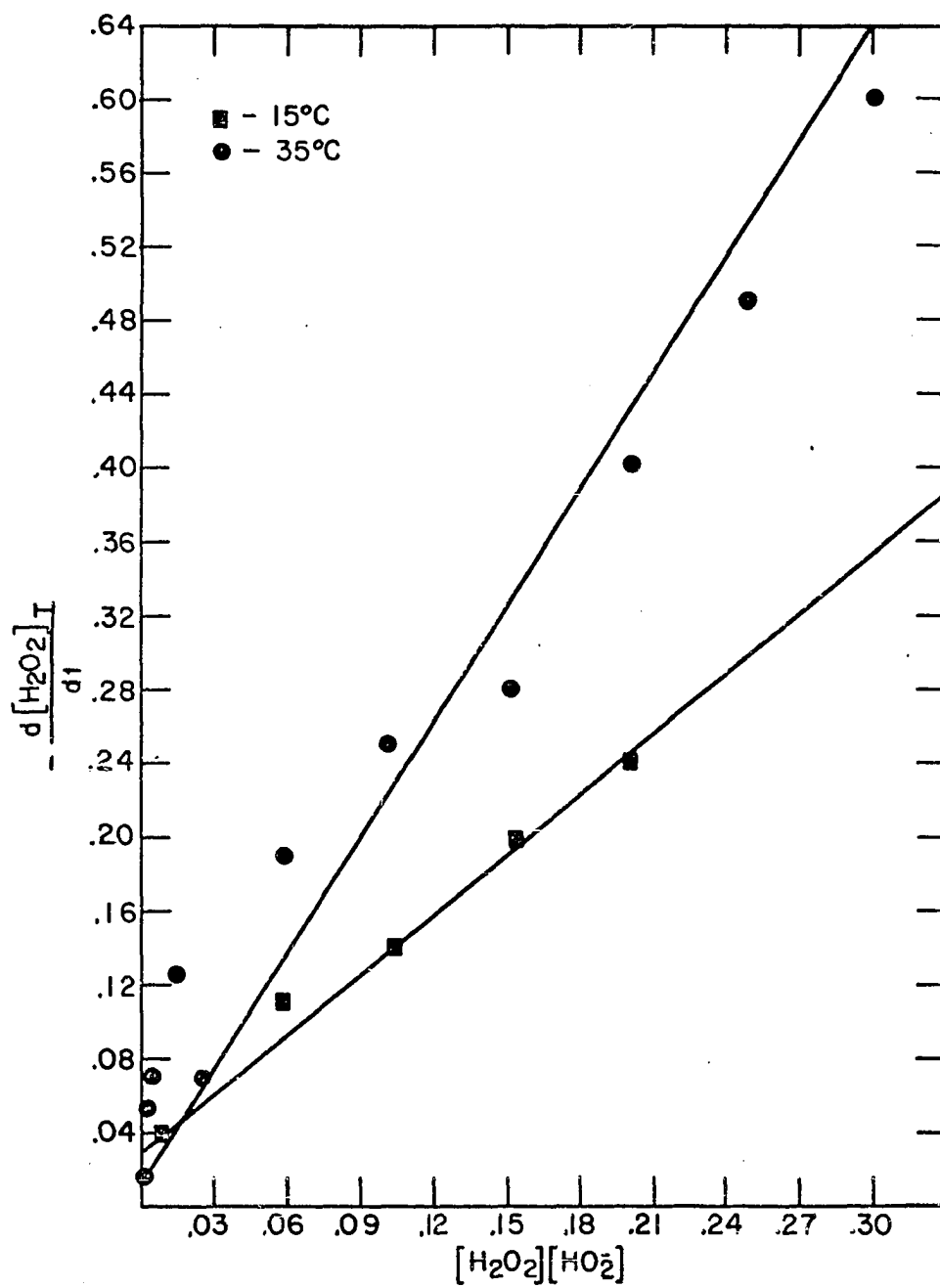


Figure 2. Plot of $-\frac{d(\text{H}_2\text{O}_2)_t}{dt}$ versus $(\text{H}_2\text{O}_2)(\text{HO}_2^-)$ for $(\text{OH}^-)_t$
= 0.5



Substituting in $(\text{OH}^-)_t = 0.5$ and $(\text{H}_2\text{O}_2)_t = 1.0$ and the value of K_{III} at 25°C one does indeed find this function equal to zero, thus indicating that these values give a maximum value to this function. That it is a maximum is easily seen by taking other values of the $(\text{OH}^-)_t$.

Thus in this manner one can predict at what value of the $(\text{OH}^-)_t$ a maximum should exist for a particular $(\text{H}_2\text{O}_2)_t$.

A test of the proposed mechanism would be to plot

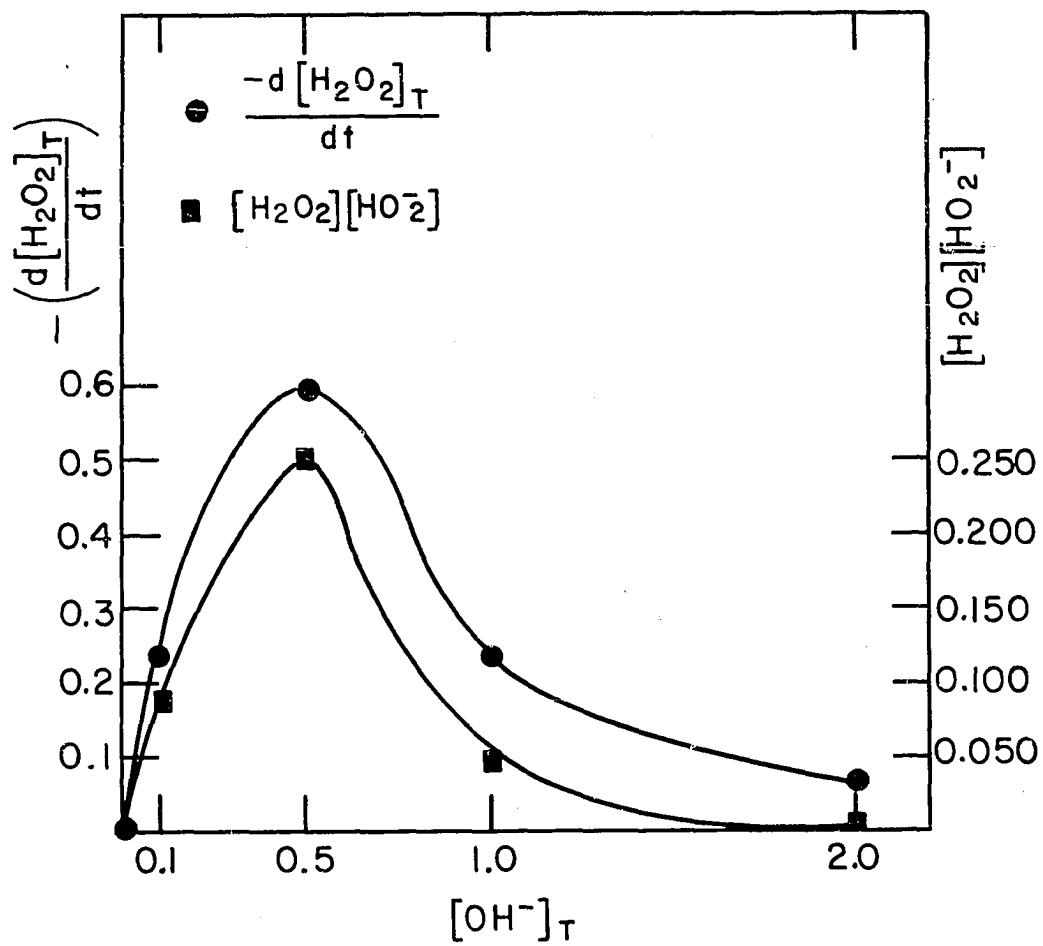
$$- \frac{d(\text{H}_2\text{O}_2)_t}{dt}$$

at $(\text{H}_2\text{O}_2)_t = 1.0$ for varying $(\text{OH}^-)_t$. Superimposed on this same plot would be values of the product $(\text{HO}_2^-)(\text{H}_2\text{O}_2)$ for $(\text{H}_2\text{O}_2)_t = 1.0$ and varying $(\text{OH}^-)_t$. The maximum found in the former case should fall at the same place the maximum in the plot of $(\text{H}_2\text{O}_2)(\text{HO}_2^-)$ versus $(\text{OH}^-)_t$ is found. Figure 3 shows that this is indeed the case. That the maximum in rate actually comes at $0.5 \text{ M } (\text{OH}^-)_t$ for $(\text{H}_2\text{O}_2)_t = 1.0 \text{ M}$ was investigated by varying $(\text{OH}^-)_t$ from 0.4 to 0.66 M . It was actually found that the maximum in rate did come at $(\text{OH}^-)_t = 0.5$. The solutions used were not made with the purest reagents and hence the actual values of

$$- \frac{d(\text{H}_2\text{O}_2)_t}{dt}$$

were not included in this graph. The qualitative conclusion that the rate maximum is actually at $(\text{OH}^-)_t = 0.5$ should

Figure 3. Plot of $-\frac{d(\text{H}_2\text{O}_2)_t}{dt}$ and $(\text{H}_2\text{O}_2)(\text{HO}_2^-)$ versus $(\text{OH}^-)_t$
for $(\text{H}_2\text{O}_2)_t = 1.0$ at 35°C



still be valid however.

The slopes of the best straight lines drawn for the plots of

$$-\frac{d(\text{H}_2\text{O}_2)_t}{dt}$$

versus $(\text{H}_2\text{O}_2) (\text{HO}_2^-)$ should give the value for k , the specific rate constant. At 35°C this value is 2.65 ± 0.40 liters-mole⁻¹-hour⁻¹ and at 15°C is 0.95 ± 0.01 liters-mole⁻¹-hour⁻¹.

The variation of k with temperature can be used to obtain the activation energy for this decomposition. The following equation can be derived (17, p. 58):

$$\frac{2.3 R(\log k_2 - \log k_1)}{-\frac{1}{T_2} + \frac{1}{T_1}} = + E^\ddagger \quad (12)$$

where

k_1 is specific rate constant at temperature. $T_1^\circ\text{K}$

k_2 is specific rate constant at temperature. $T_2^\circ\text{K}$

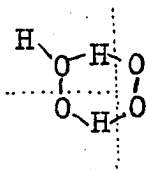
R is gas constant = $1.956 \text{ cal/}^\circ\text{K mole}$

E^\ddagger is the activation energy in cal/mole

Substitution of the proper values into equation 12 gives a value for the activation energy, E^\ddagger , of $9 \pm 1 \text{ kcal/mole}$. At first this value seems rather low. However, the activation energy for the homogeneous, uncatalyzed

decomposition is 17 to 18 kcal/mole (30). In neutral solution where this homogeneous, uncatalyzed decomposition takes place the rate is of the order of 1% per year at 30°C for 90% H_2O_2 . The base catalyzed decomposition takes place much more rapidly, hence one would expect a lower activation energy. Along these lines it is difficult to understand the value of 20 kcal/mole reported by Erdey and Inczedy (11) for the heterogeneous base catalyzed decomposition.

The mechanism proposed earlier involves the formation of the cyclic intermediate



with subsequent breaking of the bonds along the planes of the dotted lines to give the final product. This hypothesis could very easily be tested by the use of hydrogen peroxide in which both oxygens were isotopically labeled such as $\text{H}-\text{O}^{18}-\text{O}^{18}-\text{H}$. None of the common isotopes of oxygen are radioactive. O^{15} and O^{19} exist and are radioactive, but have half lives of the order of 1 minute (13). The determination of the isotopic enrichment of the water or of the oxygen evolved by this decomposition would have to be done with a mass spectrometer. This would be difficult but possible. The main reason for not carrying out this experiment is cost. The only available isotopic oxygen compound which could be of any use is $\text{O}^{18}-\text{O}^{18}$; $\text{H}-\text{O}^{18}-\text{O}^{18}-\text{H}$ is

not commercially available. The cost of O_2^{18} is very expensive and becomes more so when one realizes that this would have to be burned with Ba metal, for example, to get BaO_2^{18} from which, on acidification, $H_2O_2^{18}$ could be distilled. Overall it was not considered worth the cost to carry out such an experiment.

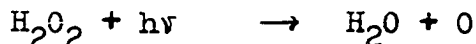
Abel (1), as discussed in the Introduction, proposed an initial step in this decomposition similar to the one proposed in this work. However he has proposed that the reaction proceeds via a free radical mechanism. However it is not felt as a result of this work that the reaction proceeds through a free radical mechanism. There are several reasons for this. First, in all but those experiments done at rate maximum, the decomposition was very slow. Free radical reactions are generally quite rapid. Free radicals once formed, such as OH, do not exist for any length of time, ordinarily. Secondly, in many free radical reactions the rate is dependent on the initial reactant concentration. This type of chain reaction depends on the quantity of radicals initially produced. The rate of decomposition as stated earlier is apparently independent of the initial $(H_2O_2)_t$.

Thirdly, free radical reactions frequently have periods of induction. None was observed for this reaction. Fourthly, the rate was found to be independent of surface area. Most free radical reactions are dependent on surface area, the vessel wall adsorbing radicals and either stabilizing them

there for future reaction or else removing them from the reaction. The last argument against a free radical reaction is that the rate was apparently not light catalyzed. Urey, et al. (28) have assumed the initial step on the photochemical decomposition to be:



while Hunt and Taube (15) suggest:



In either case it is generally agreed that the photochemical decomposition takes place with a free radical mechanism. If the base catalyzed decomposition takes place with a similar free radical mechanism it would probably be catalyzed by light.

Not all the evidence is against a free radical mechanism however. It would appear from the work of Erdey and Inczedy (11) that the heterogeneous base catalyzed decomposition has a rate equation similar to the homogeneous base catalyzed decomposition. This might be expected if both go through similar free radical mechanisms, the only difference than being the addition of a step in the mechanism in the case of the heterogeneous decomposition in glass to account for interactions of the free radicals with

the vessel walls; this interaction in polyethylene would have to be considered very small.

7. Sources of error

The entire process of analyzing the data for this reaction is very subject to error. In the first place there is that certain amount of error always present in any experimental determination. In this work the analytical determinations are subject to some errors. The taking of the samples is accomplished by using a 10 ml pipette. In those experiments where the rate was very fast the rapid evolution of oxygen tended to produce foaming. This made bringing the meniscus in the pipette to the mark somewhat difficult and measurement of the sample uncertain. There are also the usual errors met with in any titrimetric analysis.

The influence of these analytical errors can be quite profound. The eventual use of this data is to determine

$$- \frac{d(\text{H}_2\text{O}_2)_t}{dt} .$$

This quantity is extremely sensitive to how the $(\text{H}_2\text{O}_2)_t$ versus time curve is drawn. A slight error in determining the hydrogen peroxide concentration at a given time will be magnified many times when one determines the slope. This is made even worse by realizing that the method used for determining this slope is also somewhat subject to error.

Another source of error is the ignoring of activity coefficients in the determination of the quantities (H_2O_2)

and (HO_2^-) . These activity coefficients are very probably not unity and also probably vary with $(\text{H}_2\text{O}_2)_t$.

In the very slow runs one must also again be concerned with the possibility of impurity catalysis. The complete rate equation is of the form:

$$-\frac{d(\text{H}_2\text{O}_2)_t}{dt} = k_1(\text{H}_2\text{O}_2)(\text{HO}_2^-) + k_2\phi \quad (13)$$

where ϕ is some function of $(\text{H}_2\text{O}_2)_t$, $(\text{OH}^-)_t$ and impurity concentration. The evidence cited earlier shows that for faster rates the value of ϕ in relation to the term $k_1(\text{H}_2\text{O}_2)(\text{HO}_2^-)$ is very small. However a solution with $(\text{OH}^-)_t = 2.0 \text{ M}$ and $(\text{H}_2\text{O}_2)_t$ initially at 0.5 M will take well in excess of 20 days to decompose. This then is a very small rate, which is as it is predicted by the rate equation. In this case however $k_2\phi$ must surely be of sufficient magnitude to introduce great error in any determination of k_1 . This is the reason that most of the plots of

$$-\frac{d(\text{H}_2\text{O}_2)_t}{dt}$$

versus $(\text{H}_2\text{O}_2)(\text{HO}_2^-)$ that were made were done in the region of $(\text{OH}^-)_t$ from 0.1 to 1.0.

Considering then all of these possible sources of error one could not expect to have extreme precision. The scatter of points found as well as the non zero intercept found in some cases for the plots of $-\frac{d(\text{H}_2\text{O}_2)_t}{dt}$ versus $(\text{H}_2\text{O}_2)(\text{HO}_2^-)$ is not out of line. In fact it is almost surprising that they

come out as well as they do.

In concluding then a remark by Bancroft (2) seems quite proper:

"The chemistry of hydrogen peroxide is a hopeless subject for the phenomenological or Baconian experimenter because misleading experiment is everywhere."

B. Catalytic Decompositions

Before one can attempt to study the catalyzed decomposition of hydrogen peroxide one must know the uncatalyzed kinetics. Since in this work the uncatalyzed kinetics were determined the opportunity for some catalytic studies was made possible.

Lead ion is known to be one of the most active heterogeneous catalysts for this reaction (21). It was decided to study the catalysis of this ion in strongly basic solutions where PbO redissolves to form a plumbite ion. It was thought that catalysis might be an alternate oxidation-reduction of the peroxide by a plumbate to plumbite ion mechanism. It was found, however, that when the basicity was raised so that the PbO redissolved that its catalytic activity disappeared. A very slight initial reaction occurred when the $\text{Pb}(\text{NO}_3)_2$ was added to the solution due to temporary precipitation of the PbO . Beyond this no catalytic activity was found. Several lead ion concentrations and hydroxide ion concentrations were studied.

Zirconium was interesting in that when the solution of ZrOCl_2 was added to the basic solution the expected precipitate of ZrO_2 formed; however when the peroxide was added the zirconium redissolved due to the formation of some kind of complex ion. This ion was tested for its catalytic activity. Solutions at 1.0 and 2.0 molar potassium hydroxide with zirconium up to 0.01 molar were studied. No effect due to the zirconium was found. It was noted however that when the peroxide concentration became low the zirconium again precipitated out and a speeding up of the rate appeared to take place.

Arsenic, as potassium arsenite, was also tested for catalytic activity. Arsenite concentration was varied from 0.005 to 0.015 molar. No catalysis due to the added arsenic was found.

Copper is not very amphoteric and when added to these basic solutions immediately precipitated out. This hydrous oxide of copper was found to be the most active catalyst of all the catalysts studied. For example in one run a solution with $(\text{OH}^-)_t = 1.0$ molar and copper added to 5×10^{-3} molar decomposed in six hours the same amount of peroxide that uncatalyzed would have taken roughly 20 days to decompose.

It was found that copper was sufficiently amphoteric to dissolve in roughly 3 molar base. Hydrogen peroxide was added to this solution to see if the catalysis were reduced by having the copper dissolved. Unfortunately soon after the

peroxide was added a yellow precipitate formed and then the decomposition took place very rapidly.

The copper-EDTA complex was also soluble in basic solution. In this case no precipitate was formed when the peroxide was added and the decomposition rate was very much reduced.

Iron was also found to be a very active heterogeneous catalyst, although not quite as active as copper. When one adds peroxide to the solution the iron appears to darken some in color, but does not dissolve. The order in peroxide for this decomposition is one. The catalytic activity of the iron oxide appears to diminish somewhat with use probably due to coagulation of the particles resulting in a lessening of the surface area. This fact was demonstrated by adding a second portion of hydrogen peroxide to one of the decomposed solutions. The order in peroxide was still one, but the rate was somewhat slower.

It was observed that when EDTA was added to a solution with iron in it that it decomposed at a much slower rate. It was thought that this might be due to dissolution of the iron. It was found however that adding EDTA to a basic iron solution did not dissolve the iron precipitate no matter how much EDTA was added. The precipitate may have lightened in color somewhat. Interestingly, however, when peroxide was added to this solution the iron did dissolve. A very deep

purple color was formed. This solution was filtered through the finest filter paper available. The purple color passed through, but a very small amount of hydrous iron oxide remained on the filter paper. Later after sufficient peroxide had decomposed the iron began again to precipitate out. When this happened the decomposition rate increased rapidly. This is probably due to the fact that when this reprecipitation occurred the particles were quite small and hence a great surface area was exposed. The rate began to increase so rapidly in some cases that the solution became quite warm and foamed out of the beaker.

In some instances the purple color was brought back immediately by addition of more peroxide. This did not work in all cases, and in these cases where it did not work immediately addition of more EDTA or KOH had no effect. It was found that by repeated additions of hydrogen peroxide the precipitate eventually redissolved and the purple color returned.

In all cases then, for the cations studied, it can be said that when a heterogeneous catalysis is made to behave homogeneously that its activity either is lost entirely or is sharply diminished.

The catalysis of this decomposition by chloride ion has been studied extensively in acid and neutral solution (3). It was felt that it would be interesting to test its activity in a basic solution.

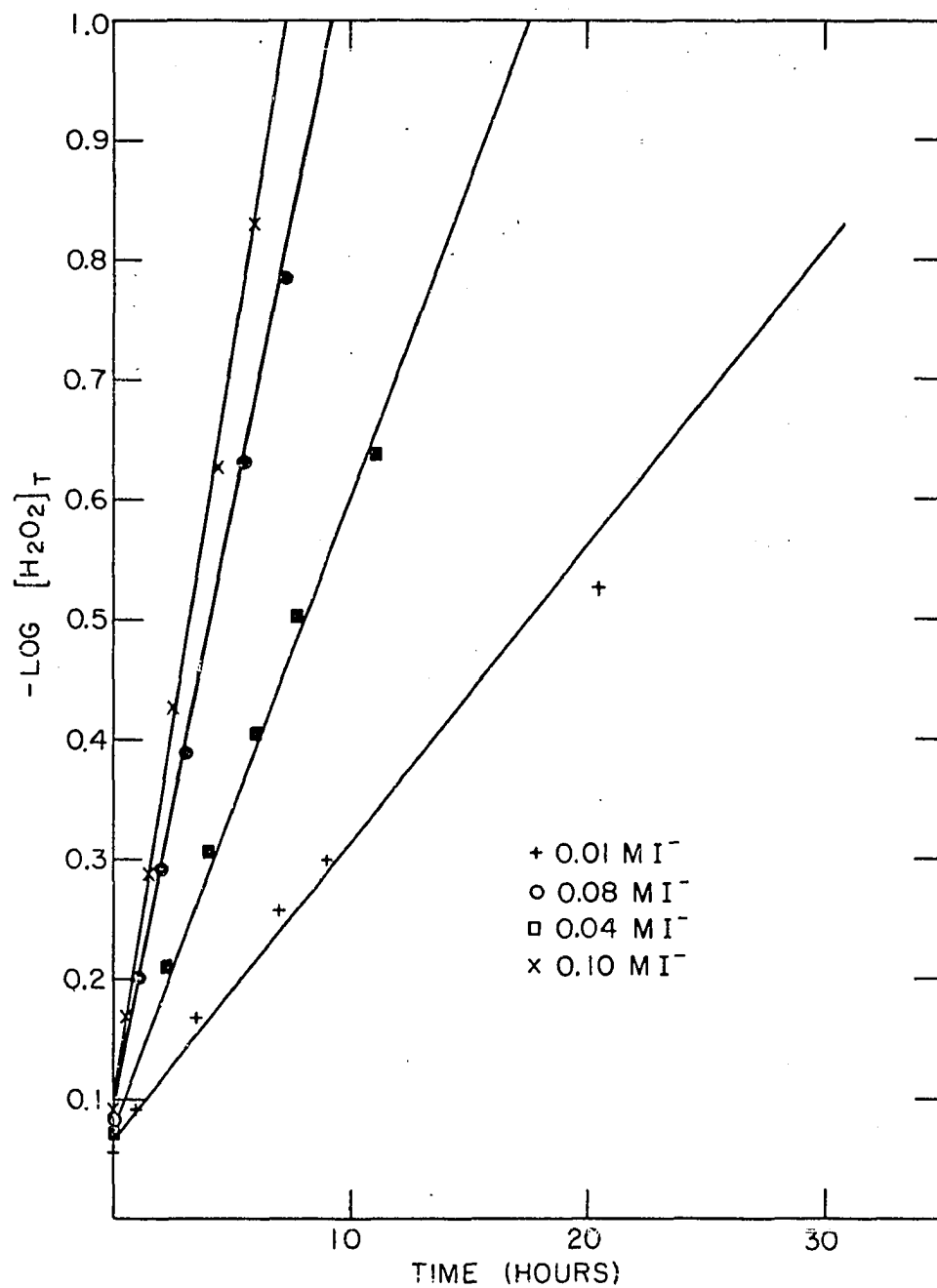
A few preliminary runs with chloride were made and the catalysis by chloride appeared negligible. At the end of these runs the solutions were analyzed for hypochlorite and chlorate as well as for total chloride. Hypochlorite and chlorate were absent in all cases. The amount of chloride added checked well with the amount found.

A more thorough study of this catalysis was then made. Chloride ion concentration was varied from 0.5 to 10^{-5} molar. Very little if any effect due to the chloride ion was found. These experiments were also carried out in the presence of the added polyethylene and also in the absence of light. The hydroxide ion concentration and initial peroxide concentration was varied. In all cases only very minor effects were found. It is concluded that in basic solution chloride ion is not a catalyst.

It was felt that if chloride was inactive that it would be instructive to see if all the halides were inactive. In acid solution iodide is the best catalyst of the halides (3) so this was tested in basic solution. It was found that iodide was a very good catalyst for this decomposition. In Figure 4 are shown some plots of $\log (H_2O_2)_t$ versus time for this reaction. These plots give very good straight lines indicating that it is of the first order in hydrogen peroxide. The rate equation is then:

$$-\frac{d(H_2O_2)_t}{dt} = k(I^-)^n (H_2O_2)_t \quad (14)$$

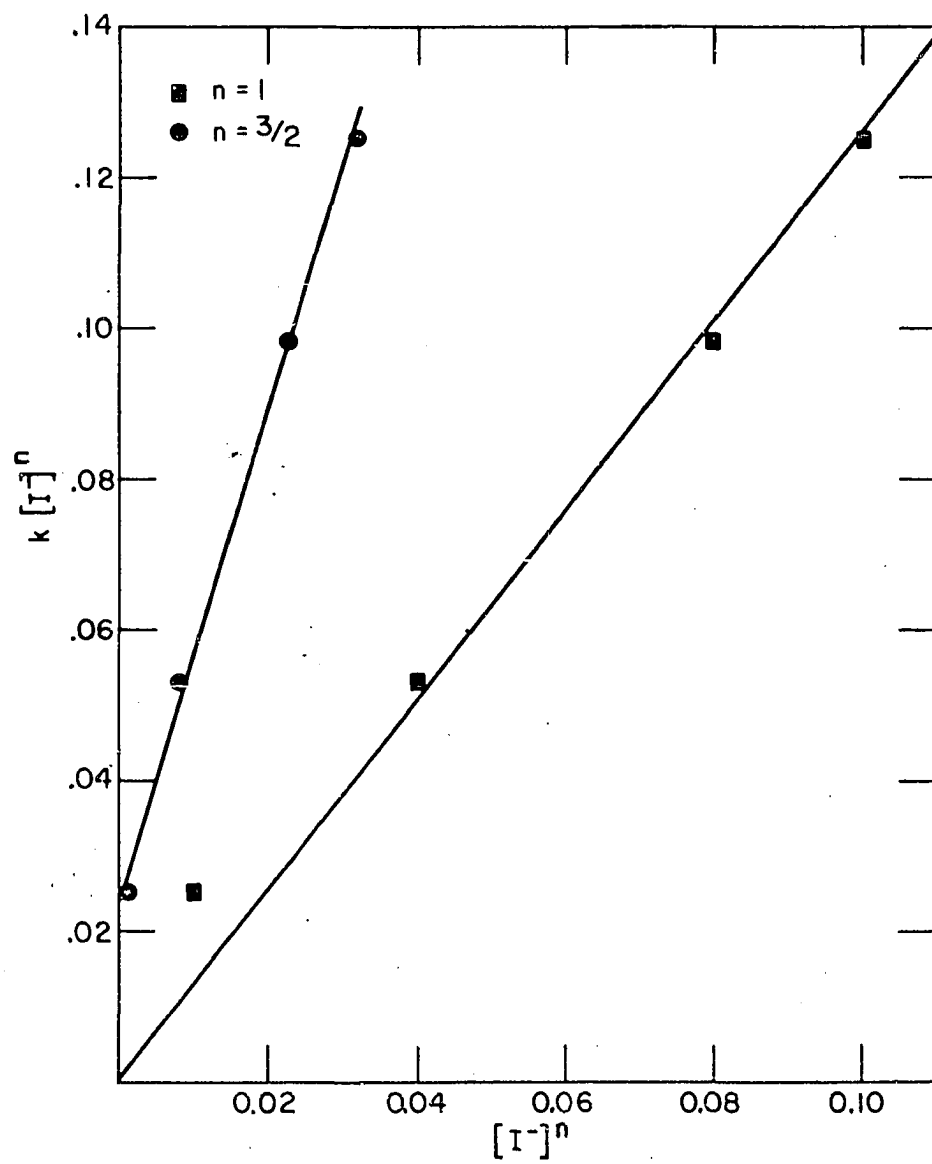
Figure 4. Graph of $-\log (H_2O_2)_t$ versus time resulting from studies on the iodide catalysis with (OH^-) 2.0 at $35^\circ C$



The order in iodide, n , can be determined by plotting the slope of the lines of the log plots versus various functions of the iodide concentration. The one giving the best straight line will give the order in iodide. Some of these are shown in Figure 5. It is hard to tell whether the order is one or three-halves from these plots. However it should be stated that in all this work the hydroxyl concentration was at 2 molar where the uncatalyzed rate is rather slow. Hence no corrections in the plots were made for this term in the rate equation. In the solutions with low iodide concentrations, however, the rate was also slow and if some corrections were made for this the slope of the lines on the log plots would have been smaller. Following this line of reasoning one would conclude that the order in iodide would be one.

Not enough information on the system was obtained to be able to work out a mechanism for this reaction. For example it would be interesting to find what effect varying the initial hydrogen peroxide concentration and also the hydroxide ion concentration would have on the rate. Further it would be interesting to start the reaction off with I_2 instead of KI to see if the same rate was obtained. This would give some information as to whether the reaction was an alternate oxidation of peroxide by free iodine followed by reduction of the peroxide by iodide ions, as it is in acidic solutions (3).

Figure 5. Plot of $k(I^-)^n$ versus $(I^-)^n$ for various n



IV. SUMMARY

The rate equation for the homogeneous, uncatalyzed decomposition of hydrogen peroxide in basic solutions is shown to be of the form:

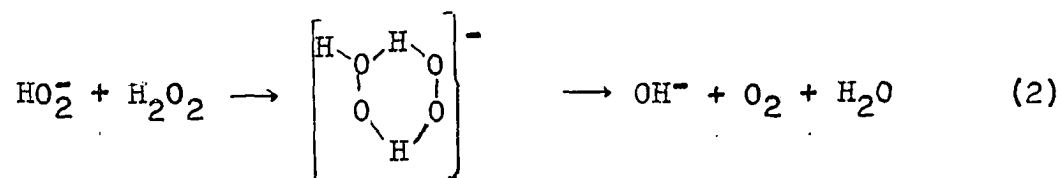
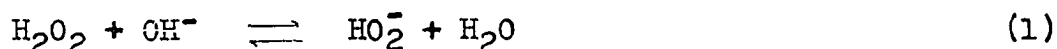
$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = k (\text{HO}_2^-) (\text{H}_2\text{O}_2)$$

A maximum in the rate is predicted by this equation when:

$$(\text{HO}_2^-) = (\text{H}_2\text{O}_2)$$

This maximum is actually found where predicted. The specific rate constant is 2.65 ± 0.4 and 0.95 ± 0.01 at 35 and 15°C respectively. The activation energy is 9 ± 1 kcal/mole.

The mechanism suggested is:



Reaction 2 is rate controlling.

Evidence is given to show that the reaction studied is actually homogeneous and that harmful impurities are absent.

Some information is also given on the catalysis of this decomposition in basic solution by iron, copper, lead, arsenic, and zirconium and chloride and iodide ions. Iron

ion and copper ion are very active catalysts. The plumbite ion, arsenite ion, and zirconium ion are found to be inactive if made to behave as homogeneous catalysts. Chloride ion does not catalyze the decomposition but iodide ion does. In the latter case the rate is first order both in iodide ion and in hydrogen peroxide.

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VII. APPENDIX

Figure 6 is included to show the general features of the $(\text{H}_2\text{O}_2)_t$ versus time curves. The perpendiculars to the tangents which are drawn by the mirror technique discussed on page 36 are not included in this figure. It should be noted that the two curves cross. This behavior is predicted by the rate equation.

All curves of this type were drawn with a flexible curve. It was found that the use of french curves tended to produce "loops". This produced great errors in the determination of the tangents.

Figure 6. Plot of $(\text{H}_2\text{O}_2)_t$ versus time at 15°C

