PHYSICAL & CHEMICAL PROPERTIES OF HYDROGEN PEROXIDE





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# Thesis.

THE PHYSICAL AND CHEMICAL PROPERTIES

OF

PURE HYDROGEN PEROXIDE.

by

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There are few compounds which have acquired such importance within recent years as hydrogen peroxide. Not only has it found a great variety of uses within the industries, but its detection as an intermediate product in the oxidation of many compounds has added to its importance in the field of theoretical chemistry particularly in connection with the difficult subject of enriched catalysis. Each year sees the literature by contributions concerning ming reactions in which hydrogen peroxide plays a part. To indicate them, even briefly, would be beyond the scope of this thesis. But it may be said that in spite of the growing importance of hydrogen peroxide, little is definitely known concerning its reactions. The researches carried out at McGill University during the past four years has led to a revision of the physical constants; in the matter of the chemical behaviour of hydrogen peroxide opinions still conflict and certain conclusions are open to doubt. In this paper, however, the discussion is confined mainly to the action of the halogens and the halogen hydrides.

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observed that when bromine is passed into dilute hydrogen peroxide the peroxide is decomposed with the formation of what appeared to be hydrobromic acid. Several years later<sup>1</sup> he described an analogous effect with iodine. No intermediate products were suggested by Schoenbein, and since he was unable to detect the presence of iodates the conclusion was drawn that the hydriodic acid is directly oxidised to iodine by the hydrogen peroxide. In 1880, Schöne<sup>2</sup> observed the analogous reaction with chlorine and concluded that the corresponding halogen hydride was formed directly without involving any intermediate product.

<sup>3)</sup>Fairley, Brit. Ass. Rep., 44, 57 (1874).

equally from the hypochlorous acid and the hydrogen peroxide. Similar conclusions had previously been reached by Brodie<sup>1)</sup>, using however, solutions of barium peroxide and calcium hypochlorite in acetic acid. In 1899 Tanatar<sup>2)</sup> using hypobromous acid observed a reaction exactly analogous to that described by Fairley with hypochlorous acid, oxygen being liberated and, in this case, hydrobromic acid formed.

Within recent years a number of papers have appeared dealing with the well known reaction between hydrogen peroxide and hydriodic acid, and the various oxy-acids of iodine have been in turn suggested as intermediate compounds. But those which have proved to be the most valuable contributions to the subject are the ones which have attacked the problem from a new angle, namely, the velocities of the reactions, especially the velocity of the catalytic decomposition of the peroxide. Bredig and Walton, for example, have shown from the rates of decomposition that iodates and periodates cannot be formed as intermediate compounds. Similarly, Brode<sup>4)</sup> has shown that there is a close relation between the rates of decom-1) Brodie, Phil. Trans., 140, 759 (1850); 152, 837 (1862). 2) Tanatar, Berichte, 32, 1013 (1899). 3) Bredig and Walton, Zeit. Elekt., 114, Vol. 9, (1903);

Zeit. phys. Chem., 47, 185 (1904).

<sup>4)</sup> Brode, Zeit. phys. Chem., 49, 207 (1904)

position and the concentration of the hypoiodite-ion. Since this investigation was begun two interesting papers on the decomposition of hydrogen peroxide by hydrobromic acid have appeared by Bray and Livingston to which further reference will be made.

No work has hitherto been done on the reaction between hydrogen peroxide and hydrochloric acid. This has probably been due to the fact that concentrated solutions of pure hydrogen peroxide have been very difficult to prepare and the opportunities for extensive experimentation have been accordingly limited. The methods devised at McGill University<sup>2)</sup> for the preparation of concentrated solutions of hydrogen peroxide on a convenient scale have opened a new field of research and have made it possible to investigate the reactions with hydrochloric acid analogous to the well known one with hydriodic acid. The opportunity for studying the reaction is all the more favorable in the case of hydrochloric acid as the reaction proceeds slower than in the case of the other halogen hydrides and the rates of decomposition can be measured with greater accuracy. This paper therefore continues the investigation into the reactions between hydrogen peroxide and the halogen hydrides from the standpoint of reaction rates and a new theory is advanced to explain their mechanism.

 Bray and Livingston, Jour. Am. Chem. Soc., 45, 1251 (1923); 45, 2048.
O. Maass, Jour. Am. Chem. Soc., 42, 2574 (1920); Maass and Hatcher, Jour. Am. Chem. Soc., 42, 2648 (1920) It was discovered that when dry hydrogen chloride gas is passed into anhydrous hydrogen peroxide chlorine is liberated even at low temperatures.<sup>1)</sup> This was unexpected as it was believed that dilute solutions of hydrochloric acid did not react upon hydrogen peroxide, in fact, hydrochloric acid has been recommended as a stabilizer to inhibit the spontaneous decomposition of hydrogen peroxide when kept in glass bottles. In the paper referred to above<sup>2)</sup> it was mentioned that it would be interesting to determine the concentrations at which chlorine would be given off and the concentrations at which hydrochloric acid would act as a stabilizer. Moreover it was thought that this might give an indication of the oxidising power of hydrogen peroxide solutions of various strengths so that a means might be obtained of standardising these solutions by means of hydrochloric acid.

and to throw some light upon the mechanism of the reactions. One of the first problems to be attacked, therefore, was the part played by the various ions or molecules in the decomposition.

The results of a preliminary investigation can be generalised briefly as follows; with the exception of hydrofluoric acid a halogen hydride causes the decomposition of hydrogen peroxide under all conditions. By increasing the concentration of either the hydrogen peroxide or the halogen hydride a point is reached where the halogen hydride itself is oxidised. The minimum concentrations at which oxidation takes place increases in the order hydrogen iodide, bromide, chloride, and fluoride. The question involved is whether the decomposition of the hydrogen peroxide is due to the hydrogen-ion, the halogen-ion, or the halogen hydride molecule. It was hoped that quantitative measurements including among others the rates of the reactions would throw some light upon this question and possibly give an inkling as to the mechanism of the reaction both when the halogen hydride is oxidised and when oxidation does not take place. Great care was taken in the preparation of the reagents as the presence of very small traces of foreign impurities was sufficient to impair seriously the accuracy of the results. All apparatus for preparing or containing the hydrogen peroxide was first allowed to stand over night in chromic acid solution, then washed in alkali, and finally in distilled water before being dried for use.

The hydrogen peroxide solutions were prepared from commercial three percent solutions in the manner described by Maass and Hatcher<sup>1)</sup>. About a hundred liters of commercial solution were concentrated by boiling in vacuo and distilled. Where solutions of ninety percent strength or over were required the concentrate was crystallised.

In the case of hydrochloric acid quantitative measurements could be carried out more accurately than in the case of the other halogen hydrides on account of its relatively smaller activity. The experimental methods used and the results obtained in the reactions between hydrogen peroxide and hydrochloric acid will therefore be first described.

Various attempts were made to discover a method of 1) Maass and Hatcher, Jour. Am. Chem. Soc., 42, 2548 (1920)

II.





analysing a mixture of hydrochloric acid, chlorine, and hydrogen peroxide in aqueous solution. It was found that very small quantities of free chlorine, .01 mg in 5 cc., could be accurately estimated by the bleaching of a standardised solution of a dye such as methyl red. But this bleaching was partially inhibited by the presence of hydrogen peroxide. An attempt was made to estimate the hydrogen peroxide in the presence of chlorine and hydrochloric acid by adding barium chloride to the mixture, together with a sufficient quantity of sodium hydroxide solution until slightly alkaline. The precipatate of barium peroxide was filtered, washed free from chloride and then analysed. The results obtained by this method were found to be inaccurate to 0.7%, and the reason for this was traced to the apparently great and variable solubility of barium peroxide. This may be due either to the decomposition of the barium peroxide or to a variation in the size of the particles in which it is precipitated. A satisfactory method was however finally devised whereby it was possible to estimate the amount of chlorine liberated and hydrochloric acid remaining, while at the same time measuring the rate of decomposition of the peroxide of hydrogen brought about by the acid. This method makes use of the apparatus shown in the accompanying diagram, Figure I.

About 10 cc. of hydrogen peroxide was introduced into the reaction flask A, by means of a pipette and weighed. It was then cooled in a salt and ice freezing mixture and the hydrogen chloride gas added. This was done by means of a capillary tube leading from a calibrated bulb filled with dry hydrogen chloride. The hydrogen chloride gas was prepared from salt and sulphuric acid and dried by passing through sulphuric acid several times before being collected over mercury. By raising and lowering a mercury reservoir it was possible to introduce into the peroxide definite volumes of hydrogen chloride gas from the calibrated bulb and the concentrations of the hydrogen peroxide, hydrochloric acid aqueous solution could therefore be accurately calculated. When however it was required to work with solutions of any particular concentration it was found to be more accurate and convenient to add the hydrogen peroxide to a solution of hydrochloric acid. For this purpose special pipettes were prepared which would deliver through capillary tubes known volumes of hydrogen peroxide solution whose strengths had been determined. The acid solutions were then made up to definite strengths so that when the hydrogen peroxide from the pipette was added to a definite weight of this acid the required concentrations would result. For example, it was desired to make up a mixture having the concentrations,

$$H_20_2$$
, 80.3%  
HC1, 0.9%  
 $H_20$ , 18.8%.

The hydrogen peroxide solution on hand was analysed and found to be 96.10%. The pipette would deliver 9.637 grams of this calculated on the density of hydrogen peroxid. It was calculated that when this is added to 1.902 grams of 5.46% hydrochloric acid the required concentrations would be reached. An acid solution of 5.46% strength was therefore carefully prepared and the proper amount weighed into the reaction flask. It was then cooled in salt and ice and the hydrogen peroxide added by means of the pipette. As a further check on the accuracy of this method the mixture could then be weighed and corrections made if necessary.

Having mixed the hydrogen peroxide and hydrochloric acid in the required proportions the reaction flask was sealed while still in the freezing mixture. The sulphuric acid bulbs B, and the potassium iodide tubes C, which had been previously sealed together were in turn sealed to the delivery tube of the reaction flask. The whole system was then placed in a thermostat and was attached by means of a short rubber tube to the gas burette and containers as shown in the diagram. The rubber tube was wired to the two glass tubes which were brought together until they touched. All other connections were glass sealed throughout to prevent any possibility of the escape of gases.

The experiments were carried out at 25°C. The thermostat was electrically controlled and was accurate to .01°C.

After the apparatus had been sealed together and the reaction had begun as indicated by the escape of bubbles of

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Maass and Hatcher, J.A.C.S., 44, 2559 (1922)

oxygen in the reaction mixture, the stop cock leading to the large reservoir, D, was closed and the stop watch was started. At the same moment the stop cock leading to the burette was opened allowing the oxygen to be collected there over water. The time from zero, i. e., the time when the apparatus was first placed in the thermostat, and the time when the reading was first begun were noted. After a suitable volume, generally about 25 cc., had been collected the two-way stop cock was again closed. The time required to collect the definite volume of the oxygen under known conditions of temperature and pressure was read off the stop watch. The oxygen was then allowed to collect in the large reservoir, D, for a time during which the burette was again filled with water by raising the levelling tube, E. In doing so the oxygen in the burette was forced into D where it was added to that which had already been collected. Another reading was then made as before, the time required to collect about 25 cc. being an indication of the rate at which the hydrogen peroxide was decomposing in the reaction flask. The operation was repeated at suitable intervals for about ten hours, or until no further reaction took place. In this manner the course of the reaction was followed. The apparatus was then cut apart and the products weighed and analysed. The oxygen collected in the large reservoir was measured and its equivalent in terms of hydrogen peroxide calculated. The hydrochloric acid oxidised was caught as chlorine in the potassium iodide tubes and estimated by means of a standardised solution

of sodium thiosulphate. The residue in the reaction flask was analysed for hydrogen peroxide by means of a standardised solution of potassium permanganate, the hydrochloric acid by means of standard alkali. Table I is a cample of the check obtained on the final products and initial constituents of the reaction.

## Table I.

Initial and Final Products of the Reaction.

HCl recovered in reaction flask; 1.6030 g. as Cl<sub>2</sub> in KI tube; .0425 g. Total; 1.6455 g. Initial HCl before reaction; 1.6490 g.

 $H_2 0_2$  recovered in reaction flask;<br/>as  $0_2$  in bulb D;.4013 g.<br/>4.1290 g.\*\*Total;4.5303 g.Initial  $H_2 0_2$  before reaction;4.5250 g.

H <sub>2</sub> 0 H H	formed	od in " from	reaction $H_2SO_4$ h HCI oxid $H_2O_2$ dec	flask; pulbs; lised; comp'd;	9.0500 .0855 .0105 1.8511	ឆ្ន ឆ្ល ឆ្ល ឆ្ល ឆ្ល ៖
Ħ	Ħ		Total;		9.1355	g.
Init Form	tial H <sub>2</sub> 0 ned from	befor HCl a	re reaction H <sub>2</sub> 0 <sub>2</sub> ;	.o <b>n</b>	7.3340 1.8616	g • g •

Total;

9**.**1956 g.

The rate of decomposition of the hydrogen peroxide could be calculated from the rate at which the oxygen was being given off. The volume collected in the burette was corrected to standard conditions of temperature and pressure and its equivalent in terms of hydrogen peroxide calculated. When divided by the reading on the stop watch, the number of grams decomposing per minute was obtained. These values are given in the last column of Table II. Since the rate was changing while the reading was being made the average rate during the interval was obtained by taking the time from zero half way between the beginning and the end of the reading.

Only the data of one experiment are given in Table II. The two parts of the experiment, A and A', were carried out several days apart and with different samples of hydrogen peroxide. As will be seen from the table, the concentrations of peroxide and acid were made the same in the two parts of the experiment, the purpose being to determine with what degree of accuracy the devised method would enable results to be duplicated. Α.

Zero Time; 1,38 p.m. Barometer; 764.3 m.m.

Time of	Temp.	Vol. O.	Stop	Time	H <sub>2</sub> O <sub>2</sub> decomp'g
Reading.	-	Collected.	Watch.	fr. zero.	per Minute.
p.m.	°C	Cc.	Min.	Min.	Grm.
1,39	19.6	35.0	5.02	2.50	.0246
1,46	19.4	27.6	3.92	8.95	.0196
1,52	19.2	20.2	2.95	14.72	.0190
1,58	19.0	20.2	3.03	20.51	.0186
2,06	19.0	20.2	3.23	28.60	.0175
2,12	19.2	20.2	3.38	34.19	.0167
2,19	19.3	20.2	3.50	41.75	.0161
2,26	19.4	20.1	3.70	48.85	.0152
2,34	19.6	20.1	3.83	56.47	.0146
2,52	19.4	20.1	4.25	75.17	.0132
3,11	19.0	20.0	4.75	94.37	.0118
3,57	19.6	20.1	5.82	140.91	.0096
4, 48	19.6	20.2	7.18	192.57	.0078
5,48	19.8	20.1	8.83	253.42	.0063
8,02	19.4	20.6	13.72	389.86	.0042
10,01	19.4	20.1	17.78	510.90	.0032
-					

A •

	Zero Time;	3,27 p.m.	Barometer;	754.0 m.m.	
3, 32	20.2	20.4	2.69	6.3	.0262
3, 38	20.0	20.5	2.83	12.4	.0199
3,45	19.8	20.5	3.02	19.5	.0190
3,50	19.8	20.5	3.13	24.6	.0179
3,56	19.8	20.4	3.23	30.6	.0174
4,01	19.8	20.5	3.29	35 <b>.6</b>	.0171
4,07	30.0	20.5	3.50	41.7	.0161
4,16	20.0	20.5	3.62	50.8	.0155
4,27	20.0	20.5	3.96	62.0	.0142
4,50	20.2	20.6	4.48	85.2	.0126
5,18	20.0	20.5	5.03	113.5	.0112
6,08	20.0	20.5	6.32	164.1	.0089
7,10	20.0	20.5	8.05	227.0	.0070
8,14	20.2	20.4	9.87	292.0	.0057
9,09	20.0	20.5	11.50	347.8	.0049
10,14	20.4	20.5	13.53	413.8	.0041
11,22	19.8	25.0	25.00	485.5	.0033



Figure II.

The data of the precedding table are represented graphically in Figure II, the time being plotted as abcissat and the amount of hydrogen peroxide decomposing per minute as ordinates. The unshaded and shaded points of Curve A in Figure II correspond to the experiments A and A' respectively. It will be seen that they both fall on the same curve A, and therefore indicate the accuracy with which the results may be duplicated with different samples of pure hydrogen peroxide even when the concentrations are above the critical, i.e., when chlorine is given off. A few other curves for which the data corresponding to Curve A are given in the appendix are also represented in Figure II. The initial conditions for these are as follows;

Curve	В;	<sup>H</sup> 2 <sup>0</sup> 2,	33.0%	Н <b>С1</b> ,	9.0%.
Ħ	C;	98	33.0%	M	8.0%
	D;	¥	19 <b>.8%</b>	HB <b>r</b> ,	1.48%
	E;	<b>98</b>	46.3%	HC1,	5.17%.

It will be seen from Figure II that in the very beginning of each reaction there is an increase in the rate at which the oxygen escapes, and after a maximum has been reached the expected diminution in rate occurs. An inhibition period of this kind was observed in every case where the acid concentration was low. It was at first thought that the curve should be drawn direct to the axis, but when this is done the area under the curve corresponds to a greater volume of oxygen than is actually given off. It was found experimentally that the volume of oxygen escaping during this inhibition period could only be correctly represented by the area under the curve itself. It will be seen that the lower the concentration of the acid the longer is the period of inhibition. It is therefore not due to the length of time required for the reaction mixture to warm up from the temperature of the freezing mixture to that of the thermostat. It may be that the greater amount of heat liberated by the reaction in the case of the higher concentrations assists the reaction mixture in reaching the temperature of the thermostat so that the inhibition period is thereby shortened. In many cases however, the inhibition period was longer than the time required to warm such a mixture to the temperature of the thermostat even when no reaction was taking place. Now, it is known that gases may remain in solution until internal pressures . of several atmospheres have been developed. It is possible therefore, that the inhibition period observed is not due to the fact that no reaction is taking place, but that the reaction is not evidenced by the escape of oxygen, an unstable equilibrium occuring whereby the oxygen remains dissolved and the solution is supersaturated with the gas.

The curves in Figure II were plotted on a large scale and divided into sections of fifty minutes each for five hundred minutes. The areas under the curve were then computed, and from the dimensions of the graph these areas were calculated in terms of hydrogen peroxide that had decomposed in the interval. Knowing the weight of peroxide initially present in the reaction flask and the weight that had decomposed, the percentage remaining in the flask could be calculated from the formula:

$$\frac{100(P-x)}{Wt.HC1 + Wt.H_0 + 0.53(P-x)} = Percent. H_20_2.$$

where <u>P</u> is the initial weight of peroxide, <u>x</u> is the weight of peroxide that has decomposed, and 0.53(P-x) is the weight of the water resulting from the decomposition of (P-x) grams of peroxide. This formula assumes that the loss in weight due to the oxidation of small quantities of hydrochloric acid and to the water carried over by the oxygen is negligible. That the latter is negligible was proven by weighing the sulphuric acid in B, Figure I, before and after the reaction. Analysis of the mixture invariably gave results in close agreement with those calculated.

From the table of percentages so obtained the molecular concentration of the peroxide was calculated from the formula:

$$\frac{1000 \text{pd}}{100 \times 34} = M$$

where <u>M</u> is the molecular concentration, <u>d</u> is the density, and <u>p</u> is the percentage. This formula assumes that for low concentrations of hydrochloric acid the change in the density of the hydrogen peroxide due to the presence of the acid is negligible. Where the concentration of the acid was high compared to that of the peroxide a correction was made accordingly for the density of the acid. The data obtained from curve A, Figure II are given in Table III.

#### Table III.

#### Data Derived From Table II.

Time	Area	HoOo	Percent	Mol. Conc.	Log(a-x)
from	below	decomp'd	H <sub>o</sub> O	(a-x)	
zero.	curve.	-	2 2		
	_ 2	-	فبر		
Min.	Cm.	Grm.	p		
0	0	C	33.00	10.85	1.0355
10	51.05	.2552	31.81	10.40	1.0170
20	90.45	.4522	30.87	10.04	1.0017
30	126.40	.6320	30.00	9.72	.9877
40	160.10	.8005	29.17	9.42	.9741
50	191.72	<b>.</b> 9586	28.40	9.16	.9619
70	349.47	1.2473	26.96	8.62	.9352
100	325.02	1.6241	25.06	7.97	.9015
150	427.17	2.1409	22.40	7.06	.8488
200	511.65	2.5582	20.16	6 <b>.32</b>	.8007
250	581.85	2 <b>.9092</b>	18.27	5.70	.7559
300	642.00	3.2100	16.60	5.18	.7143
350	694.00	3.4700	15.15	4.66	.6684
400	739.10	5 <b>.6955</b>	3.85	4.24	.6274
500	812.45	4.0622	11.74	3.50	.5441

(Twenty experiments of the type just described were carried out using different concentrations of hydrogen peroxide and hydrochloric acid. The data for these experiments corresponding to Tables II and III, together with the amount of hydrochloric acid oxidised in each case are to be found in the appendix.)

Now if the decomposition of the hydrogen peroxide is a monomolecular reaction, then  $\log \frac{a}{(a-x)} = kt$ , where a is the initial concentration,  $(\underline{a-x})$  the concentration after an amount x has decomposed, t is the time since the beginning of the reaction, and k is the value of the velocity constant. In these calculations k is



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Figure III.

evaluated on the basis of common logarithms.

When  $\log(a-x)$  is plotted against the time the value of <u>k</u> may be obtained from the slope of the curve. In Figure III several such curves have been drawn. The curve marked 10% HCl is plotted from the data of Table III and corresponds to the experiment A and A', already described. The curve marked 9% and 8% HCl were obtained in a similar manner from the Curves B, and C, in Figure II respectively. The acid concentrations are indicated on the curves, the initial concentration of the peroxide being 33.0% in each case.

It will be seen from Figure III that where the concentration of the acid is low a straight line is obtained from the very first and that the reaction is therefore a monomolecular one. No chlorine was given off in these reactions where a straight line was obtained. But where the acid concentration was higher a straight line was not obtained until the reaction had proceeded for some time when it also became monomolecular. In the latter experiments chlorine was given off as seen in the analysis of the experiment A and A'. The period during which the oxidation of the hydrochloric acid takes place may be seen from the change in the slope of the curve. All the reactions are therefore monomolecular after the concentration of the peroxide has fallen to the point where no chlorine is given off, i.e., below the critical concentration. Above the critical a monomolecular reaction does not take place until by the oxidation of the hydrochloric acid and the decomposition of the hydrogen peroxide the concentration falls to the critical toncentration or below it. The decomposition then proceeds as a monomolecular reaction, the value for k remaining the same until the reaction has gone to completion.

Bray and Livingston (loc. cit.) mention in their investigation of the catalysis of hydrobromic acid that the velocity constant <u>k</u> in the rate equation  $\frac{d(H_2O_2)}{dt} = \underline{k}(H_2O_2)$  only remained constant after the <u>steady state</u> corresponding to their outline of the mechanism of the catalysis was reached. They do not quote any of their variations in the value of <u>k</u> showing an increase before two hours. It will be observed that the curve (5%HCl) shows no variation in <u>k</u>. Only those curves above the critical concentration show a variation, and here only during the time chlorine is given off, during which the value of <u>k</u> decreases. If Bray and Livingston's explanation of the mechanism is the correct one, then the <u>steady state</u> is approached much more rapidly in the case of hydrochloric than in the case of hydrobromic acid. This question of the <u>steady state</u> will be taken up later.

From the curves of Figure III it may also be seen that the rate of decomposition and the value for the velocity constant  $\underline{k}$ , depends only upon the concentration of the acid and not upon that of the hydrogen peroxide, providing the concentrations lie below the critical value. A number of values for  $\underline{k}$  corresponding to different strengths of acid are given in Table IV. In this table  $\underline{k}$ was evaluated only after the curves similar to those in Figure III, had become straight lines and the reaction truly monomolecular. The concentrations of hydrochloric acid are calculated in gram molecules per litre on the basis of a completed reaction, that is after all peroxide had decomposed. A calculation has shown that the average change in volume and hence in concentration during the reaction is small. This is due to the fact that each gram of peroxide decomposing gives 0.53 g. of water, and the density of the peroxide solution is greater than that of an equivalent weight of water. Where oxidation of the hydrochloric acid took place the amount recovered as chlorine was subtracted from the initial weight in determining the final concentration when the reaction had gone to completion.





## Table IV.

## Value of the Velocity Constant k for Different

Concentrations of Hydrochloric Acid.

Conc. HC1.	<u>K</u> ×10	Conc. HCl (Undissod'd)
Mol./litre.	-	Mol./litre.
4.48	15.10	
4.15	14.00	
3.42	9.0	1.62
3.22	8.12	1.47
3.15	8.20	1.39
3.04	6.68	1.34
2.72	5.34	1.11
2.21	3.65	.78
2.02	3.50	.67
1.87	3.08	•59
1.45	2.33	•38
1.16	1.65	.27
1.09	1.70	.24
.979	1.70	.20
.866	1.47	.16
.633	1.00	.10
.509	.88	.073
.310	.65	.035

The data of the first two columns of the preceeding table are represented graphically in Figure IV. The last column will be referred to later.



Figure V.

The concentrations at which less than one milligram of chlorine was given off were selected as having the critical value. These concentrations were determined by trial and error. If too much hydrochloric acid had been added to the hydrogen peroxide solution considerable chlorine would be given off as was indicated by the liberation of iodine in the potassium iodide tubes. As an extreme example of this type one a experiment may be mentioned in which 8.098 grams of 84.0% peroxide solution were mixed with 2.515 grams of 37.0% hydrochloric acid in the reaction flask. The rate of reaction was too fast to be determined by the method described but it was found that an amount of chlorine corresponding to 37.2 per cent of the initial hydrochloric acid content had been swept out by the oxygen and was recovered in the potassium iodide tubes. On the other hand, if the concentrations were below the critical no hydrochloric acid would be oxidised and the potassium iodide tubes remained clear.

Velocity curves, such as were shown in Figure III, were of great assistance in determining these critical concentrations as they indicated where the critical point would lie, namely, at the point where the curve becomes a straight line.

The critical concentrations are given in Table V, and are represented graphically in Figure V. The significance of the critical concentrations in relation to the mechanism of the reactions between the halogen hydrides and hydrogen peroxide will be brought out in the discussion which follows. Table V.

Critical Concentrations of HCl and  $H_2O_2$ .

H <sup>2</sup> 0 <sup>2</sup> .	HC1.
<b>%</b> 80.2	<b>%</b>
74.1	1.5
60.1	3.0
46.3	5.2
33.0	8.0
4.9	14.8

In order to be able to infer from the experimental results the mechanism of the reaction between hydrochloric acid and hydrogen peroxide it is first necessary to recapitulate certain observations which have been made. Below what was called the critical concentration the velocity of the reaction was found to be a monomolecular one for any definite concentration of hydrochloric acid. Analysis showed that the hydrochloric acid content remained unchanged during the whole course of the reaction. Hence, if the hydrochloric acid takes a definite part in the reaction a subsequent reaction must take place in which the hydrochloric acid is reformed. The first point to be decided therefore was whether the primary cause of the reaction between the hydrogen peroxide and hydrochloric acid was due to the hydrogen chloride molecules or to the ions into which it dissociates. To decide this question a series of experiments were carried out which will now be described.

Although hydrogen peroxide when prepared pure by the method described was quite stable at low temperatures even when highly concentrated, signs of decomposition were observed at room temperatures. This was probably due to its action on the glass of the containing vessels, to the presence of light, and to the unavoidable admixture of minute traces of impurities which found their way into the solution during the course of the experiments. A blank experiment was therefore first carried out in which the "natural" rate of decomposition of the sample of hydrogen peroxide on hand was determined at 25°C and in a clean glass flask similar to those in which other experiments of this type were carried out. The flask containing a 52.8% solution of hydrogen peroxide was placed in the thermostat and samples were removed for analysis from time to time by means of a pipette. The percentages obtained from the analysis were plotted against the time when the sample was removed and a smooth curve drawn through the points. A series of values at definite times was then read from the smooth curve, these values in percentages were then calculated in terms of the molecular concentrations and the k-curve drawn as described in the previous experiments. The velocity constant k, could then be evaluated from the slope of the curve. The analysis of samples was continued for a number of days. Table VI gives the values obtained for the first five thousand minutes.

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#### Table VI.

Natural Decomposition at 25°.

Time.	Percent.	Mol. Conc.
Min.	н <mark>з</mark> 02.5	(a-x)
0	52.8	18.76
100	52.6	18.64
500	51.7	18.28
1000	50.8	17.92
2000	49.4	17.36
2500	48.7	17.04
3000	48.3	16.88
3500	47 <b>.7</b>	16.64
4000	47.5	16.56
5000	46.0	16.35

From the slope of the curve or from the formula,  $log \frac{a}{(a-x)} = kt$ , it is found that the velocity constant <u>k</u> for the natural decomposition is .00002, practically negligible in comarison with the high values for <u>k</u> which are obtained when decomposition takes place in the presence of even very low concentrations of hydrochloric acid.

Two experiments were then carried out in a similar manner in which the effect of the hydrogen-ion content were compared in the case of hydrochloric and nitric acid. In the two experiments the hydrogen peroxide concentrations and the hydrogenion concentrations were the same. The data of the two experiments are given in Tables VII, and VIII. It will be seen from a comparison of these two tables that whereas the reaction was vigorous in the gase of hydrochloric acid, in the case of nitric acid practically no decomposition took place over a long interval, and in fact, the velocity constant  $\underline{k}$ , was found to be lower than that of the natural decomposition, in other words the nitric acid acted as a stabilizer and inhibited the spontaneous decomposition of the peroxide. The reaction between hydrochloric acid and hydrogen peroxide is there-fore not due to the presence of hydrogen-ion.

### Table VII.

Decomposition Caused by 1.463 Normal Nitric Acid.

Time.	HO	Conc.
	66	Mol./liter.
Min.	%	(a-x)
0	44.75	15.42
50	44.75	15.42
100	44.70	15.40
200	44.68	15.40
<b>30</b> 0	44.60	15.38
400	44.50	15.34
500	44.20	15.22
600	43.95	15.12
700	43.80	15.06
	k = .000015	

## Table VIII.

Decomposition Caused by 1.463 Hydrochoric Acid.

Time.			H <sub>2</sub> O <sub>2</sub>	Conc.
Min.			~~~	Mol./liter.
С			44.75	15.42
50			42.90	14.70
100			41.45	14.10
200			<b>39.8</b> 8	13.58
300			36.45	12.17
400			34.40	11.40
500			32.75	10.76
600			31.25	10.18
700			29.90	9.70
• • •	k	Ħ	.00029	
A solution of potassium chloride and hydrogen peroxide was prepared similar to the nitric acid solution discussed. Here again the decomposition observed was negligible as may be seen from Table IX where the data of this experiment are tabulated.

Table IX.

Decomposition Caused by 5.50% Potassium Chloride.

Min. HO Mol /lite	r.
0 47.1 16.40	
<b>200 46.7</b> 16.23	
400 46.1 16.00	
800 45.1 15.60	
1200 44.2 15.22	
1600 43.2 14.82	
2000 42.3 14.46	
2400 41.4 14.08	

# k = .000028

It will be noticed from the value for  $\underline{k}$  in Table IX that the rate of decomposition in neutral potassium chloride solution is slightly greater than the natural rate of decomposition. The significance of this fact is brought out in the discussion of the effect of hydrogen chloride molecules on the rate of decomposition of hydrogen peroxide.

A solution of hydrochloric acid and hydrogen peroxide sontaining the same concentration of chlorine-ion as that of the potassium chloride experiment described was made up, and the rate of reaction determined. The value for <u>k</u> was found to be .000170, over six times that of the neutral potassium chloride solution. The data for this experiment are to be found in the appendix. It was evident that the hydrogen-ions or the chlorine-ions as such were not the cause of the decomposition of the hydrogen peroxide in its reactions with hydrochloric acid. The experimental results pointed to the possibility of the undissociated hydrogen chloride molecules playing a part in the reaction. This was brought out further by a final experiment of the type just described. Potassium chloride was added to the nitric acid hydrogen percxide solution (Table VII), in sufficient quantity to just double the concentration of chlorine-ion in Table IX. Samples were then removed for analysis at suitable intervals. Table X shows the results obtained.

## Table X.

Decomposition Caused by Nitric Acid and Potassium Chloride.

Time.	Percent.	Conc.
Min.	H <sub>2</sub> O <sub>2</sub> .	Mol./liter
0	40.85	13.55
60	39.9	13.31
100	39.4	13.1
200	38.3	12.7
300	37.2	12.3
<b>4</b> 00	36.1	11.9
500	35.2	11.5
1000	30.8	9.9

k = .00013

By comparison with Table VII, it is seen that the rate of decomposition immediately increased on the addition of the potassium chloride to the nitric acid solution, the value for the velocity constant <u>k</u>, increasing from .000015 to .000130. Further evidence is therefore given that the hydrogen chloride molecules





formed in the equilibrium KCl +  $HNO_3 \rightleftharpoons KNO_3$  + HCl, play a part in the reaction. To investigate this possibility the variation of the velocity constant of the hydrogen peroxide decomposition with the hydrochloric acid concentration was examined.

The curve, Figure IV, shows the relation between the velocity constant and concentration of hydrochloric acid, the latter being the sum of the concentrations of the undissociated molecules and ions. An attempt has been made in Figure VI to depict the relation between the velocity constant and the undissociated molecules alone. The values for undissociated hydrogen chloride concentrations in moles per liter are given in the last column of Table IV. The calculation of the latter was based on the ionization calculated from conductivity data. Lewis has drawn attention to the error involved in such a calculation due to the change of ionic mobility with concentration, stating that a possible dehydration of the ions would increase their mobility. Others have suggested a decrease in ionic mobility with concentration due to increased viscosity. Hence, it is not possible to estimate accurately the error involved in the calculation of the amount of dissociation from molecular conductivities, but it may be pointed out that the ionizations calculated in this way may be fairly correct relative to one another at the lower concentrations.

Kohlrausch, (Landolt, Börnstein, Roth. "Tabellen".)
Lewis, Journal Am. Chem. Soc. 34, 1631 (1912)

It will be observed, Figure IV, that at the lower concentration the curve is clearly a straight line. Within the experimental error involved in the determination of the velocity constant, and that involved in the calculation of the dissociation at higher concentrations all the points may well fall upon a straight line. If this is so, then it follows that the velocity of the reaction is proportional to the product of the concentrations of the undissociated hydrogen chloride molecules and the hydrogen peroxide. The following speculation is put forward as a tentative explanation. The hydrogen chloride molecule combines with the hydrogen peroxide to form a complex similar to a hydrate or oxonium compound;

 $H_2O_2 + HC1 \neq H_2O_2.HC1$  .....(1) This is followed by the reactions,

> $H_2 0_2 \cdot HC1 \longrightarrow H_2 0 - 0H \longrightarrow H_2 0 + HOC1 \dots (2)$ HOC1 +  $H_2 0_2 \longrightarrow H_2 0 + 0_2 + HC1 \dots (3)$

HOC1 + HC1  $\rightleftharpoons$  C1<sub>2</sub> + H<sub>2</sub>O .....(4) Reactions (3) and (4) are well known ones; reaction (2) is

analagous to the action of ethylene oxide and hydrogen chloride.

of the peroxide remains unchanged after a certain amount of hydrogen chloride has been added, all of which is in agreement with the experimental results.

Equation (1) is probably an equilibrium. The concentration of the complex  $H_2O_2$ .HCl is then proportional to the product of the concentrations of  $H_2O_2$  and HCl. Either of the steps in reaction (2) may be regarded as the rate determining step, the reaction rates of (1) and (2) being relatively great. It will be noticed that the equilibrium in reaction (4) will not appreciably affect the resultant reactions of the first three, viz.,

$$2H_2O_2 = 2H_2O + O_2$$

and therefore reaction (4) will not affect the steady state<sup>\*</sup>) if this is meant to refer to  $\frac{d(H_{10})}{dt} = k$ . To repeat, the velocity constants k are only slightly influenced by this last reaction below the critical concentrations. It is possible, for instance, that this last equilibrium is established only slowly. Reaction (4) does however explain the formation of chlorine.

The rate at which hypochlorous acid is formed depends upon the concentration of the hydrogen chloride or hydrogen peroxide so that with a constant concentration of either one, by increasing the concentration of the other the rate of production of hypochlorous acid becomes such that the equilibrium in reaction (4) is shifted to the right to an extent that appreciable amounts

\*) Vide, page 20

of chlorine are formed. From the critical curve, Figure V, it is seen that an increase in concentration of hydrochloric acid has apparently a greater effect in the production of chlorine than an increase in the concentration of peroxide. This is not quite in agreement with what has just been said, but chlorine is less soluble in hydrogen peroxide than in water and may therefore be more easily swept out by the liberated oxygen out of the more concentrated peroxide solutions.

Further evidence in favor of the views set forth above was given by experiments in which mitric acid was added to an aqueous solution of hydrogen chloride and hydrogen peroxide. The initial concentrations were  $H_2O_2$ , 36.48%, HCl, 4.21%, HNO<sub>3</sub>, 4.96%. Table XI gives the results obtained by analysis.

Table XI.

Decomposition Caused by 4.21% HCl and 4.96% HNO.

Time.	Percent.	Conc.
Min.	H202.	Mol/liter.
20	36 <b>.48</b>	12.16
20	36.20	12.08
33	35.56	11.82
84	34.43	11.40
150	33.27	10.96
280	30.70	9.96
455	28.13	9.05
	$k \times 10^4 = 2.76$	

1) Maass and Hatcher, J.A.C.S., 44, 2472 (1922)

It has been shown that nitric acid does not affect the rate of decomposition of hydrogen peroxide when added alone, except to reduce slightly the natural rate of decomposition. The velocity constant corresponding to a hydrochloric acid concentration of 2.41%, (1.15 Mols. per liter) when added alone is seen from Figure IV to be 1.65. But the velocity constant of decomposition of the above mentioned mixture of the two acids was considerably greater than that which would correspond to the hydrochloric acid content. This was to be expected as the addition of hydrogen-ion will affect the dissociation of the hydrochloric acid giving rise to a larger number of undissociated hydrogen chloride molecules, so that if the rate of decomposition depends upon the concentration of the latter, this rate will be increased.

A few words may be said with regard to the breaking up of the supposed molecular complex. Assuming that similar complexes are formed between hydrogen peroxide and other acids, then from the energy changes involved it can be readily shown that a complex with hydrogen fluoride would not break up, whereas one formed between hydrogen peroxide and hydrogen bromide would break up far more readily than the one with hydrogen chloride.

An experiment was carried out in which an aqueous solution was made containing 56.0%  $H_2O_2$ , and 13.0% HF. This was kept in a paraffin lined flask and placed in the thermostat. Samples removed for analysis from time to time gave results shown in Table XII.

## Table XII.

Decomposition Caused by 13.0% Hydrofluoric Acid.

Time.	H <sub>2</sub> O <sub>2</sub> ;	Concentration.
nours.	Percentage.	Mol./liter.
С	48.63	17.02
20	48.53	16.98
64	48.42	16.92
	$\underline{k} \times 10^4 = .0$	05

It is seen at once that the stability of the hydrogen peroxide solution is much increased by the presence of hydrofluoric acid. The value of  $\underline{k}$  is a tentative one, the decomposition rate being so slow that although the analysis was continued for several days,  $\underline{k}$  could not be measured with any great degree of accuracy, although a similar solution of peroxide with hydrochloric instead of hydrofluoric acid would have reacted with almost explosive violence.

Experiments were carried out with hydrobromic acid, the experimental methods used being the same as those described with hydrochloric acid. Due to the much greater velocity of reaction the experimental results could not be determined with the same degree of accuracy since only small quantities of hydrobromic acid could be added. At medium concentrations bromine was liberated so vigorously that no experiments could be carried out at high concentrations. The liberated oxygen sweeps out the bromine thus altering the composition of the reaction mixture with regard to the hydrobromic acid content. In Table XIII is given a sample of the data obtained in a manner similar to that described in the case of hydrochloric acid, and analagous to Tables II and III. The data of Table XIII are represented graphically in Figure II, Curve D. The data for a number of other experiments using different concentrations of hydrogen peroxide and hydrobromic acid are to be found in the appendix.

III.

# Table XIII.

Decomposition Caused by 1.48% Hydrobromic Acid. Initial Concentration, 19.82% Hydrogen Peroxide.

Temp.	Volume 0 collected.	Stop watch.	Time from zero.	H <sub>2</sub> O <sub>2</sub> decomp'g per minute.
•C	Cc.	Min.	Min.	Grm.
20.4	25.1	14.73	7.4	.0047
20.4	25.9	10.47	21.7	.0068
20.4	25.1	10.08	34.0	.0068
20.4	25.1	10.12	45.0	.0067
20.6	25.0	10.60	55.3	.0065
20.8	25.0	10.86	67.9	.0063
20.8	25.0	11.66	101.3	.0059
19.6	25.8	13.56	156.7	.0053
19.0	25.6	18.32	332.6	.0039
20.0	25.1	20.06	403.C	.0034

Barometer; 756.0 m.m.

Time.	H <sub>2</sub> O <sub>2</sub> decomp'd.	H <sub>2</sub> 02 percent.	H <sub>2</sub> O <sub>2</sub> conc.	Log(a-x).
Min.	Grm.	*	Mol/1.	
0		19.82	6.20	.7924
50	.2915	18.67	5.83	.6757
100	.6040	17.44	5.42	.7340
150	.8822	16.32	5.07	.7050
200	1.1347	15.31	4.72	.6739
250	1.3675	14.35	4.40	.6435
300	1.5800	13.48	4.12	.61.47
350	1.7745	12.68	3.84	.5843
400	1.9550	11.91	3.61	.5575
450	2.1210	10.96	3.32	.5211
500	2.2757	10.55	3.20	.5051
	HBr c	xidised; .00	83 g. <b>i.e</b>	., 2.4%.
	<u>k</u> ×	10 <sup>4</sup> ; 6.0		

Concentration HBr at the end of the reaction .2014 Mol./liter.

The values for <u>k</u> corresponding to different concentrations of hydrobromic acid are given in Table XIV. This table is analogous to Table IV where hydrochloric acid was employed, and is represented graphically on the same figure, Figure IV.

# Table XIV.

Value of the Velocity Constant, k, for Different Concentrations of Hydrobromic Acid.

Conc'n HBr. (Moles/liter)	k×10 <sup>4</sup>
.256	6.74
.201	6.00
.139	3.20
.125	1.50
.117	2.16

The critical concentrations could not be determined in the same way as was done with hiddrochloric acid, because in every case traces of bromine found their way into the potassiun iodide solution. The attempt was made to obtain a curve analogous to the critical concentration curve of hydrochloric acid by measuring the minimum concentration of hydrobromic acid which, for a given concentration of hydrobromic acid which, for a given concentration of hydrogen peroxide, would produce an appreciable coloration due to liberated bromine within an hour. The experiments were carried out under the same conditions of temperature as in the case of hydrochloric acid. At concentrations of two percent of hydrogen peroxide and lower, the color change is not nearly so definite as at the higher concentrations, the time factor being considerably longer than one hour. Table XV gives the values obtained. This table does not give the critical concentrations as arbitrarily defined in the case of hydrochloric acid, but, as was pointed out above, analogous values. The analogy is emphasised in Figure V where these values are depicted along with the critical concentrations of hydrochloric acid. The abcissa of the HBr curve are  $\frac{1}{14.7}$  of those of the HCl curve.

## Table XV.

Concentrations of H2C2 and HBr Analogous to Critical Concentrations.

<sup>н</sup> 2 <sup>0</sup> 2.	HBr.
60.4	0.17
48.3	0.35
33.3	C.52
19.0	0.75
12.3	C • 90
8.2	1.00
2.0	1.10
0.5	1.15

The method of measuring the rate of decomposition for small concentrations of hydrobromic acid by means of the evolved gas does not give results that are as consistent as those obtained where hydrochloric acid was used. The few values obtained by the author are however in good agreement with those obtained by another method by Bray and Livingston, taking into account that the velocity constants here given have to be multiplied by 2.3 to be compared with theirs which were calculated on the basis of natural logarithms.

The curve for hydrobromic acid, Figure IV, shows how greatly the velocity constant is affected by a slight variation in the concentration of the hydrobromic acid as compared to the change caused by a corresponding variation in the concentration of hydrochloric acid. Although the same apparatus was used as in the case of the latter acid and the concentrations made up in the same way, the degree of accuracy was not sufficient for the large changes caused by small amounts of bydrobromic acid. The errors involved are connected with the establishment of the hydrobromic acid concentration and not with the constant k, which was determined accurately. This was shown by the fact that the points giving the relation between time and weight of hydrogen peroxide decomposed fell upon a straight line. One fact was established, namely, that the velocity constant did not alter appreciably after the first thirty minutes, that is, k was constant long before the "steady state" as measured by Bray and Livingston by the rise in bromine concentration had been reached.

1) That time may be required to reach hydrolysis equilibrium has been found in some cases, e.g., Arrhenius, Zeit. phys. Chem., 13, 407 (1900) and, Shaeffer and Jones, Am. Chem. Jour., 49, 240 (1913).





Livingston<sup>1</sup> for the rate of decomposition of hydrogen peroxide in the presence of hydrobromic acid, and calculating the concentration of hydrogen bromide molecules from conductivity data, the curve shown in Figure VII is obtained. It may be seen that a straight line represents the relation between concentration and the rate of decomposition.

It has already been pointed out that if the rate of decomposition is dependent on the concentration of the undissociated acid molecules, then the rate should be increased by the addition of a substance which will tend to decrease the dissociation of the halogen hydride. The action of the hydrogen-ion has already been described in the case of hydrochloric acid. A number of similar experiments were carried out with hydrobromic acid of which a few examples will now be given. It has just been pointed out that an increase in the concentration of hydrobromic acid when a fixed concentration of hydrogen peroxide is used, produces a definite color due to the formation of bromine. Thus, a 5% solution of hydrogen peroxide became definitely colored when the concentration of the hydrobromic acid was increased from 0.95% to 1.10%. A 5% peroxide solution containing C.66% HBr was colorless. Solutions were made up having the latter concentration of hydrobromic acid and at the same time having varying amounts of hydrochloric acid, sulphuric acid, and potassium

Bray and Livingston, J.A.C.S., Table II. page 2051, 45, (1923)
Ostwald, ("Tabellen", Landolt, Bornstein, Roth.)

bromide respectively. Table XVI shows the minimum concentrations of these substances which were found to just cause bromine coloration to appear.

#### Table XVI.

"Critical" Concentrations of Hydrobromic Acid with HCl, KBr, etc.

<sup>H</sup> 2 <sup>0</sup> 2'	5.0%;	HBr,	C.66%;	HC1,	0.91%.
Ħ	5.0%	31	0.66%	H2\$04,	1.82%
15	5.0%,	Ħ	0.66%	KBr,	1.95%.
*	23.8%,	11	C.46%	HCl,	0.18%.

(It will be noticed by comparison with the values for hydrochloric acid that 0.91%HCl and 0.18% HCl are far below the critical concentrations for this acid so that ne appreciable decomposition is caused by the concentrations of hydrochloric acid listed in Table XVI).

Bromine coloration, according to the mechanism put forward above, means that the rate of formation of hypobromous acid has just been reached which will cause appreciable amounts of bromine to form. A solution containing 0.66% HBr and 0.91% HCl has a combined content of 0.33 gran nolecules of acid. Taking the degree of ionization of the hydrobromic and hydrochloric acids to be the same this corresponds to a concentration having an ionization of 98.1%, so that the concentration of the undissociated hydrogen bromide nolecules has been changed from .0056 tp .010 moles per liter. The critical concentration of hydrobromic acid is 1.05% when the concentration of the peroxide is 5.0%, (See Table XV), which corresponds to . 11 moles per liter of undissociated hydrogen bromide molecules. The addition of the hydrochloric acid has therefore increased the concentration of the hydrogen bromide molecules to the critical value. As seen from Table XVI, 1.82% sulphuric acid has the same effect as 0.91% hydrochloric acid. These percentages of acid correspond to 0.37 and 0.25 moles per liter respectively.on the basis of complete dissociation. The difference in value between the sulphuric and hydrochloric acid is in agreement with the idea set forth, for it is well known that sulphuric acid is dissociated to a much smaller extent than hydrochloric, and therefore the true hydrogen ion concentration, and consequently the increase in the undissociated hydrogen bromide molecules is less in the presence of the sulphuric than in the presence of an equimolecular quantity of hydrochloric acid. Hence, the smaller effect of the sulphuric acid on the rate of decomposition is accounted for.

Finally the addition of the bromine-ion should cause an increase in the undissociated molecules, and this is plainly shown by the fact that the addition of potassium bromide gave the critical coloration of bromine to the hydrogen bromide harogen peroxide mixture, whereas a much higher concentration of potassium bromide alone gave no effect whatever.

Before concluding this section it may be worth while describing one more experiment in which chlorine was passed into a 43.0% solution of hydrogen peroxide. The mixture was placed in the thermostat and samples removed from time to time were analysed for acid and peroxide content. Within an hour the chlorine had disappeared and the acid value remained constant thereafter. Table XVII gives the values found.

## Table XVII.

Decomposition Caused by Chlorine.

Time.	Percent.	Mol. Conc.
Min.	H802.	Mol./liter.
100	43.7	14.90
100	42.6	14.77
200	41.5	14.26
300	40.4	13.77
500	38.4	12.75
700	36.7	12.15
1000	34.3	11.25
2000	28.3	9.05

 $k \times 10^4 = 1.30$ 

Acid Concentration after one hour corresponded to 3.65% HCL. Acid Concentration at the end of the reaction corresponded to 1.28 moles per liter of hydrochloric acid.

The rate of decomposition of the hydrogen peroxide corresponded to the rate for a hydrochloric acid solution having the acid value found. This is in agreement with reactions (1) to (4) outlined in the preceeding which are based on the assumption that hypochlorous acid is the intermediate compound. Since the hydrolysis constant of bromine is so very much lower than that of chlorine,

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it follows that the critical concentrations of hydrobromic acid, that is, the concentrations at which bromine is visibly liberated, are very much lower than the critical concentrations for hydrochloric acid.

Bray and Livingston make use of the activity coefficient for hydrobromic acid in the relationship;

 $\frac{-d(H_2O_2)}{dt} = \chi (H_2O_2)(H^+)(Br^-) \Upsilon^2_{HBr}$ 

where  $\underline{X}$  is a constant, and  $\underline{Y}_{HBr}$  is the activity coefficient of hydrobromic acid. They did not test this equation at ionic strengths higher than 0.25 because of lack of activity data. In the case of hydrochloric acid where the activity data have been accurately determined a similar relationship does not hold at any concentration as measured by the author.

A final word may be stid with regard to the use of conductivity data for the calculation of the undissociated molecules. The author realizes that an uncertainty exists as to the soundness of this method in giving absolute values, but considers that it may be the best means available at present for measuring the undissociated halogen hydride concentrations. The term, "undissociated halogen hydride concentration" is considered by some investigators as unjustifiable. The term may be replaced by that of "ions within the sphere of their mutual attraction" as has been suggested by

1) Lewis and Randall, "THERMODYNAMICS", McGraw-Hill Book Co., page, 335, Edition 1923.

others. If this is done, then the formation of the complex  $H_2O_2$ .HCl may be looked upon as depending on the concentration of the hydrogen peroxide molecules and the concentration of those pairs of hydrogen and chlorine ions which are "within the sphere of their mutual attraction."

It has been shown that with the exception of hydrofluoric acid, which acts as a stabilizer, halogen hydrides cause the decomposition of hydrogen peroxide under all conditions. Below certain critical concentrations the reaction is monomolecular and no halogen is set free. Above certain critical concentrations of either the hydrogen peroxide or the halogen hydride, the latter is itself oxidized. These critical concentrations increase in the order, hydrogen iodide, bromide, chloride, fluoride.

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The velocity of reaction over a wide range of concentrations has been studied for the case of hydrochloric acid, and it has been shown that the velocity coefficient is proportional to (1 - 4) times the acid concentration, where 4 is the dissociation calculated from electrical conductivities. It has also been shown that neither hydrogen-ion nor chlorine-ion cause the decomposition of hydrogen peroxide. Hence it has been suggested that the mechanism of the reaction is as follows:

 $H_{2}O_{2} + HC1 \text{ (undissociated)} \xrightarrow{\longrightarrow} H_{2}O_{2} \cdot HC1$   $H_{2}O_{2} \cdot HC1 \xrightarrow{\longrightarrow} H_{2}O - OH \xrightarrow{\longrightarrow} H_{2}O + HOE1$   $HOC1 + H_{2}O_{3} \xrightarrow{\longrightarrow} H_{2}O + O_{2} + HC1$   $HOC1 + HC1 \xrightarrow{\longrightarrow} C1_{3} + H_{2}O$ 

IV.

Similar experiments were carried out with hydrobromic acid, analogous results were obtained and the same explanation was advanced. The rates of reaction were found to be considerably greater than in the case of hydrochloric acid, and the critical concentrations were found to be lower due to the greater rate of reaction and to the fact that bromine is hydrolyzed to a smaller extent than chlorine. The reactions were found to be of the same general character as those with hydrochloric acid.

5 5

The decomposition of the hydrogen peroxide by the halogens is due to the hydrolysis of the latter, forming oxy-acids which decompose the hydrogen peroxide and yield the halogen hydride. SECTION II.

PHYSICAL PROPERTIES OF PURE HYDROGEN PEROXIDE.

It was pointed out in the first section of this thesis that most of the physical constants of hydrogen peroxide have undergone a revision within the last few years; t'e determination of the physical properties has been hampered by the difficulty of obtaining pure hydrogen peroxide in sufficient quantities. In the case of certain physical constants the investigations have been attended with peculiar difficulties owing to the unstable nature of hydrogen peroxide itself. This is particularly so in the determination of such properties as vapor pressures, conductivities, etc., which involve the use of mercury manometers and metallic electrodes since the hydrogen peroxide is immediately decomposed when brought in contact with a metal. The data have therefore been meagre and unreliable. For example, only two vapor pressures for hydrogen peroxide have hitherto been determined; one by Wolffenstein<sup>1)</sup> at sixty five degrees. and another by Brühl<sup>2</sup>) at eighty five degrees. In both cases the accuracy of the values published has been open to question. The vapor density, on the other hand, has never been determined.

The determination of the vapor pressures and the vapor density is of considerable importance. By means of the vapor density the problem as to the molecular aggregation of gaseous hydrogen per-<sup>1)</sup> Wolffenstein, Ber. deut. chem. Ges., 27, 3307, (1894). <sup>2)</sup> Bruhl, Ber. deut. chem. Ges., 28, 2847 (1895). oxide may be settled which in turn may throw light upon its constitutional formula. Furthermore, from an accurate knowledge of the vapor pressures over a large temperature range valuable information may be derived, such as the boiling point, the latent heat of evaporation, the critical temperature, and the value of Trouton's Constant. Even from the meagre data of Wolffenstein and Brühl, Lewis and Randall have made important thermodynamic deductions. This section therefore deals with the determination of the vapor pressures and the vapor density.

The difficulties to be overcome in the determination of the vapor pressure of hydrogen peroxide were those which have already been mentioned, namely, that hydrogen peroxide could not be brought in contact with mercury owing to the fact that mercury brings about its immediate decomposition. A mercury manometer could therefore not be used directly. Nor was it practicable to use a sulphuric acid manometer owing to the solubility of hydrogen peroxide in sulphuric acid and subsequent decomposition. Furthermore, on account of the low vapor pressure of hydrogen peroxide at room temperatures, condensation would occur in all parts of the apparatus not artificially heated. An apparatus which avoids these difficulties was devised. This apparatus makes use of an oxygen screen between the peroxide and a mercury manometer, the oxygen being supplied by the hydrogen peroxide vapor itself.



A diagram of the apparatus used is shown in Figure VIII. The flask, A, of about 150 cc capacity was sealed by means of a side tube to a tube, B, containing granular manganese dioxide. This in turn was sealed to two drying tubes, C, and D, containing calcium chloride and phosphorus pentoxide respectively. From these a tube led to the manometer and a T-tube to a large sulphuric acid vacuum pump,<sup>1)</sup> both tubes being provided with taps E, and F, as shown in the diagram. The flask, A, was fitted with an extra side tube for introducing the peroxide, and with a magnetic stirrer, MM, as shown. The long neck of the flask which was necessary to permit of the stirring rod was covered with a layer of asbestos as was also the tube containing the manganese dioxide. Around the asbestos was wound nichrome wire leading from the neck of the flask and around the manganese dioxide tube as shown; both could then be heated by an electric current through the wire. The wire was surrounded with an another layer of asbestos, both layers of asbestos being allowed to dip into the water of the thermostat so as to prevent cracking of the flask due to the sudden change of temperature between the hot wire and the comparatively cool water of the thermostat. The neck of the flask and the side arm of the manganese dioxide tube were wired as described to within a quarter of an inch of the surface of the water. The side arms of the flask were well underwater so that conden-

1) 0. Maass, Jour. Am. Chem. Soc., 42, 2570, (1920) sation in any part of the flask was prevented when a current was sent through the wire.

A preliminary experiment in which a receiving flask and condenser were substituted for the drying tubes showed that when a current was passed through the nichrome wire and hydrogen peroxide distilled in the flask under vacuum, no trace of the hydrogen peroxide passed through the manganese dioxide tube into the receiving flask. The manometer was carefully calibrated, the limit of error being 0.1 mm., and the system was tested for defects. It was found that the vacuum pump maintained a constant pressure of 0.2 mm. when the amparatus was dry.

About twenty grams of pure hydrogen peroxide analysing 90.98 % H<sub>2</sub>O<sub>2</sub>, were introduced into the flask, A, through the side tube by means of a capillary pipette extending to the neck of the flask. After sealing the tube the thermostat was filled with ice water and the system exhausted. A current of two to three amperes was sent through the nichrome wire until the manometer showed that no further temperature change was taking place.

It was found that when the tap, F, leading to the vacuum pump was closed pressure equilibrium throughout the system was established within a few seconds, the peroxide being vigorously stirred and the stirrer so arranged that it would break right through the surface of the liquid peroxide with each stroke. The vapor pressure could then be read directly from the manometer. At higher temperatures a correction was necessary which will be discussed later.

Between each reading at the different temperatures the system was exhausted, the hydrogen peroxide boiling vigorously. When the tap, F, was closed the vapor pressure of the peroxide in the flask forced some of the peroxide vapor into the hot manganese dioxide tube where it was decomposed into oxygen and water. The oxygen was dried by the calcium chloride and phosphorus pentoxide, and thus only dry oxygen was permitted to come in contact with the mercury of the manometer.

The temperature changes in the thermostat were made as quickly as possible, the time element being a factor of considerable importance for ensuring accuracy by preventing any undue decomposition of the peroxide. A large vacuum tank of thirty liters capacity previously evacuated to C.5mmm pressure was attached in series between the apparatus and the vacuum pump. The system could thus be quickly evacuated between each reading. The peroxide was stirred constantly by means of the magnetic stirrer throughout the run. The thermostat was kept constant at any temperature to within C.1°.

A slight decomposition of the peroxide was observed at temperatures above 50°, and a slight but steady increase in pressure occurred after equilibrium had been reached due to the evolution of oxygen within the peroxide. In order to obtain the equilibrium pressure at the higher temperatures a series of readings was made at definite intervals, depending upon the rate at which the gas was



Figure IX.

being evolved. These readings, on being plotted against the time, gave a straight line after equilibrium pressure had been reached. By extrapolating the line to zero time, that is, the time when the tap, F, was closed and the stop watch started, the equilibrium pressure was obtained. In Table XVIII is given a typical series of readings so obtained. Further data of this nature are to be found in Appendix B. The data of Table XVIII together with those of several other series at different temperatures are shown graphically in Figure IX.

#### Table XVIII.

Manometer Readings at 80.0°C.

Interval. Manometer. (Right Arm)

Sec.	mm.
0	90.0
15	102.0
30	104.0
45	105.0
60	105.8
90	107.0
120	108.0
150	109.0

After the vapor pressure had been determined to as high a temperature as was considered safe, the flask was cooled and determinations were again made at lower temperatures as a check upon those previously determined before the higher temperatures had been reached. The change in vapor pressure due to the decomposition of the peroxide was found to be negligible. The peroxide was then cooled in ice, the apparatus was cut apart and the peroxide analysed. It





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was found that the drop in concentration was 0.4 percent.

The vapor pressures of hydrogen peroxide as obtained from two samples of peroxide by the method described above are given in Table XIX, and are represented graphically in Figure X. It will be seen that the two sets of values are in close agreement, and that although the determinations were made with different samples of peroxide the values obtained fall upon the same curve.

Second Sample.

#### Table XIX.

First Sample.

Vapor Pressures of Hydrogen Peroxide.

Temperature.	Vapor Pressure.	Temperature.	Vapor Pressure.
°C	mm .	°C	mm.
4.5	0.55		
15.0	1.1		
24.2	1.9	23.6	1.8
		29.2	2.6
35.2	4.4	35.8	4.1
		40.8	6.2
45.0	7.8	45.4	8.6
		51.5	11.8
56.8	15.8	56.7	15.0
62.6	21.4	62.4	21.4
70.2	31.1	70.0	31.1
75.2	40.1		
		80.0	49.7
		89.1	72.6

In Table XX, Column I, are given a number of values of vapor pressures of hydrogen peroxide taken from the vapor pressure curve, Figure X, at temperatures from ten to ninety degrees. In the second column are given the logarithms of these vapor pressures. In the third column are given the temperatures corresponding to the





vapor pressures, and in the fourth column the reciprocals of these temperatures on the absolute scale. In Figure XI the logarithms of the vapor pressures are plotted against the reciprocals of the absolute temperatures.

Table XX.

Ρ.	Log10 P.	Temp.	<u> </u>
0.9	.0045	10°	.003 <b>532</b>
1.1 1.5	.0414 .1761	15 20	.003471 .003412
2.0	.3010	25	.003355
2.8	.4472	30	.003299
4.1	.6128	35	.003246
5.8	.7634	40	.003194
8.2	.9138	45	.003144
10.8	1.0334	50	.00 <b>3095</b>
14.3	1.1553	55	.003048
18.5	1.2672	60	.003002
24.1	1.3820	65	.002958
31.2	1.4942	70	.002915
40.0	1.6021	75	.002873
48.7	1.6875	80	.002832
61.5	1.7889	85	.002792
75.3	1.8768	90	.002754

It is seen that the relationship is represented by a straight line. The equation for this curve is found to be;

$$\log P = \frac{-2600}{T} + 9.046$$

where P is the vapor pressure and T the absolute temperature.

The boiling point of hydrogen peroxide calculated from the above equation is found to be 147.2°C
The equation in terms of natural logarithms is,

$$\ln P = \frac{-5987}{T} + 20.82$$

Since this corresponds to the theoretical,

$$\ln P = \frac{-L}{R} \cdot \frac{1}{T} + K,$$

L, the molecular latent heat of evaporation is found to be 11850 cal., and Trouton's Constant,  $\frac{L}{T_b}$ , is found to be 28.21, where  $T_b$  is the boiling point on the absolute temperature scale.

A knowledge of the vapor pressures of a substance makes it possible to determine its vapor density by what is known as the dynamic method for determining vapor pressures. This method consists of passing a known volume of an inert gas through the liquid at constant temperature, the rate of passage of the gas being so regulated as to make certain that it is saturated with the vapor. The inert gas is in turn passed through an absorber which removes the vapor, and the amount is estimated by the usual methods of analysis. From the volume, temperature, and assumed density, the vapor pressure of the liquid can be calculated. Conversely, when the vapor pressure is known the vapor density can be determined.

A known volume of nitrogen was passed through hydrogenperoxide kept in a thermostat at 50°. The nitrogen was then passed through a wash bottle containing ether kept cold at a temperature of -78°, and then through a second wash bottle containing water. The vapor pressure of hydrogen peroxide at 50° is 1.1 centimeters. Using this value and the results obtained from an analysis of the hydrogen peroxide absorbed by the ether, the values for the density of hydrogen peroxide vapor were always found to be less than that corresponding to the formula,  $H_2O_2$ . This was due to the decomposition of the hydrogen peroxide vapor which it was found impracticable to prevent. Moreover, at that low vapor pressure it was found very difficult to ensure that the nitrogen passed through was completely saturated. The vapor density experiments are therefore by no means conclusive in showing that in the vapor state the molecule corresponds to  $H_2O_2$  and not to a multiple of this formula. The work on vepor density is being continued and with a modified apparatus more conclusive results may be obtained.

An attempt was made to determine the vapor density by the Victor Meyer method since the boiling point of hydrogen peroxide is now known. A long cylinder of pyrex glass was filled with oil and heated electrically to a constant temperature at 200°, and the Victor Meyer apparatus inserted. It was thought that the sudden vaporisation of the hydrogen peroxide would take place before decomposition had occurred. It was found that .0248 grams of peroxide gave a volume of 26.4 cc. at 23° and 744 m.m. pressure within half a minute. This gives a molecular weight of 23, corresponding to  $H_2O + \frac{1}{3}O_2$ , that is, the hydrogen peroxide had decomposed inmediately so that this method cannot be used.

#### CONCLUSION.

It was pointed out by Maass and Hatcher<sup>1)</sup> that certain physical properties of liquid hydrogen peroxide are very similar to those of water. Thus, total surface energy, Ramsay and Shield's Constant, show that the association is very much the same for these two substances in the liquid state. The value calculated above for Trouton's Constant is in very close agreement with this. The value for water, 26.2, is exceptionally high, 21 being the value for all unassociated substances. This similarity between hydrogen peroxide and water makes it possible to calculate the boiling point, molecular latent heat of evaporation, with a much higher degree of accuracy than has been done above. Thus, when the boiling point of water is calculated from the vapor pressure curve taken over the same range from 0° to 80°, the boiling point is found to be 98.6°, that is, 1.4° too low. It would seem likely, therefore, that the boiling point of hydrogen peroxide as calculated above is also too low.

On account of the similarity between hydrogen peroxide and water it is permissible to apply the method of Ramsay and Young<sup>2</sup>) in determining the boiling point:

$$\frac{T_1}{T_2} = \frac{T_2}{T_2}$$

<sup>1)</sup> Maass and Hatcher, Jour. Am. Chem. Soc., 42, 2548, (1920).
<sup>2)</sup> Ramsay and Young, Phil Trans., 21, 37 (1886)

where  $T_1$  and  $T_2$  are the temperatures of the water and hydrogen peroxide respectively at the same pressure. Substituting the temperatures at 50 and 760 m.m. pressure, that is  $T_1 = 311.4$ ,  $T_1' = 373.1$ ,  $T_2 = 353.8$ , then  $T_2'$  is equal to the boiling point of hydrogen peroxide which is found to be 150.2°C.. This temperature for the boiling point is probably correct to within a few tenths of one degree and may now be used for the calculation of Trouton's Constant and for the latent heat of evaporation.

The molecular latent heat of evaporation, L, of hydrogen peroxide is given by the expression;

$$L = \frac{RTT'}{T'-T} \ln \frac{p}{p'}$$

Substituting the values, T' = 423.3, T = 353.3, p' = 760, p = 50, R = 1.98, the molecular latent heat of evaporation is found to be 11520 calories. The latent heat for one gram is therefore 338.7 calories These new values give 27.2 for Trouton's Constant, a value in much closer agreement with that for water, which is in conformity with the expectations.

Again, by taking advantage of the similarity between hydrogen peroxide and water it is possible to estimate the critical temperature of hydrogen peroxide from the boiling point of water, namely, 0.58 on the "corresponding temperature" scale. This gives the critical temperature of hydrogen peroxide as 456°C. The information obtained in this investigation together with the data determined by Maass and Hatcher now enables one to determine the slope of the univariant systems passing through the triple point. This is of interest in comparing hydrogen with water. The slopes of the vapor-solid and vapor-liquid curves are given by the equation:

$$\frac{dp}{dT} = \frac{L}{R} \frac{p}{T^2}$$

where L stands for the molecular latent heats of sublimation and evaporation respectively, p and T being the pressure and temperature at the triple point. The slope of the solid-liquid system is given by

$$\frac{dp}{dT} = \frac{1}{T(v_1 - v_8) 24.19}$$

where 1 is the latent heat of fusion,  $v_1$  and  $v_s$  are the volume of one gram liquid and solid respectively.

Table XXI shows the values calculated in this way, the symbols V, L, and S, standing for the vapor, liquid, and solid phases respectively.

Table XXI.

	F. P.	<b>V</b> .P.	L-V.	S-V.	L-S.
H203	-1.7°	C.305	*.024	+.029	+152
H <sub>2</sub> 0	0.0	4.58	+.300	+.345	-131



Figure XII.

The accompanying diagram, Figure XII, shows the triple points in which the liquid-vapor and solid-vapor systems are drawn on a different scale from the liquid-solid systems. The vapor pressure of water at its triple point is fifteen times as great as that of the hydrogen peroxide, and the variation of the vapor pressures with the temperature of both solid and liquid phases is about twelve times as great.

The solid-liquid systems slope in opposite directions. Hydrogen peroxide differs markedly in this respect from water, and undergoes, like the vast majority of substances, a decrease in volume on solidification. The value obtained for Trouton's Constant, quite in agreement with the other physical constants which are affected by molecular association in the liquid state, showed that hydrogen peroxide and water in the liquid condition are associated to the same extent. Yet the density curve of liquid hydrogen peroxide shows no inflexion corresponding to that of water. Since the tha association shows that triple hydrogen peroxide molecules corresponding to trihydrol exist, these must have a smaller volume than the unassociated peroxide molecules with which they are in equilibrium. It would be of great interest to subject hydrogen peroxide crystals to X-ray analysis since the information obtained from such experiments taken in conjunction with the facts pointed out above would throw light upon the anomalous behaviour of water.

The vapor pressure curve of hydrogen peroxide has been determined with considerable degree of accuracy. The latent heat of evaporation, the boiling point, Trouton's Constant, and the critical temperature of hydrogen peroxide have been derived. The physical properties of hydrogen peroxide and water have been compared and the importance of this comparison has been indicated.

# APPENDIX A.

# Experiment 1.

•

Initial	Concentrations;	<sup>H</sup> 2 <sup>O</sup> 2	, 80.2%;	нсі,	0.90%.
Temp.	Volume of oxygen collected.	Stop watch.	Time from zero.		H <sub>2</sub> O <sub>2</sub> decomposing per minute.
•C	Cc.	Min.	Min.		Grm.
22.5	25.C	39.56	22.8		.0017
21 8	25.2	36.50	64.2		.0019
21.2	24.6	39.37	144.7		.0017
21.8	<b>25</b> .8	43.50	187.7		.0016
21.4	24.9	44.22	255.0		.0015
19.4	24.5	49.05	350.0		.0013
19.4	25.0	57.15	535.0		.0012

Barometer; 746.8 m.m.

Time from	H <sub>2</sub> O <sub>2</sub> decomposed.	H <sub>2</sub> 02 pe <b>rcent</b> .	H <sub>2</sub> 0 <sub>2</sub> concentration	Log(a-x).
zero.			(a-x)	
Min.	Grm.	Percent.	Mols/liter.	
50	.0700	<b>79</b> .68	31.28	1.4953
100	.1615	79.36	31.14	1.4934
150	.2480	78.89	30.90	1.4900
200	.3295	78.36	30.60	1.4857
300	.4810	77.56	30.20	1,4800
400	.6165	76.79	29.82	1.4745
500	.7415	76.08	29.24	1.4660

HCl oxidised; .0005 g.

 $k \times 10^4$ ; .65

,

# Experiment 2.

	Initial	Concentrations	; H <sub>2</sub> 0 <sub>2</sub> ,	80.3%;	H <b>C1,</b>	1.17%.
Temp	•	Volume Og collected.	Stop watch.	T fro	ime m zero	H <sub>2</sub> O <sub>2</sub> dec'g per minute.
•C		Cc.	Min.		Min.	Grm.
20.05		24.7	22.70		13.3	.0030
20.02		25.0	21.42		36.7	.0032
20.02		25.0	22.66		59.3	.0030
20.0		25.0	25.47	1	21.8	.0027
20.03		25.0	29.58	2	20.8	.0023
20.2		25.0	32.92	3	02.5	.0021
20.0		25.0	<b>35.5</b> 0	3	67.7	.0019
		Barometer;	759.5 M.m.	,		

Time	HgOg decomp'd.	H2 <b>02</b> percent.	H2O2 conc'n.	Log(a-x).
Min.	Grm.	%	Mols/1.	
50	.1414	79.55	31.20	1.4942
100	.2905	78.74	30.74	1.4877
150	.4255	78.00	30.40	1.4829
200	.5505	77,28	30.06	1.4780
250	.6640	76.62	29.72	1.4731
300	.7710	76.01	29.41	1.4684
350	.8710	75.45	29.14	1.4645
400	.9695	74.92	28.90	1.4609
450	1.0650	74.30	28.56	1.4557
500	1.1570	73.74	28.28	1.4514

HC1	oxidise	1;	.0021	g.
k >	< 10 <sup>4</sup> ;	.88		

# Experiment 3.

Initial Concentrations; H<sub>2</sub>O<sub>2</sub>; 74.13%; HCl, 1.5%.

Temp.	Volume 02	Stop	Time	H202 decomp'g	
	collected.	watch.	from zero.	per minute.	
•C	Cc.	Min.	Min.	Grm.	
20.4	25.0	25.50	15.8	.0027	
8.08	25.0	22.15	41.1	.0031	
21.6	25.0	22.22	65.1	.0031	
21.0	25.0	25.93	127.0	.0027	
21.6	25.0	27.50	163.7	.0025	
21.2	25.3	30.00	236.0	.0023	
21.0	25.1	32.32	298.0	.0021	
22.0	25.0	38.00	504,	.0018	

Barometer; 766.5 m.m.

Time.	H <sub>2</sub> O <sub>2</sub> decompld	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	Log(a-x).
	accomb a.	har carres	GOUG II.	
Min.	Grm.	%	Mols/1.	
50	.1290.	73.47	28.14	1.4493
100	.2775	72.69	27.80	1.4440
200	.5380	71.27	27.10	1.4330
300	.7665	70.06	26.52	1.4235
400	.9585	69.00	26.00	1.4150
500	1.1140	68.14	25.58	1.4079

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HCl oxidised; .0006 g. k \ge 10^4; 1.0
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Experiment 4.

	Initial	Concentratio	ons; H <sub>2</sub> 0 <sub>2</sub>	, 73.96%;	HC1,	2.03%.	
Temp.		Volume Og collected.	Stop watch.	T: from	ime zero.	H <sub>2</sub> O <sub>2</sub> dec per minu	omp'g te.
°C		Cc.	Min.	Mi	<b>1.</b>	Grms.	
19.5		42.5	20.53	16.7	7	.0057	
19.5		42.5	22.50	47.7	7	.0052	
19.6		87.0	56.10	99.8	5	.0043	
19.8		49.0	33.92	164.9	5	.0040	
19.8		43.0	34.51	239.2	3	.0035	
20.0		50 <b>.0</b>	47.12	349.1	3	.0029	
20.0		42.5	45.25	442.0	6	.0026	
20.0		42.5	50.86	540.4	4	.0023	

Barometer; 763.3 m.m.

Time.	H202	H202	H <sub>2</sub> O <sub>2</sub>	Log(a-x).
	decomp'd.	percent.	conc'n.	
Min.	Grm.	at jo	Mols/1.	
80	.1166	73.3	28.08	1.4484
40	.2271	72.7	27.60	1.4409
60	.3314	72.2	27.54	1.4399
100	.5252	71.0	27.00	1.4314
200	.9436	68.6	25.80	1.4116
300	1.2852	66.6	24.84	1.3952
400	1.5776	64.8	24.02	1.3804
500	1.8352	63.2	23,28	1.3670
700	2.3708	59.7	21.55	1.3334
1000	2.7808	56.5	20.25	1.3064

HCl oxidised; .0026 g.  $k \times 10^4$ ; 1.47

Experiment 5.

Initial Concentrations; H<sub>2</sub>0<sub>2</sub>, 75.64%; HC1, 3.41%.

Temp.	Volume Og	Stop	Time	H <sub>2</sub> O <sub>2</sub> decomp'g	
	collected.	watch.	from zero.	per minute.	
•C	Cc.	Min.	Min	Grms.	
21.0	42.5	5.66	4.4	.0208	
21.0	42.5	6.86	12.4	.0171	
21.0	42.5	7.85	21.0	.0150	
21.0	42.5	8.75	31.4	.0134	
21.0	42.5	9.55	41.7	.0123	
21.0	42.5	10.30	53.1	.0114	
21.0	42.5	11.28	67.6	.0104	
21.0	42.5	13.00	88.0	.0090	
21.0	42.5	16.60	146.8	.0071	
21.0	44.0	22.00	222.5	.0056	
21.0	42.5	26.16	301.6	.0045	
21.0	42.5	35.50	454.0	.0033	

Barometer; 764.5 m.m.

Time.	HaOa	H <sub>o</sub> O <sub>o</sub>	HgOg	Log(a-x).
	decomp'd.	percent.	concin.	
Min.	Grm.	×	Mols/1.	
10	.2028	74.51	28.55	1.4556
30	.5105	72.61	27.60	1.4409
50	<b>.75</b> 95	71.32	26.95	1.4305
120	1.4180	67.25	25.05	1.3988
150	1.6400	66.07	24.45	1.3882
200	1.9550	63.82	23.50	1.3710
250	2.2300	61.91	22.55	1.3531
300	2.4650	60.39	21.75	1.3374
350	2.6680	58.91	21.25	1.3273
400	2.8470	57.69	20.75	1.3170
450	3.0090	55.24	19.76	1.2958
600	3.4490	53.27	18.94	1.2774

HCl oxidised; .0401 g.

 $k \times 10^4$ ; 2.33

# Experiment 6.

Initial Concentrations;	H202,	60.10%;	HCl,	2.98%.
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Temp.	Volume Og collected.	Stop watch.	Time from zero.	H <sub>2</sub> O <sub>2</sub> decomp'g per minute.
°C	Cc.	Min.	Min.	Grm.
20.0	25.1	19.20	11.6	.0036
20.0	25.1	16.68	30.3	.0041
20.4	25.1	17.15	48.6	.0040
20.2	25.0	18.50	92.3	.0037
20.0	26.0	21.50	161.7	.0033
19.5	27.0	27.37	317.6	.0027
20.02	26.0	30.25	458.1	.0023

Barometer; 750.0 m.m.

Time.	HgOg decomp'd.	Hg0g percent.	Hg0g conc'n.	Log(a-x).
Min.	Grm.	ø,	Mols/1.	
50	.1650	59.13	21.48	1.3320
100	.3540	58.09	21.00	1.3222
200	.6880	56.13	20.16	1.3045
300	<b>.97</b> 80	54.43	19.43	1.2885
400	1.2350	5 <b>2.85</b>	18.78	1.2737
500	1.4725	51.39	18.16	1.2591
,				

HCl oxidised; .0003 g.

$$k \times 10^4;$$
 1.6

.65

### Experiment 7.

	Initial Concentrat	ions; H <sub>2</sub> 0	2, 33.0%;	HC1, 5.02%.
Temp.	Volume O <sub>2</sub> collected.	Stop watch.	Time from zero.	Hg0 decomp'g per minute.
•0	Co.	Min.	Min.	Grm.
21.0	20.5	27.50	17.7	.0031
21.4	20.5	22.50	44.2	.0035
21.2	20.7	24.00	68.0	.0024
21.2	20.8	24.08	94.1	.0023
20.0	20.3	25.08	176.5	.0022
20.4	20.5	26.00	207.0	.0022
21.0	20.4	26.88	261.5	.0021
21.0	20.5	28.50	337.3	.0020

Barometer; 774.0 m.m.

Time.	H <sub>2</sub> O <sub>2</sub> decomp'd.	H <sub>2</sub> 0 <sub>2</sub> percent.	H <sub>2</sub> O <sub>2</sub> conc.	Log(a-x).
Min.	Grm.	%	Mols/1.	
55	.1170	32.40	10.62	1.0261
100	.2235	31.90	10.44	1.0187
200	.4457	30.82	10.02	1.0008
300	.6530	29.83	9.66	0.9850
400	.8495	28.85	9.31	0.9689
500	1.0390	27.90	9.00	0,9542

In this experiment no hydrochloric acid was oxidised.

$$k \times 10^4$$
; 1.70

### Experiment 8.

Initial Concentrations;  $H_20_2$ , 46.36%; HCl, 5.17%.

Temp.	Volume 02 collected.	Stop watch.	Time from zero.	H <sub>2</sub> O <sub>2</sub> decomp'g
	0011000041			re-
•0	Cc.	Min.	Min.	Grm.
22.4	25.0	16.82	9.4	.0040
22.4	24.9	14.75	28.0	.0046
22.2	25.0	15.33	42.0	.0047
22.2	25.0	15.66	58.8	.0044
22.0	24.9	16.82	87.4	.0040
21.6	25.0	20.32	181.1	.0034
21.0	25.0	23.10	263.0	.0030
19.6	25.1	27.40	373.7	.0025

Barometer; 755.0 m.m.

Time	H <sub>2</sub> O <sub>2</sub> decomp'd.	H202 percent.	Hg <sup>0</sup> g conc.	Log(a-x).
Min.	Grm.	%	Mols/1.	
<b>5</b> 0	.2005	44.89	15.51	1.1906
100	.4105	43.37	14.88	1.1727
150	.5945	42.02	14.32	1.1559
200	.7630	40.76	13.82	1.1405
250	.9170	39.56	13.36	1.1258
300	1.0605	38.45	12.94	1.1120
350	1.1960	37.38	12.51	1.0972
400	1.3225	36.38	12.16	1.0849

HCl oxidised; .COO3 g.

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### Experiment 9.

# Initial Concentrations; H<sub>2</sub>O<sub>2</sub>, 49.17%; HCl, 6.10%.

Temp	Volume O.	Stop	Time	H <sub>2</sub> O <sub>2</sub> decomp'g
	collected.	watch.	from zero.	per minute.
۰C	Cc.	Min.	Min.	Grm.
20.5	42.5	18.25	9.62	.0063
20.5	42.5	18.93	34.95	.0061
20.5	42.5	20.32	57.67	.0056
20.5	42.2	23.42	108.21	.0049
20.5	42.5	34.08	278.94	.0034
20.5	42.5	39. 32	363.16	.0029
20.5	42.5	42.98	420.96	.0027

### Barometer; 744.0 m.m.

Time.	Hg <sup>O</sup> g decomp'd.	HgOg percent.	H <sub>2</sub> O <sub>2</sub> conc.	Log(a-x).
Min.	Grm.	al p	Mols/1.	
40	.2469	44.26	15.24	1.1829
80	.4696	42.4	14.50	1.1614
120	.6696	40.1	13.56	1.1322
160	.8512	<b>39</b> .5	13.34	1.1252
<b>2</b> 00	1.0160	38.2	12.84	1.1086
280	1.3048	<b>35</b> .8	11.92	1.0760
400	1.6680	32.7	10.74	1.0311
600	2.1480	28.46	9.18	0.9628

HCl oxidised; .0008 g.  $k \times 10^4$ ; 3.65

### Experiment 10.

Initial Concentrations; H<sub>2</sub>O<sub>2</sub>, 33.0%; HCl, 8.0%.

Temp.	Volume O <sub>2</sub> collected.	Stop watch.	Time from zero.	H202 decomp'g per minute.
۰C	Cc.	Min.	Min.	Grm.
20.2	20.5	6.11	6.0	.0091
20.0	21.8	6.23	15.6	.0095
20.0	20.6	6.17	30.1	.0091
20.0	30.5	6.28	41.1	.0089
20.5	20.5	7.62	109.8	.0073
21.0	20.4	8.27	144.1	.0069
21.5	20.5	9.20	185.6	.0060
21.5	23.4	11.50	238.7	.0055
21.5	21.9	11.13	247.5	.0053
21.0	20.7	11.83	279.9	.0047
80.5	20.6	13.26	372.6	.0042

Barometer; 749.1 m.m.

Time.	H <sub>2</sub> 0 decomp'd.	H <sub>2</sub> O <sub>2</sub> percent.	H <sub>2</sub> O <sub>2</sub> conc.	Log(a-x).
Min.	Grm.	<b>6</b>	Mols/1.	
10	.0907	32.51	<b>10.6</b> 6	1.0278
20	.1855	32.10	10.50	1.0212
30	.2786	31.64	10.32	1.0136
60	.5445	30.37	9.86	0.9939
80	.7110	29.56	9.55	0.9800
100	.8683	28.80	9.30	0.9685
130,	1.0887	27.73	8.90	0.9494
160	1.2921	26.66	8.49	0.9289
200	1.5263	25.46	8.10	0,9085
250	1.8013	24.05	7.60	0.8808

HCl oxidised; .0009 g.  $k \times 10^4$ ; 5.34

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### Experiment 11.

Initial Concentrations; H<sub>2</sub>O<sub>2</sub>, 33.0%; HCl, 9.0%.

Temp.	Volume Og collected.	Stop wa <b>tc</b> h.	Time from zero.	Hg0g decomp'g per minute.
•0	Cc.	Min.	Min.	Grm.
21.4	20.0	4.83	6.4	.0112
21.4	19.9	3.83	13.9	.0141
21.4	20.0	3.95	20.0	.0197
21.4	20.0	4.05	27.0	.0133
21.4	20.0	4.32	37.1	.0125
21.4	20.0	4.65	54.3	.0116
21.4	20.0	5.08	82.5	.0106
21.4	19.9	5.60	107.8	.0096
22.0	19.5	6.78	162.4	.0078
22.4	20.5	7.98	195.5	.0069
21.8	20.1	9.70	273.9	.0056
21.8	19.5	11.08	337.5	.00475
22.0	20.0	13.41	403.7	.0040
22.2	20.15	15.03	464.5	.0036

Barometer; 750.0 m.m.

Time.	HgOg decomp'd.	H202 percent.	H <sub>2</sub> O <sub>2</sub> co <b>nc</b> .	Log(a-x).
Min.	Grm.	d.	Mols/1.	
10	.1428	32.35	10.50	1.0253
20	.3885	31.68	10.30	1.0128
50	.6638	29.87	9 <b>.5</b> 8	.9857
100	1.2036	27.20	8.70	.9405
160	1.7301	24.55	7.80	.8921
200	2.0232	23.03	7.25	.8597
250	2.3407	31.34	6.71	.8267
300	2.6203	19.82	6.21	.7931
350	2.8663	18.54	5.74	.7619
400	3.0813	17.36	5.38	.7308
450	3.2740	16.29	5.04	.7084
500	3.4490	15.30	4.71	.6730

HCl oxidised; .0023 g.

$$k \times 10^4$$
; 6.68

### Experiment 12.

Initial Concentrations; H<sub>2</sub>O<sub>2</sub>, 33.2%; HCl, 9.55%.

Temp.	Volume Og collected.	Stop watch.	Time from zero.	H202 decomp'g per minute.
°C	Ce.	Min.	Min.	Grm.
22.5	19.0	6.0	5.5	.0084
22.5	30.3	8.0	9.0	.0112
22.5	34.6	9.0	20.5	.0103
22.5	41.1	12.0	34.5	seoo.
22.5	34.5	11.0	48.5	.0084
22.5	28.7	11.0	85.5	.0069
22.5	29.5	13.5	116.7	•005 <b>8</b>
22.5	25.0	13.0	166.5	.0052
22.5	30.2	22.0	249.0	.0040
22.5	23,0	27.0	358.5	.0023

Barometer; 744.0 m.m.

Time.	H <sub>2</sub> O <sub>2</sub> decomp'd.	Hg0g percent.	H202 conc.	Log(a-x).
Min.	Grm.	*	Mols/1.	
20	.2240	31.2	10.15	1.0064
40	.4152	29.6	9.55	.9800
60	.5812	28.3	9.08	.9581
80	.7292	27.2	8.70	<b>.939</b> 5
100	.8644	26.7	8.55	.9320
150	1.1568	23.6	7.45	.8722
200	1.3988	21.5	6.76	.8312
250	1.6020	19.7	6.16	.7924
300	1.7704	18.3	5.60	.7520

H <b>C1</b>	03	cidi	sød;	.0035	g.
k	X	104	; 8	.12	

### Experiment 13.

H20g decomp'g per minute. Volume Og collected. Stop Temp. Time from zero. watch. °C Min. Cc. Min. Grm. 4.27 .0301 22.0 52.0 6.63 .0279 22.0 4.93 14.9 50.3 .0236 22.0 50.1 5.81 23.4 22.0 6.68 .0205 50.2 32.8 7.70 50.1 .0178 32.0 43.3 22.0 50.1 11.39 83.1 .0122 22.0 50.0 16.50 132.9 .0081 32.0 50.0 29.30 234.1 .0043 22.0 50.0 43.59 329.8 .0031

Barometer; 757.0 n.m.

54.50

383.2

Time.	H202 decomp'd.	H <sub>2</sub> O <sub>2</sub> percent.	H <sub>2</sub> O <sub>2</sub> conc.	Log(a-x).
Tima.	Grm.	of F	M/1.	
20	.5770	30.4	8.10	.9948
60	1,3430	21.1	6.61	.8202
80	1.6190	19.1	5.91	.7716
120	3.0415	15.8	4.88	.6884
160	2.3500	13.5	4.12	.6149
200	3.5875	11.6	3.52	•5465
260	2.8495	9.4	2.80	.4472
300	2.9908	8.3	2.48	.3945
380	3.2216	6.3	1.84	.2648

HC1 oxidised; .0486 g.  $k \times 10^4$ ; 16.1

Initial Concentrations;

H<sub>2</sub>O<sub>2</sub>, 30.42%; HC1, 13.7%.

.0025

22.0

50.0

### Experiment 14.

Initial Concentrations; H<sub>2</sub>O<sub>2</sub>, 13.8%; HCl, 13.26%.

Temp.	Volume 0,	Stop	Time	H <sub>2</sub> O <sub>2</sub> decomp'g
	collected.	watch	from zero.	per minute.
•0	Cs.	Min.	Min.	Grm.
23.5	30.0	15.5	10.7	.0053
23.5	30.5	16,25	29.2	.0051
23.5	30.2	19.0	46.5	.0046
23.5	30.3	26.5	74.3	.0031
23.5	30.1	32.5	129.3	.0025
23.5	3043	44.0	272.0	.0019
28.5	30.9	61.0	<b>338.</b> 5	.0014

Barometer; 758.0 m.m.

H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	Log(a-x).
decomp'd.	percent.	conč.	
Grm.	et k	M/1.	
.1052	13.9	4.05	<b>.607</b> 45
.2056	12.0	3.78	<b>.57</b> 75
.2825	11.39	3.58	•5539
.3878	10.48	3.30	.5185
.4981	9.50	2.88	.4594
.5723	8.85	<b>2.64</b>	.4216
.6841	7.80	2.32	.3655
.7834	6.97	2.07	.3160
.8703	6.18	1.80	.2553
	H <sub>2</sub> O <sub>2</sub> decomp'd. Grm. .1052 .2056 .2825 .3878 .4981 .5723 .6841 .7834 .8703	H <sub>2</sub> O <sub>2</sub> decomp'd. H <sub>2</sub> O <sub>2</sub> percent. Grm. 5 .1052 12.9 .2056 12.0 .2825 11.39 .3878 10.48 .4981 9.50 .5723 8.85 .6841 7.80 .7834 6.97 .8703 6.18	$H_2O_2$ $H_2O_2$ $H_2O_2$ $H_2O_2$ decomp'd.percent.conc.Grm. $\checkmark$ M/1105212.94.05.205612.03.78.282511.393.58.387810.483.30.49819.502.88.57238.852.64.68417.802.32.78346.972.07.87036.181.80

HCl oxidised; .0040  $k \times 10^{4}$ ; 14.0

### Experiment 15.

Initial Concentrations;  $H_20_2$ , 4 91%; HCl, 14.85%.

Temp.	Volume Og collected.	Stop watch.	Time from zero.	H202 decomp'g
•C	Cc.	Min.	Min.	Grm.
23.5	25.1	17.80	13.0	.0038
23.5	25.1	12.37	29.3	.0055
23.5	25.1	13.82	43.6	.0052
23.5	25.1	16.83	102.0	.0041
23.5	25.1	22.35	175.0	.0031
23.0	25.1	43.83	358.4	.0015

Barometer; 758.0 m.m.

Time.	H <sub>2</sub> O <sub>2</sub> decomp'd.	H <sub>2</sub> 02 percent.	H <sub>2</sub> O <sub>2</sub> conc.	Log(a-x)
Min.	Grm.	a,	м/1.	
50	.2150	4.25	1.20	్ర.0792
100	.4400	3.58	1.03	0.0128
150	.6835	3.02	.85	<b>1.9294</b>
200	.7735	2.56	.71	<b>I.8513</b>
250	.8985	2.18	.58	<b>I.</b> 7634
300	1.0020	1.86	.50	<b>I.6990</b>
350	1.0880	1.56	. 42	<b>I.6232</b>

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HCl oxidised; .0014 g. k \times 10^4; 15.1
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### Experiment 16.

Initial	Concentrations;	<sup>H</sup> 2 <sup>0</sup> 2'	10.95%;	HC1,	18.84%.
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H222 decomp'g per minute. Volume O<sub>2</sub> Stop collected. watch. Temp. Time watch. from zero. •C Cc. Min. Min. Grm. 22.0 7.5 7.2 .0108 30.3 32.0 30.4 9.5 .0086 18.7 22.0 33.5 14.0 33.0 .0065 22.0 30.8 16.5 49.8 .0050 32.0 33.3 26.0 73.0 .0035 22.0 29.8 43.0 127.5 .0019

Barometer; 748.0 m.m.

Time.	H_O_	H <sub>2</sub> O <sub>2</sub>	H_O_	Log(a-x).
	decomp'd.	percent.	cõnč.	
Min.	Gro.	۶.	M/1.	
10	.1130	9.5	2.90	.4624
20	.2056	8.3	2.52	.4014
40	.3449	6.5	1.95	.2900
60	.4440	5.2	1.55	.1903
80	.5171	4.2	1.24	.0934
100	.5737	3.5	1.00	.0000
120	.6187	2.9	•85	I.9294
150	.6737	2.1	•3	1.4771

HCl oxidised; .0350 g.  $k \times 10^4$ ; 54.2

### Experiment 17.

Initial Concentrations; H<sub>2</sub>O<sub>2</sub>, 18.61%; HCl, 19.26%.

H202 decomp'g per minute. Volume 0, Time Temp. Stop collected. watch. from zero. °C Min. Grm. Cc. Min. 21.0 32.7 .0255 3.5 5.2 21.0 31.0 6.0 9.0 .0141 21.0 30.5 8.0 17.0 .0103 21.0 31.3 10.0 27.0 .0085 21.0 34.6 15.0 34.0 .0063 31.2 17.5 21.0 64.0 .0049 21.0 30.8 23.0 85.0 .0036 21.0 28.1 31.0 117.0 .0025 21.0 30.2 276.0 .0007 120.0

Barometer; 752.0 m.m.

Time.	HO2 decomp'd.	H 0 pe <b>rcent</b> .	H <sub>2</sub> O <sub>2</sub> conc.	Log(a-x).
Min.	Grm.	<b>6</b>	M/1.	
10	.2400	15.3	4.75	.6767
20	.4670	12.2	3.70	.5682
40	.6430	9.7	2.90	.4624
60	.7710	7.9	2.40	.3810
100	<b>.960</b> 0	5.1	1.50	1761
150	1.0980	3.1	<b>.</b> 85	1.9294
200	1.1840	1.7	.45	<b>1.6532</b>
250	1.2420	.8	.25	<b>T.116</b> 1

HCl oxidised; .1930 g.

 $k \times 10^4$ ; 103.2 to 57.7

In this experiment the value of k dropped from the very first, and continued to drop until the reaction had gone to completion.

# · Experiment 19.

# Initial Concentrations; H<sub>2</sub>O<sub>2</sub>; 20.0%; HBr, 1.00%.

X

Temp.	Volume Og collected.	Stop watch.	Time from zero.	H202 decomp'g per minute.
۰C	Cc.	Min.	Min.	Grm.
22.4	25.0	19.92	13.1	.0034
22.4	25.0	18.75	33.3	.0036
8.82	25.1	19.05	53.5	.0036
32.8	25.1	20.58	119.3	.0033
82.8	35.1	22.33	185.1	.0029
22.0	25.9	24.35	243.1	.0029
21.6	25.1	25.16	313.6	.0027
21.0	25.2	30.23	499.1	.0023

Barometer; 759.1 m.m.

Time.	H <sub>2</sub> O <sub>2</sub> decomp'd.	H <sub>2</sub> O <sub>2</sub> percent.	HO mol. Conc.
Min.	Grm.	<b>r</b>	M/1.
0		30.0	6.26
50	.1730	19.32	6.02
100	.3480	18.62	5.80
150	.5130	18.00	5.60
200	.6170	17.55	5.44
250	.8155	16.76	5 <b>.20</b>
300	.9555	16.20	5.00
350	1.0905	15.63	4.80
400	1.2175	15.04	4.60
450	1.3385	14.62	4.46
500	1.4530	14.15	4.32

HBr oxidised to  $Br_2$ ; .52% <u>k × 10<sup>4</sup></u>; 3.20

### Experiment 20.

Initial Concentrations; H<sub>2</sub>O<sub>2</sub>, 19.86%; HBr, 0.83%.

Temp.	Volume Og collected.	Stop watch.	Time from zero.	H <sub>2</sub> O <sub>2</sub> decomp'g per minute.
°C	Cc.	Min.	Min.	Grm.
23.4	25.1	28.45	15.2	.0021
23.0	25.6	21.42	40.6	.0032
23.0	25.1	21.33	63.1	.0031
22.8	25.0	22.10	97.3	.0030
22.23	25.0	24.66	238.8	.0027
22.2	25.4	28.38	382.2	.0024
22.0	25.6	31.70	498.5	.0022

Barometer; 748.0 n.m.

H <sub>2</sub> O <sub>2</sub> decomp'd.	H <sub>2</sub> 0 <sub>2</sub> percent.	H202 mol. conc.
Grm.	of.	N/1.
	19.86	6.22
.1150	19.50	6.10
.2675	10.02	5.93 .
.4135	18.55	5.78
.6385	17.84	5.54
.8190	17.27	5.36
.9440	16.86	5.22
1.0635	16.47	5.11
1.1750	16.11	4.92
1.2865	15.74	4.85
	H <sub>2</sub> O <sub>2</sub> decomp'd. Grm. .1150 .2675 .4135 .6385 .6385 .8190 .9440 1.0635 1.1750 1.2865	$H_2O_2$ $H_2O_2$ decomp'd.percent.Grm. $\%$ 19.86.115019.50.267519.02.413518.55.638517.84.819017.27.944016.861.063516.471.175016.111.286515.74

<u>k×10</u><sup>4</sup>; 2.16

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"Br concentration at end of reaction, .117 moles/liter.

### Experiment 21.

Initial Concentrations; H<sub>2</sub>O<sub>2</sub>, 5.05%; HBr, 2.02%.

Temp.	Volume O <sub>2</sub> collected.	Stop watch.	Time from zero.	H <sub>2</sub> O <sub>2</sub> decomp'g per minute.
•C.	Cc.	Min.	Min.	Grm.
20.4	25.0	27.42	15.3	.0025
20.4	25.1	18.17	39.1	.0038
20.4	26.4	23.78	151.9	.0031
20.4	25.2	26.75	238.4	.0026
20.4	29.3	34.80	308.4	.0023
20.4	25.1	31.68	343.8	.0022
20.0	25.0	35.63	404.8	.0017

Barometer; 762.5 m.m.

Time.	H <sub>2</sub> O <sub>2</sub> decomp'd.	H 0 2 percent.	H <sub>2</sub> O <sub>2</sub> mol. conc.
Min.	Grm.	s fo	M/1.
0	-	5.05	1.48
50	.1445	4.86	1.40
100	.3250	4.48	1.28
150	.4870	4.15	1.20
200	.6325	3.84	1.10
350	.7655	3.56	1.02
300	.8870	3.31	.92
350	.99990	3.07	.86
400	1.0965	2.87	.80

Conc. HBr at end of reaction; .260 moles per liter.

$$k \times 10^4$$
; = 6.74

Experiment 22.

Initial Concentrations; H<sub>2</sub>O<sub>2</sub>, 5.01%; HBr, 0.96%.

Temp.	Volume 0	Stop watch.	Time from zero	H202 decop8g
		W G C C III		
°C	Cc.	Min.	Min.	Grm.
21.4	51.2	116.60	67.0	.coc7
21.8	25.3	66.83	161.4	.0010
22.8	30.8	88.25	274.0	.0010
22.8	23.7	68.92	357.5	.0094

Barometer; 759.0 m.m.

Time.	H <sub>2</sub> O <sub>2</sub> decomp'd.	H <sub>2</sub> 02 percent.	$H_2O_2$ (a-x)
Min.	Grm.	7	mol/liter.
$\hat{}$	-	5.01	1.45
100	.060	4.89	1.40
200	.160	4.69	1.35
300	.260	4.49	1.30
400	.320	4.36	1.24
	$k \times 10^4 =$	1.50	

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Concentration HBr at end of reaction; .125 moles per liter

#### APPENDIX B.

The following tables give the readings on the right arm of the manometer at intervals of fifteen seconds for the different temperatures at which the vapor pressure of hydrogen peroxide was determined. The actual pressures were obtained by extrapolating these readings to zero time as described in the thesis and referring them to a calibration curve in which the difference between the two arms of the manometer were plotted against the height of the right arm. The values for the calibration curve are given below.

### Calibration of Manometer.

Left Arm.	Right Arm.	Difference.
1.38	14.79	13.41
3.03	12.94	9.91
4.52	11.32	6.80
5.93	9.77	3.84
7.01	8.60	1.59
7.67	7.88	0.21

### Manometer Readings at Intervals of Fifteen Seconds.

Temperature 62.5°

1	8.0	8.3
2	9.0	8.88
3	9.1	8.90
4	9.2	8.93
5	9.28	8.99
6		9.03
7		9.10
8		9.20
9		9.3

	Temp. 56	.7°	Tem	p, 70.0	•
0	8.00	8.64	0	8.30	8.50
1	8.55	8.60	1	9.25	9.30
2	8.60	8.60	2	9.43	9.42
3	8.63		3	9.48	9.48
4	8.64	8.64	4.	9.52	9.52
8	8.71	8.72	6	9.58	ି •58
12	8.75	8.80	8	9.63	S.64
20	8.80	8.89	12	9.73	9.75
	Temp. 8	0.0°.	Tem	p. 89.1	0

C	0.00		Õ	^ <b>.</b> 50	9.50	
1	10.20	10.30	1	11.57	11.51	11.52
2	1.0.40	10.4	2	11.82	11.75	11.78
3	10.5	10.5	3	12.00	11.92	11.91
4	10.58	10.6	4	12.12	12.03	12.03
6	10.70	10.71	5	12.23	12.18	12.18
8	10.80	10.87	6	12.32	12.28	
10	10.90	10.95				

# Temp. 51.59

Temp. 62.5°

10 sec.	8.30	1	8.80
40 "	8.40	2	8.90
80	8.44	3	8.93
135	8.50	4	8.99
175	8.51	6	9.03
		8	9.10
		12	9.20

-	Temp. 24	.2°
0	7.82	7.83
1	7.86	7.86
2	7.87	7.88
3	7.88	7.89
5	7.89	7.89
6	7.00	7.90
7	7.91	7.90

Eenp. 35.2°

0	7.88	7.90
1	7.98	7.99
2	8.01	8.01
3	8.02	8.02
4	8.03	8.03
5	8.03	8.03
6	8.04	
7	8.05	8.04
8	8.06	8.05

	Temp. 45.0°	I	emp. 56.9°
1	8.00	С	8.05
2	8.10	1	8.58
3	3 <b>.21</b>	2	8.63
4	8.22	3	8,68
5	8.24	4	8.71
6	8.25	5	8.73
7	8.27	6	8.77
		7	8.80
		8	8.32

Temp. 70.1°

\*

Temp. 75.1°

0	8.23	0	9.20
2	9.35	1	9.85
3	9.43	3	9.92
4	9.49	3	9.99
5	9.52	4	10.03
6	9.56	5	10.08
7	9,59	6	10.12
<b>8</b> ·	8.62		
9	9.64		

• •	Temp. 45.0°	Temp	. 56.9°
1	8.00	C 8	.05
2	8.10	1 8	•58
3	8.21	28	.63
4	8.22 .	3. 8	.68
5	8.24	4 8	.71
6	8.25	5 8	.73
7	8.27	6 8	.77
		7 8	8.80
		8 8	8.82

Temp. 70.1°

-

Temp. 75.1°

0	8.23	0	9.20	
2	9.35	1	9.85	
3	9.43	2	9.92	
4	9.49	3	9.99	
5	9.52	4	10.03	
6	9.56	5	10.08	
7	9.59	6	10.12	
8	9.62			
9	9.64			

