

These joints thus hold a vacuum at least as well as a glass stopcock greased with Ramsay grease, and have the great advantages of holding at 150° and of not evolving any organic vapors when the flux is efficiently removed.

It has also been found possible to coat hard glass and porcelain with lead, but no attempts have been made to construct joints with these. There is no obvious reason, however, why such joints should not be as successful as those with glass and silica.

No difficulty has been experienced in constructing joints up to 16 mm. in diameter.

In conclusion the author wishes to acknowledge the assistance afforded by a maintenance grant from the Board of Scientific and Industrial Research.

Summary

A method is given for coating soft glass, hard glass, silica or glazed porcelain, with homogeneous lead films, and for soldering material so coated to metal. The method can be applied to sheet or tube. A metal-to-glass, or metal-to-silica joint made by this method will hold a vacuum up to 10^{-4} mm. at 150° for some days, and up to 10^{-6} mm. for shorter periods.

LONDON, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF MCGILL UNIVERSITY]
**THE PROPERTIES OF PURE HYDROGEN PEROXIDE. IV.
ACTION OF THE HALOGENS AND HALOGEN HYDRIDES**

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This paper deals with a further investigation of the properties of pure hydrogen peroxide. When dry hydrogen chloride is passed into anhydrous hydrogen peroxide, chlorine is liberated even at low temperatures.¹ 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. It was mentioned in the paper referred to above² 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.

Experiments carried out by the authors revealed from the first the fact that even at low concentrations hydrochloric acid would bring about the decomposition of fairly dilute solutions of hydrogen peroxide apparently without the liberation of chlorine. The investigation was therefore ex-

¹ Maass and Hatcher, *THIS JOURNAL*, **44**, 2472 (1922).

² Ref. 1, p. 2477.

tended to cover a wider field, its object being not only to determine the critical concentrations at which chlorine would be given off, but also to investigate the action of the other halogen hydrides upon hydrogen peroxide and to throw some light upon the mechanism of the reactions. Since this investigation was begun, two interesting papers on the decomposition of hydrogen peroxide by bromine and hydrobromic acid have been published by Bray and Livingston³ to which further reference will be made.

The results of a preliminary investigation can be generalized 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 halogen hydride or the hydrogen peroxide a point is reached where the halogen hydride itself is oxidized. The minimum concentrations at which the oxidation takes place increase in the order, hydrogen iodide, bromide, chloride, fluoride. The question which arises 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 reactions would throw light upon this question and possibly give an inkling as to the mechanism of the reaction both when oxidation of the halogen hydride takes place and when it does not take place.

In the preparation of the reagents great care was taken to ensure their purity, 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 peroxide was first allowed to stand overnight in chromic acid solution, then washed in sodium hydroxide solution and finally in distilled water before being dried for use.

The hydrogen peroxide solutions were prepared in the manner described by Maass and Hatcher⁴ using the sulfuric acid concentrator. About 100 liters of commercial 3% solution was concentrated and distilled. Where solutions of 90% strength or over were required the concentrate was crystallized.

In the case of hydrochloric acid, quantitative measurements could be carried out most accurately on account of its relatively smaller reactivity than in the case of the other halogen hydrides. The experimental methods used and the results obtained with hydrochloric acid will therefore be first described. Various attempts were made to discover a means of analyzing a mixture of hydrochloric acid, chlorine and hydrogen peroxide in aqueous solution. It was found that very small quantities of free chlorine, 0.01 mg. in 5 cc., could be accurately estimated by the bleaching of a standardized solution of a dye such as methyl red. But this bleaching was inhibited by the presence of hydrogen peroxide. An attempt was made to estimate the hydrogen peroxide in the presence of free chlorine and hydrochloric

³ Bray and Livingston, *THIS JOURNAL*, 45, 1251 (1923); 45, 2048 (1923).

⁴ Maass and Hatcher, *ibid.*, 42, 2548 (1920).

acid by adding barium chloride together with sodium hydroxide solution until the mixture was slightly alkaline. The barium peroxide precipitated was filtered off, washed free from chloride and analyzed. 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 the barium peroxide. This may be due to decomposition of the barium peroxide or to a variation in the size of the precipitated particles. A satisfactory method of analysis was, however, finally devised whereby it was possible to estimate the amount of chlorine liberated and the amount of hydrochloric acid remaining while at the same time measuring the rate of decomposition of the hydrogen peroxide caused by the acid. The method makes use of the apparatus shown in the accompanying diagram, Fig. 1.

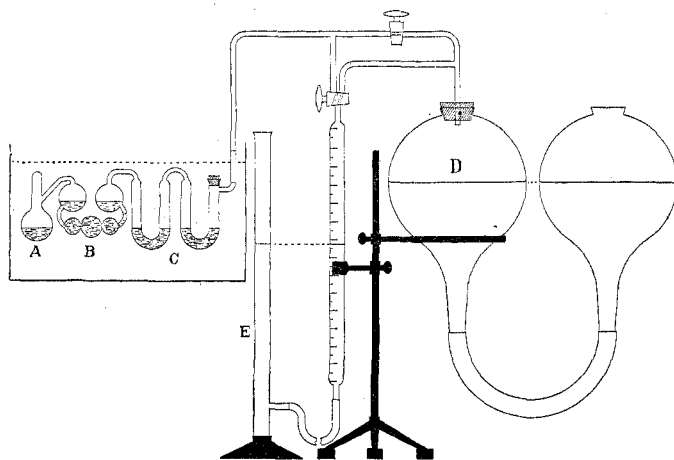


Fig. 1.

About 10 cc. of hydrogen peroxide solution was introduced into the reaction flask, A, by means of a pipet and weighed. It was then cooled in a salt-and-ice freezing mixture and the hydrogen chloride added. This was done by means of a capillary tube leading from a calibrated bulb filled with dry hydrogen chloride. The hydrogen chloride was prepared from salt and sulfuric acid and was dried by passing through sulfuric acid before being collected over mercury. By raising and lowering a mercury reservoir it was possible to introduce into the hydrogen peroxide definite volumes of hydrogen chloride from the calibrated bulb, and the concentrations of the hydrogen peroxide, hydrochloric acid and aqueous solution could therefore be accurately calculated. When, however, it was required to work with solutions having any particular concentration it was found to be more accurate and convenient to add the hydrogen peroxide to the hydrochloric acid in solution. For this purpose special pipets were prepared which would deliver through capillary tubes known volumes of hydrogen peroxide solution whose strength had been determined. The acid solutions were then made up to definite strengths so that, when the hydrogen peroxide from the pipet was added to a definite weight of the acid, the required concentrations would result. For example, it was desired to make up a mixture having the concentrations, H_2O_2 , 80.3%; HCl , 0.9%; H_2O , 18.8%. The hydrogen per-

oxide solution on hand was analyzed and was found to be 96.10%. The pipet delivered 9.637 g. calculated on the density of hydrogen peroxide.⁵ It was calculated that when this amount is added to 1.902 g. of 5.46% hydrochloric acid the required concentrations would be reached. An acid solution of strength 5.46% hydrochloric acid 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 pipet. As a further check on the accuracy of the method the mixture could then be weighed and corrections made if necessary.

Having thus mixed the peroxide and acid in the required proportions the reaction flask was sealed while still in the freezing mixture. The sulfuric acid bulbs, B, and the potassium iodide tubes, C, previously sealed together, were in turn sealed to the delivery tube of the reaction flask as shown. The whole system was then placed in the thermostat and attached by means of a short rubber tube to the gas buret. 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° in a shaded room. The thermostat was electrically controlled and was accurate to 0.01°.

After the apparatus had been sealed together and the reaction had begun as indicated by the escape of bubbles of oxygen in the reaction mixture, the stopcock leading to the large reservoir, D, was closed and the stop watch was started. At the same moment the stopcock leading to the buret was opened, allowing the oxygen to be collected there over water. The time from zero, that is, the time when the apparatus was first placed in the thermostat, and the time when the reading was begun were noted. After a suitable volume, generally about 25 cc., had been collected the 2-way stopcock was again closed. The time required to collect the definite volume of the oxygen under known conditions of temperature and pressure was read from the stop watch. The oxygen was then allowed to collect in the large reservoir, D, for a time, during which the buret was again filled with water by raising the leveling tube, E. In doing so the oxygen in the buret 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 analyzed. The oxygen collected in the large reservoir was measured and its equivalent in terms of hydrogen peroxide calculated. The hydrochloric acid oxidized was caught as chlorine in the potassium iodide tube and estimated by means of standard sodium thiosulfate. The sulfuric acid bulbs acted as an absorbent for any water vapor which might be carried over so that this might be calculated. The residue in the reaction flask was analyzed, the hydrogen peroxide being estimated by means of a standard potassium permanganate solution and the hydrochloric acid by means of standard alkali. A check on the final products and initial constituents was thus obtained.

The rate of decomposition of the peroxide could be calculated from the rate at which the oxygen was being given off. The volume of the oxygen collected was corrected for pressure, temperature and water vapor 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 I. 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 halfway between the beginning and the end of the reading.

⁵ Ref. 4, p. 2559.

The data only of one experiment are given in Table I. The two parts of the experiment, A and A', were carried out several days apart and with different samples of peroxide. The concentrations were as nearly as possible the same in the two parts of the experiment, A and A', namely, H₂O₂ 33.0%; HCl, 10.0%. In the case of A the amount of hydrochloric acid oxidized was 0.38% of the total added; in the case of A', 0.36% was oxidized.

TABLE I
TYPICAL EXPERIMENTAL DATA

EXPERIMENT A					
Zero time: 1:38 P.M.			Barometer: 764.3 mm.		
Time when reading was begun P.M.	Temp. °C.	Volume of oxygen collected Cc.	Stop watch Min.	Time from zero Min.	H ₂ O ₂ decomposing per minute G.
1:39	19.6	35.0	5.02	2.50	0.0246
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

EXPERIMENT A'					
Zero time: 3:27 P.M.			Barometer: 754.0 mm.		
Time when reading was begun P.M.	Temp. °C.	Volume of oxygen collected Cc.	Stop watch Min.	Time from zero Min.	H ₂ O ₂ decomposing per minute G.
3:32	20.2	20.4	2.69	6.3	0.0262
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	35.6	.0171
4:07	20.0	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
11:22	19.8	25.0	25.00	485.5	.0033

The data of the preceding table are represented graphically in Fig. 2, the time being plotted as abscissas and the amount of peroxide decomposing per minute as ordinates. The unshaded and shaded points of Curve A in this figure correspond to Expts. A and A', respectively, and 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 and chlorine is given off. A few other curves for which the data corresponding to Curve A are not given are also represented in Fig. 2.

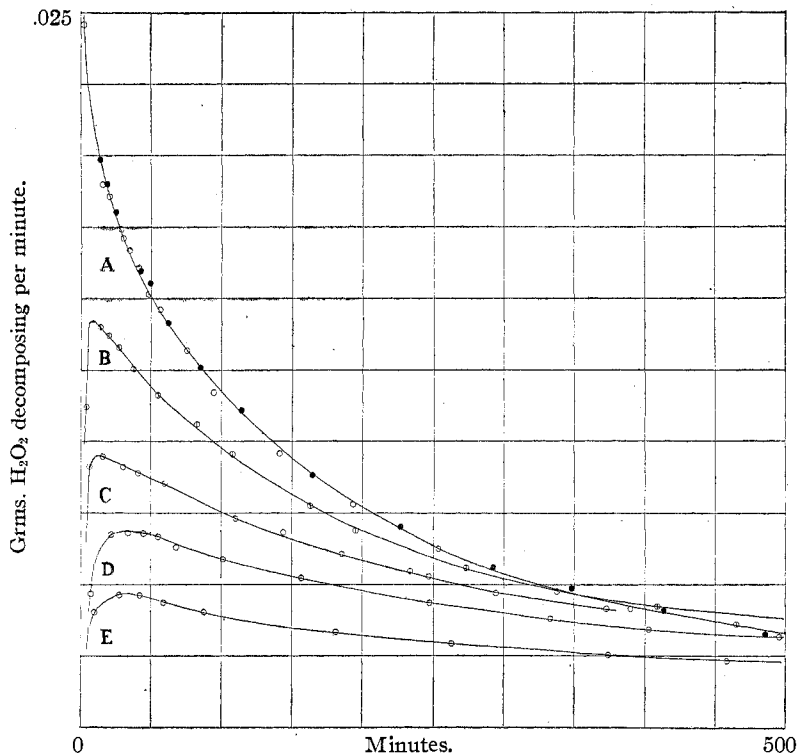


Fig. 2.

The initial conditions for these are as follows: B, 33.0% H_2O_2 , 9.0% HCl ; C, 33.0% H_2O_2 , 8.0% HCl ; D, 19.8% H_2O_2 , 1.48% HBr ; E, 46.3% H_2O_2 , 5.17% HCl .

It will be seen from Fig. 2 that in the very beginning of each reaction the rate at which the oxygen escapes increases, a maximum being reached, after which the expected diminution in rate occurs. This *inhibition period* was observed in all cases where the acid concentration was low. It was found experimentally that the volume of oxygen escaping during this inhibition period was correctly represented by the area under the curve itself. It will be seen that the lower the rate of decomposition at

the start and irrespective of the nature of the acid (hydrochloric or hydrobromic) the longer is the period of inhibition which is therefore not due to the length of time required for the mixture to warm up from the temperature of the freezing mixture to that of the thermostat. The inhibition period is probably due, in part at least, to an unstable equilibrium, the oxygen remaining dissolved in a supersaturated condition although the flask and contents were shaken at the start after being placed in the thermostat. This explanation is probably the correct one, as once the evolution of

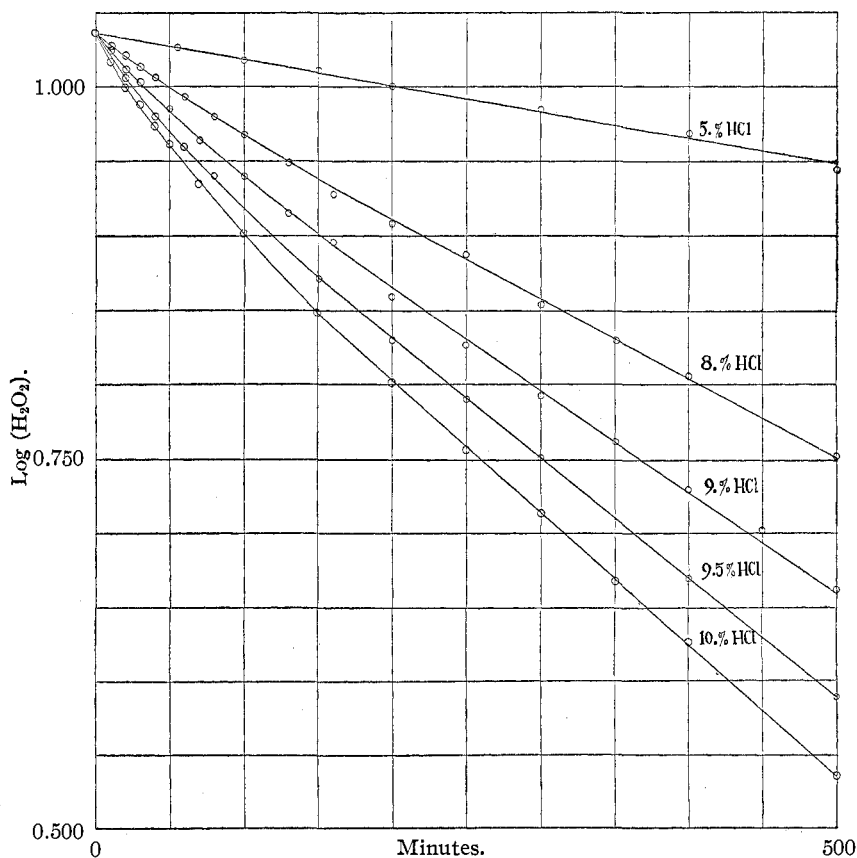


Fig. 3.

oxygen was well under way true equilibrium as regards dissolved oxygen was reached. This was shown by the fact that the area enclosed by the curve between zero time and the time shortly after the maximum had been reached gave a point in the curve depicting the relation between $\text{log}(\text{H}_2\text{O}_2)$ and time (Fig. 3), which was in line with the logarithm of the initial concentration and the remaining points in the curve.

The curves in Fig. 2 were plotted on a large scale and divided into sections of 50 minutes each for 500 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 during 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

$$\frac{100(P-x)}{\text{Wt. HCl} + \text{Wt. H}_2\text{O} + 0.53(P-x)} =$$

Percentage of H_2O_2 , where P is the initial weight of peroxide, x 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 proved by weighing the sulfuric acid in B, Fig. 1, 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 $1000 p d / (100 \times 34) = M$, where M is the molecular concentration, d is the density, and p 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

TABLE II
DATA DERIVED FROM TABLE I

Time from zero Min.	Area below curve Sq. cm.	H_2O_2 decomposed G.	H_2O_2 %	Mol. concn. ($a-x$)	$\text{Log}(a-x)$
0	0	0	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	0.9877
40	160.10	.8005	29.17	9.42	.9741
50	191.72	.9586	28.40	9.16	.9619
70	249.47	1.2473	26.96	8.62	.9352
100	325.02	1.6251	25.06	7.97	.9015
150	428.17	2.1409	22.40	7.06	.8488
200	511.65	2.5582	20.16	6.32	.8007
250	581.85	2.9092	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	3.6955	13.85	4.24	.6274
500	812.45	4.0622	11.74	3.50	.5441

presence of the acid is negligible. Where the concentration of the hydrochloric 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, Fig. 2, are given in Table II.

Now if the decomposition of the peroxide is a monomolecular reaction then $\log a/(a-x) = kt$, where a is the initial concentration, $(a-x)$ is the concentration after an amount, x , has decomposed, t is the time since the beginning of the reaction and k is the velocity constant.⁶ When $\log(a-x)$ is plotted against the time the value of k may be obtained from the slope of the curve. In Fig. 3 several such curves have been drawn. The curve marked "10% HCl" is plotted from the data of Table II and corresponds to the Expt. A and A', already described. The curves marked 9% and 8% HCl were obtained in a similar manner from the Curves B and C, in Fig. 2, 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 Fig. 3 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 Expt. AA'. 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, that is, below the critical concentration. Above the critical point 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 value 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 Livingston³ mention in their investigation of the catalysis by hydrobromic acid that the velocity constant k in the rate Equation $d(\text{H}_2\text{O}_2)/dt = k(\text{H}_2\text{O}_2)$ remained constant only after the *steady state*, corresponding to their outline of the mechanism of the catalysis, was reached. They do not quote any of their variations in the value of k showing an increase before two hours. It will be observed that the curve, (5% HCl), shows no variation in k . 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 k decreases. If Bray and Livingston's explanation of the mechanism is a correct one, then the *steady state* is approached much more rapidly in the case of hydrochloric than in the case of hydrobromic acid. This question of the *steady state* will be taken up later.

From the curves of Fig. 3 it may also be seen that the rate of decomposition and the value for the velocity constant, k , depend only upon the

⁶ In these calculations k is evaluated on the basis of common logarithms.

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 k corresponding to different strengths of acid are given in Table III. In this table k was evaluated only after the curves, similar to those in Fig. 3, had become straight and the reaction truly monomolecular. The concentrations of hydrochloric acid are calculated in gram molecules per liter 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 in the potassium iodide tubes was subtracted from the initial weight in determining the final concentration when the reaction had gone to completion.

TABLE III
VALUE OF THE VELOCITY CONSTANT, k , FOR DIFFERENT CONCENTRATIONS OF
HYDROCHLORIC ACID

Concn. HCl Moles/liter	$k \times 10^4$	Concn. undissoc. HCl Moles/liter	Concn. HCl Moles/liter	$k \times 10^4$	Concn. undissoc. HCl Moles/liter
4.48	15.1	..	1.87	3.08	0.59
4.15	14.0	..	1.45	2.33	.38
3.43	9.00	1.62	1.16	1.65	.27
3.23	8.12	1.47	1.09	1.70	.24
3.16	8.20	1.39	0.979	1.70	.20
3.05	6.68	1.34	.866	1.47	.16
2.72	5.34	1.11	.633	1.00	.10
2.21	3.65	0.78	.509	0.88	.073
2.02	3.50	.67	.310	.65	.035

The data of the first two columns of Table III are represented graphically in Fig. 4. The last column will be referred to later.

The concentrations at which less than 1 mg. of chlorine was given off were selected as having the critical values. These concentrations were determined by trial and error. If too much hydrochloric acid had been added to the peroxide considerable chlorine was given off, as indicated by the liberation of iodine in the potassium iodide tubes. If the concentrations were below the critical no hydrochloric acid was oxidized and the potassium iodide tubes remained clear. Velocity curves such as were shown in Fig. 3 were of great assistance in determining these critical concentrations as they indicated where the critical point would lie, namely, at the point where the curves became a straight line. The critical concentrations are given in Table IV, and are represented graphically in Fig. 5.

In order to be able to infer from the experimental results the mechanism of the reaction between hydrochloric acid and hydrogen peroxide the follow-

ing observations can be made; below what we 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

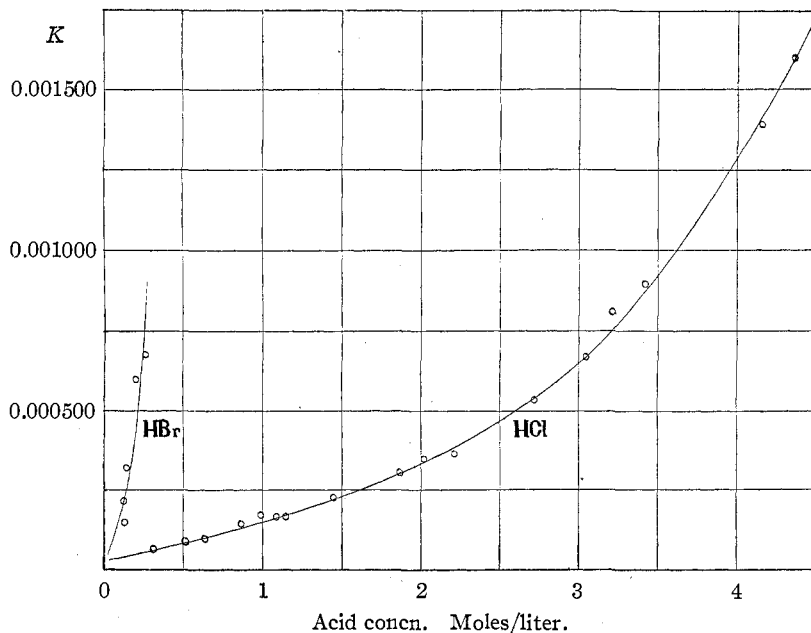


Fig. 4.

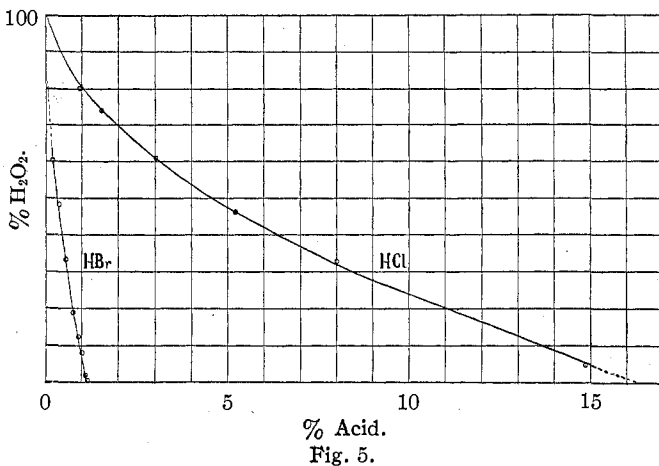
hydrochloric acid is reformed. The first point to be decided was whether the hydrogen chloride molecules or the ions into which it dissociates were the primary cause of the action with the hydrogen peroxide. This was determined by the following experiments: first, an aqueous solution of hydrogen peroxide and nitric acid was made up so that the hydrogen-ion

TABLE IV

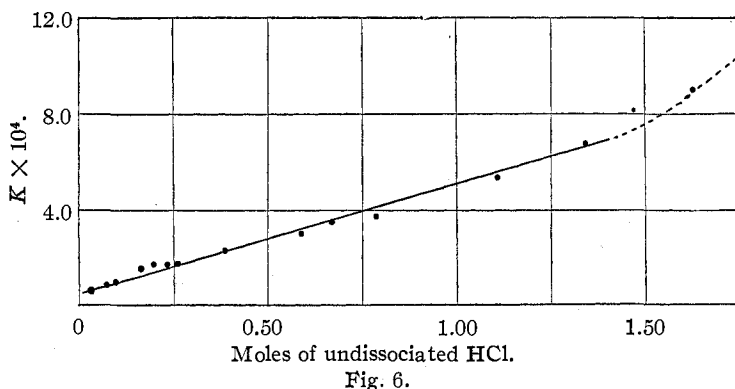
CRITICAL CONCENTRATIONS OF HYDROCHLORIC ACID AND HYDROGEN PEROXIDE						
H ₂ O ₂ , %.....	80.2	74.1	60.1	46.3	33.0	4.9
HCl, %.....	0.9	1.5	3.0	5.2	8.0	14.8

content corresponded to that of a hydrochloric acid solution where vigorous reaction had been found to occur. Samples of the mixture removed for analysis showed that even after four days no decomposition of the peroxide had taken place. A similar sodium chloride solution of hydrogen peroxide was prepared, and here again a negligible decomposition was observed. Evidently the hydrogen ions or chlorine ions as such are not the cause of

the decomposition of the hydrogen peroxide. It was not far fetched therefore, to consider the possibility of the undissociated hydrogen chloride molecules playing a part in the reaction. To examine this possibility the variation of the velocity constant of the hydrogen peroxide decomposition with the hydrochloric acid concentration was investigated.



The curve, Fig. 4, shows the relation between velocity constant and concentration of hydrochloric acid, the latter being the sum of the concentrations of the undissociated molecules and the ions. An attempt has been made in Fig. 6 to depict the relation between the velocity constant



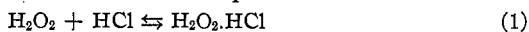
and the undissociated molecules alone. The values for undissociated hydrogen chloride concentrations in moles per liter are given in the last column of Table III. The calculation of the latter was based on the ionization calculated from conductivity data.⁷ Lewis⁸ has drawn attention

⁷ Kohlrausch, in Landolt-Börnstein-Roth, "Tabellen."

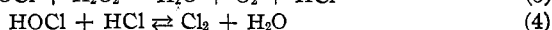
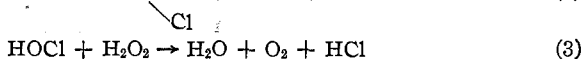
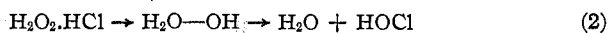
⁸ Lewis, THIS JOURNAL, 34, 1631 (1912).

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.

It will be observed (Fig. 4) that at the lower concentrations 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.



This is followed by the reactions,



Reactions 3 and 4 are well known; Reaction 2 is analogous to the action of ethylene oxide and hydrogen chloride.⁹

In Reaction 1 the velocity is proportional to the product of the concentrations of undissociated hydrogen chloride and hydrogen peroxide. In the subsequent reactions the hydrogen chloride is reformed. Hence, the velocity constant of the rate of decomposition of the peroxide remains unchanged after a certain amount of hydrogen chloride has been added, all of which is in agreement with experimental results.

Equation 1 is probably an equilibrium. The concentration of the complex $\text{H}_2\text{O}_2 \cdot \text{HCl}$ is then proportional to the product of the concentration of hydrogen peroxide and hydrochloric acid. 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, namely, $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$, and therefore Reaction 4 will not affect the *steady state* if this is meant to refer to $d(\text{H}_2\text{O}_2)/dt = k$. To repeat, the velocity constants k are only slightly influenced by this last reaction below the critical concentrations. It is possible, for instance,

⁹ Maass and Boomer, *THIS JOURNAL*, **44**, 1724 (1922).

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 of chlorine are formed. From the critical curve, Fig. 5, 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 water² and may therefore be more easily swept out by the oxygen liberated from the more concentrated peroxide solutions.

Further evidence in favor of the views set forth above was given by experiments in which nitric acid was added to an aqueous solution of hydrogen chloride and hydrogen peroxide.¹⁰ As has been mentioned, nitric acid does not affect the rate of decomposition when added alone. But the velocity constant of decomposition of the above-mentioned mixture 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 the formation of a larger number of undissociated hydrogen chloride molecules so that if the rate of decomposition of the peroxide depends on 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 shown readily that a complex with hydrogen fluoride would not break up, whereas one formed between the peroxide and hydrogen bromide would break up far more readily than that with hydrogen chloride. An experiment was carried out in which an aqueous solution containing 55% of hydrogen peroxide and 13% of hydrogen fluoride was kept in a paraffin-lined bottle and the latter placed in the thermostat. No measurable decomposition of the peroxide occurred during the course of several days, although a similar solution with hydrochloric in place 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 for hydrochloric acid. Due to the much greater velocity of the reaction the experimental results

¹⁰ The initial concentrations in this experiment were 36.48% of H_2O_2 , 4.21% of HCl , 4.96% of HNO_3 . The value of the velocity constant $k \times 10^4$ was found to be 2.76, whereas the velocity constant corresponding to 4.2% (1.15 moles per liter) is much less, namely, 1.65.

could not be obtained with any great degree of accuracy because only small quantities of hydrobromic acid could be added. At medium concentrations bromine was liberated vigorously so 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. The values are given in Table V, and are shown graphically in Fig. 4.

TABLE V
VALUE OF THE VELOCITY CONSTANT, k , FOR DIFFERENT CONCENTRATIONS OF HYDROBROMIC ACID

Conc. HBr, moles/liter.....	0.260	0.201	0.139	0.124	0.117
$k \times 10^4$	6.7	6.0	3.2	1.5	2.1

The critical concentrations could not be determined in the same way as with hydrochloric acid because in every case traces of bromine found their way into the potassium 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 hydrogen peroxide, would produce within an hour an appreciable coloration due to the liberation of bromine in the original solution. The experiments were carried out under the same conditions of temperature as in the case of hydrochloric acid. At concentrations of peroxide equivalent to 2% 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 VI 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 emphasized in Fig. 5 where these values are depicted. The abscissas of the curve for hydrobromic acid are 1/14.7 of those of the curve for hydrochloric acid.

TABLE VI
CONCENTRATIONS OF HYDROGEN PEROXIDE AND HYDROBROMIC ACID ANALOGOUS TO CRITICAL CONCENTRATIONS

H ₂ O ₂ , %.....	60.4	48.3	33.3	19.0	12.3	8.2	2.0	0.5
HBr, %.....	0.17	0.35	0.52	0.75	0.90	1.00	1.10	1.15

The method of measuring the rate of decomposition for low 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 authors are, however, in fair 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, Fig. 4, shows how greatly the velocity constant is affected by a slight variation in the concentration of hydrobromic acid as compared to the change caused by a corresponding variation in the concentration of hydrochloric acid. The same apparatus that was employed in the case of the latter acid was used, but the degree of accuracy of the concentrations which were made up in the same way was not sufficient for the large changes caused. The errors involved are connected with the establishment of the hydrobromic acid concentration, and not with the constant k which was determined accurately as was shown by the fact that the points giving the relation between time and hydrogen peroxide decomposed fell on a straight line. One fact was established, namely, that the velocity constant for hydrobromic acid did not vary 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.

The dehydrolysis in the bromine hydrolysis equilibrium may take some time to be established.¹¹ As was pointed out in the case of hydrochloric

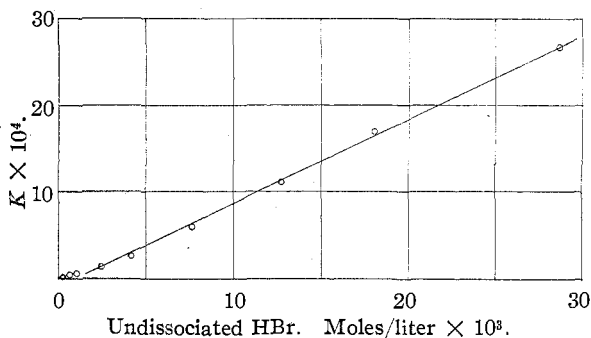


Fig. 7.

acid, Reaction 4 may not affect the velocity constant $d(\text{H}_2\text{O}_2)/dt$ appreciably except at very low concentrations of hydrogen peroxide. Taking the values obtained by Bray and Livingston^{12a} for the rate of decomposition of hydrogen peroxide in the presence of hydrobromic acid, and calculating the concentration of the hydrogen bromide molecules from conductivity data,^{12b} the curve shown in Fig. 7 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

¹¹ That time may be required to reach hydrolysis equilibrium has been found in some cases, for instance, Shaeffer and Jones, *Am. Chem. J.*, **49**, 240 (1913), and Arrhenius, *Z. physik. Chem.*, **13**, 407 (1894).

^{12a} Bray and Livingston, *THIS JOURNAL*, **45**, 2051 (1923), Table II.

^{12b} Ostwald, in Landolt-Börnstein-Roth, "Tabellen".

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 the 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 peroxide became definitely colored when the concentration of hydrobromic acid was increased from 0.95% to 1.10%. A 5% peroxide solution containing 0.66% of hydrobromic acid was colorless. Solutions were made up having the latter concentration and at the same time having various amounts of hydrochloric acid, sulfuric acid, and potassium bromide, respectively. The following concentrations show the minimum amounts of these substances which will just cause bromine coloration to appear: 5.0% of H_2O_2 , 0.66% of HBr, 0.91% of HCl;¹³ 5.0% of H_2O_2 , 0.66% of HBr, 1.82% of H_2SO_4 ; 5.0% of H_2O_2 , 0.66% of HBr, 1.95% of KBr. Bromine coloration according to the mechanism put forward above means that that rate of formation of the hypobromous acid has just been reached which will cause appreciable amounts of bromine to form. A solution containing 0.66% of hydrobromic acid and 0.91% of hydrochloric acid has a combined content of 0.33 gram mole of acid. Taking the degree of ionization of the hydrobromic and hydrochloric acids to be the same, this concentration corresponds to an ionization of 88.1%, so that the concentration of the undissociated hydrogen bromide molecules has been changed from 0.0056 to 0.010 mole per liter. The critical concentration of hydrobromic acid is 1.05% when the concentration of the peroxide is 5.0% (see Table VI), which corresponds to 0.011 mole 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 above, 1.82% of sulfuric acid had the same effect as 0.91% of hydrochloric acid. These percentages of acid correspond to 0.37 and 0.25 mole per liter, respectively, on the basis of complete dissociation. The difference in value between the sulfuric and hydrochloric acids is in agreement with the idea set forth, for it is well known that the sulfuric acid is dissociated to a much smaller extent than hydrochloric, and therefore the true hydrogen-ion concentration and consequently the increase in undissociated hydrogen bromide molecules is less in the presence of the sulfuric than in the presence of an equimolecular quantity of hydrochloric acid. Hence, the smaller effect of the sulfuric acid on the rate of decomposition is accounted for.

Finally, the addition of bromine ion should cause an increase in the undis-

¹³ It will be noticed by comparison with the values for hydrochloric acid that 0.91% of HCl is far below the critical concentration for this acid, so that no appreciable decomposition is caused by it.

sociated molecules and this is plainly shown by the fact that the addition of potassium bromide gave the critical coloration of bromine whereas a much higher concentration of potassium bromide alone had no effect whatever.

Before concluding it may be worth while to describe one more experiment in which chlorine was passed into a 43% solution of hydrogen peroxide. The mixture was placed in the thermostat, and samples removed from time to time were analyzed for acid and peroxide content. Within an hour the chlorine had disappeared and the acid value remained constant thereafter. The rate of decomposition of the hydrogen peroxide corresponded to the rate for a hydrochloric acid solution having the acid value found. This experiment is in agreement with the Reactions 1 to 4 outlined in the preceding which are based on hypochlorous acid being the intermediate compound. Since the hydrolysis constant of bromine is so very much lower than that of chlorine 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; $-\frac{d(\text{H}_2\text{O}_2)}{dt} = X(\text{H}_2\text{O}_2)(\text{H}^+)(\text{Br}^-) \cdot \gamma_{\text{HBr}}^2$. 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 determined¹⁴ a similar relationship does not hold at any concentration as measured by the authors.

A final word may be said with regard to the use of conductivity data for the calculation of undissociated molecules. The authors realize the uncertainty which exists as to the soundness of this method in giving absolute values but consider that it may be the best means available at present for estimating 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." If this is done, the formation of the complex, $\text{H}_2\text{O}_2 \cdot \text{HCl}$, may then 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."

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Summary

1. Hydrofluoric acid does not decompose hydrogen peroxide but acts as a stabilizer. The other halogen hydrides cause the decomposition of hydrogen peroxide at all concentrations.

¹⁴ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 335.

2. The rate of decomposition of the hydrogen peroxide by hydrochloric acid was examined over the whole range of possible concentrations. For any given concentration of hydrogen peroxide below 100% a "critical concentration" of hydrochloric acid was found below which the rate of decomposition was monomolecular, the acid concentration remaining unchanged, and above which chlorine was liberated to an extent such that the liberated oxygen swept the chlorine out of the reaction mixture. The relationship between acid concentration and velocity constant was determined and it was suggested that the rate constant was proportional to $(1 - \alpha)$ multiplied by the acid concentration, where α is the dissociation of the acid calculated from conductivity data.

3. The mechanism of the reaction involved may possibly be represented by the formation of a complex, $H_2O_2 \cdot HCl$, which breaks down into hypochlorous acid and water. This is followed by a reaction between hypochlorous acid and hydrogen peroxide, and above the critical concentrations by the liberation of chlorine due to the displacement of the equilibrium among hypochlorous acid, hydrochloric acid and chlorine.

4. 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 bromine was liberated at far lower concentrations due to this greater rate and to the smaller extent to which bromine is hydrolyzed.

5. The decomposition of the hydrogen peroxide by the halogens is due to the hydrolysis of the latter, the resulting oxy-acid causing the decomposition of the peroxide accompanied by the formation of the halogen hydride.

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THE HYDRATES OF LIME

BY R. T. HASLAM, G. CALINGAERT AND C. M. TAYLOR

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An exhaustive study of the literature on the system, calcium oxide plus water, shows many discrepancies as to the compounds capable of existing in such a system. Following a suggestion of the National Lime Association, the present study was undertaken to determine whether there was any other hydrate than the well-known monohydrate $Ca(OH)_2$, or $CaO \cdot H_2O$.

Review of the Literature

Karcz¹ claims to have prepared a white granular powder of the formula $CaO \cdot 2H_2O$, by digesting calcium oxide with water for several days at 60°. He also gives data on

¹ Karcz, *Chem.-Ztg.*, **22**, 38 (1898).