cathode rays, it has been shown that peroxide, water vapor and ozone are formed as primary products.

A kinetic study at varying concentrations of hydrogen and oxygen shows that the rate of peroxide formation is almost independent of concentration, whereas the rate of water vapor formation varies over a five-fold range, and ozone over a ten-fold range.

The rates of formation of ozone and water vapor parallel one another very closely at all the concentrations studied, suggesting that the same primary mechanism is responsible for the formation of both.

The gross rate of reaction parallels that observed by Lind for the same reaction under the influence of α-particles.

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THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN AN ACID CHLORINE-CHLORIDE SOLUTION. II. AN INTERPRETATION OF THE RATE MEASUREMENTS IN CONCENTRATED SOLUTION

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The velocity of decomposition of hydrogen peroxide in an acid chlorine-chloride solution can be represented, with approximate accuracy, by the following equation[1]

$$v = \chi(H_2O_2)(H^+)(Cl^-)f^2_{HCl} \qquad (1)$$

where χ is a constant (0.00010) and f_{HCl} is the activity coefficient of hydrochloric acid. In dilute solutions the equation apparently represents the experimental data within the limits of error; in more concentrated solutions the value of χ decreases systematically to a value of 0.00005 at an ionic strength of 5μ. Equation 1 may be considered as a simplified form of the general reaction velocity equation, presented by J. N. Brönsted.[2] The exact form of the Brönsted equation for this reaction is

$$v = K\,H_2O_2(H^+)(Cl^-)f^2_{HCl} \cdot f_{H_2O_2}/f_x \qquad (2)$$

where f_x is the activity coefficient of the "reaction complex," $(H_2O_2 \cdot HCl)$. If we assume that $f_{H_2O_2}/f_x$, the ratio of the activity coefficients of two neutral molecules, is equal to unity, Equation 2 reduces to the form of Equation 1.

It has been demonstrated, both on theoretical[3] and on experimental[4]

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[1] Livingston and Bray, THIS JOURNAL, **47**, 2069 (1925); **48**, 405 (1926).

[2] (a) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); (b) "The Velocity of Ionic Reactions," Columbia Press, **1927**.

[3] Debye and McAuley, *Physik. Z.*, **26**, 22 (1925).

[4] A review of existing data has been recently presented by Randall and Failey, *Chem. Reviews*, **4**, 271, 285 (1927). This summary demonstrates that the formula holds

grounds, that the variation of the activity coefficient of a non-electrolyte in an aqueous salt solution may be represented by an equation of the following form

$$\log f_0/\mu = k \qquad (3)$$

where f_0 is the activity coefficient of the non-electrolyte and k is a constant the value of which depends upon the properties of the salt and the non-electrolyte present.

Since both hydrogen peroxide and the reaction complex are neutral molecules, we may write

$$\log (f_{H_2O_2}/f_x) = \mu(k_{H_2O_2} - k_x) = \mu k' \qquad (3a)$$

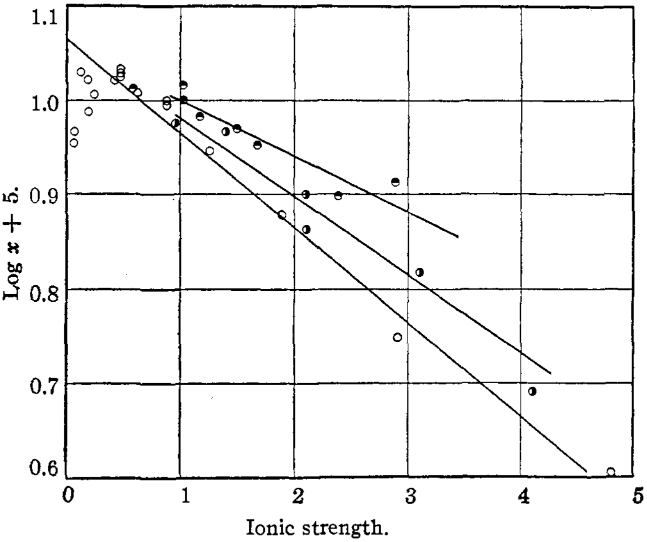
Substituting this relation in Equation 2, we obtain

$$v = K(H_2O_2)(H^+)(Cl^-)f^2_{HCl} \cdot 10^{\mu k'} \qquad (4)$$

or

$$\log K = \log \chi - \mu k' \qquad (4a)$$

We may test this relation by plotting log χ against μ. Such a plot is given in Fig. 1. The data are taken from Table I of reference 1. The points, representing experiments performed in hydrochloric acid solutions, fall on a straight line within the limits of experimental error. The experi-



○, HCl; ◑, HCl + NaCl; ●, HCl + HClO$_4$.

Fig. 1.—The velocity of decomposition of hydrogen peroxide in an acid chlorine–chloride solution.

with reasonable accuracy for all of the non-electrolytes investigated, even at high ionic strengths. Linderström-Lang, *Compt. rend. trav. lab. Carlsberg,* **15**, No. 4 (1924), measured the solubilities of quinone, hydroquinone, succinic acid and boric acid in the presence of varying concentrations of a number of different salts, and found that the ratio of the logarithm of the activity coefficient of the non-electrolyte to the equivalent concentration of the salt was practically constant.

ments at the lowest concentrations show a negative departure of 10 to 20%; however, this is probably due to experimental error, since the absolute values of these rates are very small.[5] The experiments performed in mixtures of hydrochloric acid and perchloric acid or sodium chloride may be also represented by straight lines the slopes of which differ from that determined by the experiments in hydrochloric acid. At the higher concentrations these mixtures may be regarded as practically pure solutions of perchloric acid or of sodium chloride, and therefore we should expect the straight line relation to hold. Unfortunately the experiments were not planned to illustrate this effect and several of the experiments at low ionic strength were performed in mixtures containing relatively large amounts of hydrochloric acid. The values of the ionic strength given are based upon concentrations expressed in moles per liter rather than in molality.[6]

An additional test of Equation 4 may be made by combining the rate measurements (that is, values of χ) with experimentally determined values of $f_{H_2O_2}$. If the reaction complex has properties similar to those of a stable neutral molecule, we may expect that

$$\log f_x = \log (K/\chi) f_{H_2O_2} = \mu k_x \qquad (5)$$

The Activity of Hydrogen Peroxide in Sodium Chloride and Sodium Sulfate Solutions[7]

The activity of hydrogen peroxide in aqueous salt solutions can be readily determined by "partition" experments with a suitable immiscible solvent. A variety of organic solvents have been investigated;[8] of these *iso*-amyl alcohol is probably best adapted to the purpose.[9]

The following *experimental procedure* was adopted. The aqueous peroxide solution, containing a known amount of salt (weighed out as anhydrous material), was made up in a glass-stoppered cylinder and placed in a 25° thermostat to attain thermal equilibrium. After an hour or more a definite amount of *iso*-amyl alcohol (also at 25°) was added to the aqueous solution. The cylinder was then shaken vigorously until the two phases formed a fine emulsion and then returned to the thermostat and allowed to remain for two hours. At the end of this time the two phases had separated into clear, apparently homogeneous layers and samples were withdrawn for analysis.[10]

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[5] See pp. 2072–2073, ref. 1.

[6] Compare footnote 4.

[7] These experiments were performed at the University of California in 1925.

[8] See Walter and Lewis, This Journal, **38**, 633 (1916).

[9] (a) H. Calvert, *Z. physik. Chem.*, **38**, 512 (1901); (b) A. Joyner, *Z. anorg. Chem.*, **77**, 103 (1912).

[10] The experiments of Joyner (ref. 9b) indicate that the partition equilibrium is attained very rapidly.

Materials.—The salts were purified by repeated crystallization of the "C. P." materials. The stock hydrogen peroxide solution was made by diluting "perhydrol." The *iso*-amyl alcohol was purified by twice distilling "C. P." material in an all-glass still, discarding the first and last fractions.

In the presence of *iso*-amyl alcohol, hydrogen peroxide cannot be titrated with permanganate solution.[9a] After a number of preliminary experiments, the following analytical procedure was adopted. To determine the aqueous solution: add the sample (2 cc.) to a glass-stoppered flask containing 50 cc. of distilled water, 1 cc. of concentrated sulfuric acid and 4 g. of potassium iodide, allow to stand for thirty minutes and titrate the resulting iodine with thiosulfate to a starch end-point. To determine the alcohol solution: add the sample (10 cc.) to a glass-stoppered flask containing 200 cc. of distilled water, 4 cc. of concentrated sulfuric acid and 4 g. of potassium iodide, allow to stand for thirty minutes and titrate with thiosulfate, shaking frequently, until the yellow color disappears from the floating droplets of alcohol.[11] These methods give results reproducible within 0.5%. The method for the aqueous solution was shown to give results identical with those obtained by direct titration with permanganate in the absence of the alcohol.

Samples of the alcohol (upper) layer were withdrawn and measured with an ordinary pipet. Samples of the aqueous layer were obtained by introducing a sealed glass tube into the solution, breaking the thin glass seal[12] against the bottom of the vessel and forcing a sample of the lower layer out by air pressure.

Results and Calculations.—The experiments of Joyner[9b] at 0° and of Calvert[9a] at 25° demonstrate that the activity of hydrogen peroxide in aqueous solution is practically independent of its concentration for concentrations between 0.10 and 2.0 *M*. In light of these results, all of our experiments were performed with hydrogen peroxide solutions of about 1.5 *M*. The results of the partition experiments are summarized in Table I. The concentration of the added salt, in moles per liter, is given in the second column; the mean value of the distribution constant, *D*, in the third; and the number of separate experiments, upon which the mean value was based, in the fourth column.

TABLE I

THE ACTIVITY OF HYDROGEN PEROXIDE IN AQUEOUS SALT SOLUTIONS AT 25°

No.	Added salt	$D = m_{aq.}/m_{alc.}$	No. of expts.	$f_{H_2O_2}$	$-\log f_{H_2O_2}/\mu$
1[9a]	None	7.03 ± 0.05	8	1.00	
2	None	6.87 ± 0.07	11		
3	0.25 m, NaCl	7.21 ± 0.01	2	0.96	0.064
4	0.50 m, NaCl	7.33 ± 0.05	4	.95	.045
5	1.00 m, NaCl	7.52 ± 0.07	4	.92	.034
6	2.00 m, NaCl	8.16 ± 0.01	2	.85	.035
7	4.00 m, NaCl	9.21 ± 0.04	2	.76	.031
8	0.25 m, Na_2SO_4	7.62 ± 0.04	2	.91	.054
9	0.50 m, Na_2SO_4	7.96 ± 0.05	2	.87	.039
10	1.00 m, Na_2SO_4	8.65 ± 0.10	3	.80	.032

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[11] As was pointed out by Calvert (ref. 9a), it is impossible to obtain a starch iodine color in the presence of the alcohol phase. He overcame this difficulty by adding sufficient water at 55° to render the titration mixture homogeneous.

[12] Compare Abbott and Bray, THIS JOURNAL, **31**, 738 (1909).

The values of $f_{H_2O_2}$ listed in the fifth column are based upon the assumption that the value for pure aqueous solution is unity.[13] In these computations we have used a value of 6.95 for the distribution coefficient between alcohol and pure water; this is an average of the value presented here (6.87) and that given by Calvert (7.03).

We would predict from Equation 3 that $\log f_{H_2O_2}/\mu$,[14] given in the last column, should have a constant value. While the observed trend may be real,[15] it is also possible that it is due to an error in the average value chosen for the distribution coefficient with pure aqueous solutions. The trend could be eliminated by choosing a value 2% higher.

The Measured Velocity and the Activity of Hydrogen Peroxide.—By combining values of $f_{H_2O_2}$ with velocity measurements which were performed in sodium chloride solution, we may test the validity of Equation 5. The results of such a comparison are summarized in Table II. The first five columns are taken from Table I, ref. 1. The values of $f_{H_2O_2}$, Col. 6, were interpolated from Table I. In computing k_x, Col. 7, K was obtained by extrapolating χ to infinite dilution (Fig. 1) and has a value of 11.7×10^{-5}.

TABLE II

INTERPRETATION OF THE REACTION VELOCITY IN SODIUM CHLORIDE SOLUTIONS

No.	(HCl)	(NaCl)	μ	$\chi \times 10^5$	$f_{H_2O_2}$	$\frac{\chi}{f_{H_2O_2}} \times 10^5$	k_x	a_{H_2O}	$K'_a \times 10^5$
1	0.444	0.50	0.94	9.5	0.92	10.3	0.059	0.97	11.3
2	.444	1.00	1.44	9.3	.89	10.5	.033	.95	12.2
3	.098	2.00	2.10	7.3	.85	8.6	.064	.93	10.7
4	.222	1.89	2.11	8.0	.85	9.4	.045	.93	11.7
5	.098	3.00	3.10	6.6	.80	8.25	.049	.89	11.7
6	.098	4.00	4.10	4.9	.75	6.55	.062	.85	10.8

While there is considerable erratic variation in the values of k_x, there is no apparent trend. This may be considered as definite evidence in support of Equation 5. It follows from this that when due allowance is made for the variation of the activity coefficients of the neutral molecules involved, the rate of decomposition of hydrogen peroxide in acid chlorine–chloride solutions at ionic strengths between 0.1 and 4.0 is accurately represented by the Brönsted formula, and that it is unnecessary in this case to make allowance for any change in the nature of the solvent.[16] It is interesting to note that k_x has a value typical of normal non-electro-

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[13] For a discussion of factors, presumably negligible in this case, which can affect the accuracy of activity determinations based upon distribution measurements, see Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, **1923**, p. 262.

[14] Here, as in the rate measurements, the values of the ionic strength are based upon concentrations expressed in moles per liter rather than in moles per 1000 g. of water.

[15] Compare the data recorded by Randall and Failey, ref. 4.

[16] See Brönsted, *Z. physik. Chem.*, **115**, 359–363 (1925).

lytes[3] and unlike $k_{H_2O_2}$ is positive in sign; that is, the fugacity of the complex is increased by the addition of salts.

It is also possible to interpret these data in terms of the "activity rate" theory.[17] According to this theory the reaction velocity is proportional to the product of the activities of the components, and the velocity equation is

$$v = K_a a_{H_2O_2} a_{H^+} a_{Cl^-} \qquad (6)$$

However, the data of Col. 7, Table II, demonstrate that K_a ($= \chi/f_{H_2O_2}$) is not a constant. It was suggested by G. N. Lewis[18] that the departure from constancy of K_a might be due to the solvent entering directly into the reaction. As is demonstrated by the data in the last column of Table II, we may obtain an empirical fit if we introduce[19] $a^3_{H_2O}$ into Equation 6. This corresponds to the assumption that three molecules of water take part in the reaction.[20] It is, unfortunately, not possible to determine $a_{H_2O_2}$ in the presence of hydrochloric acid by the distribution method used, both because of the decomposition of hydrogen peroxide in hydrochloric acid and because of the solubility of the acid in *iso*-amyl alcohol. In order to give K' a constant value of about 11.7×10^{-5} for the measurements in concentrated hydrochloric acid, we must assume that hydrochloric acid and sodium chloride have about the same effect on the activity of hydrogen peroxide. However, if this is done, the experiments in dilute solution exhibit a departure which is apparently too great to be attributed entirely to experimental error. Therefore, in spite of the constancy of K' for the measurements in sodium chloride solutions, it seems improbable that the modified form of the "activity rate" theory represents the facts.

A Discussion of Two Analogous Reactions.—The velocity of the decomposition of hydrogen peroxide in a bromine–bromide solution[21] and the velocity of rearrangement of chloro-acetylaminobenzene in an acid chloride solution[22] can be represented by laws analogous to the law determined for the decomposition of hydrogen peroxide in an acid chlorine–chloride solution.

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[17] See for example Harned and Seltz, THIS JOURNAL, **44**, 1476 (1922).

[18] Private communication.

[19] The values of a_{H_2O} given in Table II were computed from the values of γ_{NaCl} presented by Lewis and Randall, ref. 13, p. 351.

[20] It is not at all improbable that water does enter into the reaction, although there is, of course, no *a priori* reason for selecting the third or indeed any positive power. It is a suggestive fact that Walton and Jones, THIS JOURNAL, **38**, 1955 (1916), find that certain hydrogen peroxide decomposition reactions occurring in non-aqueous solvents are of second order.

[21] (a) Bray and Livingston, THIS JOURNAL, **45**, 1251 (1923); (b) Livingston and Bray, *ibid.*, **45**, 2048(1923); (c) Livingston, *ibid.*, **48**, 53 (1926).

[22] (a) Rivett, *Z. physik. Chem.*, **82**, 201; **85**, 113 (1913); (b) Harned and Seltz, THIS JOURNAL, **44**, 1480 (1922); (c) Åkerlöf, *Medd. K. Vetenskapsakad. Nobelinstitut*, **6**, No. 2 (1922); (d) Soper, *J. Phys. Chem.*, **31**, 1192 (1927).

The decomposition of hydrogen peroxide in acid bromine–bromide solutions has been studied chiefly at ionic strengths less than unity. Under these conditions its velocity may be represented with fair accuracy by the following equation.

$$v = \chi_{HBr}(H_2O_2)(H^+)(Br^-)f^2_{HBr} \qquad (7)$$

However, an examination of the data shows that there is apparently a systematic decrease in the value of χ_{HBr} with increasing ionic strength. A plot of log χ against μ shows that the data are consistent with an equation analogous to Equation 4. The measurements performed in hydrobromic acid solutions (at ionic strengths between 0.01 and 0.4) indicate a value of about -0.07 for k'. The experiments performed in solutions containing potassium bromide and sulfuric acid (at ionic strengths[23] between 0.05 and 4.3) exhibit considerable erratic variation but are consistent with a value of about -0.04 for k'.

The velocity of rearrangement of chloro-acetylaminobenzene was measured by Rivett[22a] in solutions of hydrochloric acid up to one molal and in solutions containing 0.25 *M* hydrochloric acid and one of a number of different chlorides (as well as sulfuric acid) at a variety of concentrations up to an ionic strength of about 4. More recently Harned[22b] has repeated Rivett's measurements in hydrochloric acid solutions. Åkerlöf[22c] measured the rate in solutions containing 0.25 *M* hydrochloric acid and aluminum chloride at concentrations up to 2 *N*. It has been demonstrated that the rate-determining step in the reaction is $C_6H_5 \cdot NHClAc + H^+ + Cl^- \longrightarrow X$. This mechanism should lead to a rate equation similar to Equation 4, and therefore the plot of log $[k/(H^+)(Cl^-)f^2_{HCl}]$ (where k is the first order constant) against μ should be a straight line. We may use the measurements of Harned[24] to obtain approximate values of f_{HCl} in alkali chloride solutions. The experimental values for alkali chloride solutions fall approximately on straight lines with slopes of about -0.09; but these lines do not appear to extrapolate to the same point in dilute solution. Rivett's experiments in pure hydrochloric acid give a straight line with a slope of 0.06; the values of Harned and Seltz are practically constant, but show a slope of about -0.01 if recent values[25] of f_{HCl} are used. These apparent inconsistencies are probably due to a factor which has been discussed by

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[23] Based upon concentrations expressed in moles per liter rather than in molality. This probably introduces a considerable error in the more concentrated solutions. See note b, Table II, ref. 20. As has already been stated (ref. 21 c, p. 55), the values of χ_{HBr} measured in KBr–sulfuric acid solutions are consistently 10% higher than those measured in hydrobromic acid solutions, or in solutions containing HBr and metallic bromides. This difference must be due to some unknown difference in experimental conditions.

[24] Harned, THIS JOURNAL, **42**, 1808 (1920); also Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922).

[25] Randall and Young, *ibid.*, **50**, 989 (1928).

Soper.[22d] He has shown that there are two possible products of the reaction, one of which is an oxidizing agent, and that, therefore, the iodimetrically measured rate is always less than the actual rate. This effect is greatest when $a_{H^+} \times a_{Cl^-}$ is small. A correction for this factor would raise all of the values of k for dilute solution experiments, especially those performed in dilute hydrochloric acid solutions. If proper allowance were made for this factor and the correct values of f_{HCl} were employed, it is very probable that the velocity could be accurately expressed in terms of an equation similar to Equation 4.

In conclusion we may state that for the type of reaction considered here,[26] Brönsted's equation is sufficient to represent the reaction velocity measurements at all concentrations investigated. Taken in conjunction with the success of the theory in interpreting the results of velocity measurements for widely different types of reactions in dilute solutions,[27] this constitutes strong empirical evidence for the general validity of the Brönsted hypothesis as applied to reactions in aqueous solution. The application of the theory to other types of reactions in concentrated solutions will be considered in another paper.

Acknowledgment should be made to Professor W. C. Bray and to Professor F. H. MacDougall for their kind interest and criticism.

Summary

1. The Brönsted reaction velocity equation has been combined with the Debye and McAuley equation for the activity of non-electrolytes to obtain an expression for the rate of decomposition of hydrogen peroxide in acid chlorine-chloride solutions

$$v = K\,(H_2O_2)(H^+)(Cl^-)\,f^2_{HCl}\cdot 10^{\mu k}$$

It has been shown that this expression is in agreement with the experimental material.

2. The activity of hydrogen peroxide in sodium chloride and sodium sulfate solutions has been determined by distribution measurements. These results have been used to test a prediction based upon the reaction velocity theory.

3. Some discussion of the velocity measurements of two analogous reactions has been presented.

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[26] A reaction between two ions having charges of similar magnitude but of unlike sign, and a neutral molecule. This is practically the same as Brönsted's reactions type VI (compare reference 2a, p. 177).

[27] (a) Brönsted, ref. 2a and b; (b) Brönsted and Delbanco, *Z. anorg. Chem.*, **144**, 248 (1925); (c) Livingston, ref. 21c; (d) Brönsted and Livingston, THIS JOURNAL, **49**, 435 (1927).