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THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN A BROMINE-BROMIDE SOLUTION, AND A STUDY OF THE STEADY STATE

BY WILLIAM C. BRAY AND ROBERT S. LIVINGSTON

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Introduction

Preliminary experiments showed that in acid solution at room temperature hydrogen peroxide not only oxidizes bromide to bromine,

$$H_2O_2 + 2Br^- + 2H^+ = Br_2 + 2H_2O \qquad (1)$$

but also reduces bromine to bromide,

$$H_2O_2 + Br_2 = O_2 + 2Br^- + 2H^+ \qquad (2)$$

The transformation of bromide to bromine is favored by high concentration of hydrogen and bromide ions, and that of bromine to bromide by low concentration of these substances.[1] However, both reactions can be demonstrated at a single intermediate concentration of hydrogen ion by starting with bromine at zero concentration in one case and at high concentration in the other.

The sum of Reactions 1 and 2 is the decomposition of hydrogen peroxide.

$$2H_2O_2 = 2H_2O + O_2 \qquad (3)$$

This reaction accompanies (1) and (2) in gradually increasing proportion. In each case *a steady state* is finally reached where the decomposition of hydrogen peroxide is the only measurable reaction. Thus, we have a catalytic reaction which is closely related to two ordinary chemical reactions, and in which the concentrations of two forms of the catalyst (bromide and bromine) can be measured experimentally at the steady state.

The results of two typical experiments are shown in Fig. 1, where concentrations of bromine are plotted against time in minutes. Curves I and II correspond to the experiments summarized in Tables VII and IX, respectively. In the first case the bromine concentration starts at zero and rises to a constant value, while in the second case it decreases from an initially high value until a definite concentration is reached.

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[1] The liberation of a small amount of chlorine by the action of concentrated H_2O_2 solution on HCl was noted in 1870 by Engler and Nasse [*Ann.*, **154**, 215 (1870)]. The catalytic decomposition of H_2O_2 in KBr solution and to a much less extent in KCl or NaCl solution, was demonstrated by Schöne in 1879 [*Ann.*, **195**, 228 (1879)]. Very recently Maass and Hatcher [THIS JOURNAL, **44**, 2476-7 (1922)] have studied the reactions of the halogens and halides with concentrated solutions of H_2O_2 and with the anhydrous material. They state that the peroxide is gradually decomposed when in contact with any of the halogens, that bromine or chlorine is liberated in the reaction with HBr or HCl, and that bromine is liberated in the reaction with KBr. These results in general are in agreement with our results in *dilute* solutions, but we have found no evidence of the formation of bromine in a neutral bromide solution.

When the bromine concentration is constant the concentrations of hydrogen ion and bromide ion, of course, also have fixed values.

Since the two hydrogen peroxide reactions, 1 and 2, are irreversible there is no doubt that they continue to take place at the steady state. It is the purpose of the present investigation to determine whether the bromine-bromide catalysis can be completely accounted for by this chemical theory. The following determinations have been undertaken: (1) the kinetics at the steady state, (2) the functional relation between the concentrations of bromine, hydrogen ion, bromide and hydrogen peroxide at the steady state, and (3) and (4) the kinetics of Reactions 1 and 2 at a distance from the steady state.

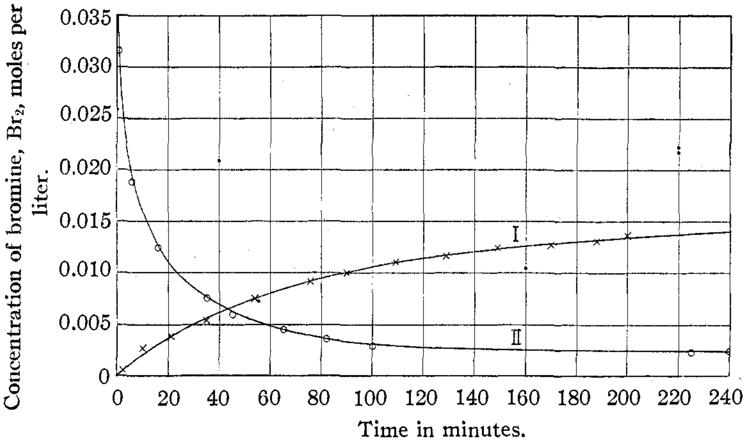

Fig. 1.

Analogous Reactions

Numerous examples might be cited of a close relationship between a catalyzed reaction and ordinary chemical reactions, but we will mention only a few involving hydrogen peroxide.

There is a close analogy between the bromine-bromide reactions and the iodine-iodide reactions with hydrogen peroxide, which Abel[2] has been studying for several years. Thus, hydrogen peroxide oxidizes iodide ion to iodine in acid solution, reduces iodine to iodide ion in alkaline solution and at very low concentrations of hydrogen ion. and is catalytically decomposed under intermediate conditions. In this iodine-iodide catalysis Abel has shown that a steady state is reached, and has studied this both theoretically and experimentally. In agreement with the chemical theory, the rate at the steady state is equal to the sum of the rates of the two opposing or compensating chemical reactions. However, the rate of the iodine-hydrogen peroxide reaction, which could be measured only when the concentration of hydrogen ion was held within the limits 10^{-7} to 10^{-6} M by means of buffer solutions, follows a very complicated law; and, although the iodide-iodine mechanism has been demonstrated, and hypo-iodite is prob-

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[2] Abel, *Z. Elektrochem.*, **14,** 598 (1908); *Monatsh.*, **41,** 405 (1920); *Z. physik. Chem.*, **96,** 1 (1920).

ably an important intermediate substance, a complete theory of the mechanism has not been realized.

The iodic acid-iodine catalysis has been shown by Bray and Caulkins[3] to be closely related to two reactions of hydrogen peroxide in which iodine is converted into iodic acid, and iodic acid into iodine, respectively. The unusual phenomenon of periodicity discovered in this case demonstrates the complicated nature of the reactions. Instead of a gradual approach to a steady state which depends on the concentrations of iodine, iodate, acid and peroxide (the substances present in measurable amounts), it appears that under suitable conditions the reaction can proceed beyond a theoretical steady-state position and then oscillate back and forth about such a position.

The chromate-chromate ion catalysis investigated by Spitalsky[4] is also complicated, but is clearly intermediate between the reduction of dichromate ion to chromic ion (Cr^{+++}) by hydrogen peroxide in acid solution and the oxidation of trivalent chromium to chromate ion in alkaline solution, and depends upon the rates of these two opposing reactions. The existence of a steady state during catalysis has been demonstrated; but, since analyses could be made only after the hydrogen peroxide had been completely decomposed, the steady state function was determined only for the limiting case of zero concentration of hydrogen peroxide. It involves the concentrations of chromic ion, dichromate ion and hydrogen ion.

It seems fairly certain that in any homogeneous catalytic reaction there must be postulated a steady state in which the catalyst exists in at least two forms. Moreover, if the mechanism consists of a single series of intermediate reactions, the absolute rates of each of these reactions must be equal at the steady state. An example in which the catalyst seems to exist as one molecular species is, therefore, simply the limiting case in which the specific reaction rate of the disappearance of this form of the catalyst is very small compared with that of its re-formation.

The Choice of Catalysts by Means of Free-Energy Data

The theory that a homogeneous catalytic reaction consists of compensating chemical reactions requires that each of the latter has a tendency to take place under steady-state conditions and, therefore, involves a decrease in free energy. Conversely, when the necessary free-energy data are available, we may determine whether each of a series of compensating reactions has a tendency to take place, and thus decide in advance whether the series is a possible mechanism for the catalysis.

Thus the choice of the bromine-bromide couple as a catalyst for the decomposition of hydrogen peroxide was based on calculations of the free energies of Reactions 1 and 2. The following revised values of F°_{298}, the free energy of formation at 25°, in calories, were kindly furnished by Lewis and Randall, and differ slightly from the values first published.[5]

H_2O_2(aq.), —31470; Br^-, —24595; Br_2(aq.), 977; H^+, 0; O_2(g), 0; H_2O (l), —56560; BrO_3^-, 2300.

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[3] Bray and Caulkins, This Journal, **43**, 1262 (1921).

[4] Spitalsky, *Z. anorg. Chem.*. **53**, 184 (1907); **56**, 72 (1907); **69**, 179 (1910).

[5] Lewis and Randall. This Journal, **36**, 1992 (1914); **38**, 2356 (1916).

From these data values of $\Delta F°_{298}$ were calculated.

(1)—$H_2O_2 + 2Br^- + 2H^+ = Br_2 + 2H_2O$; $\Delta F°_{298} = -31483$ cals.

(2)—$H_2O_2 + Br_2 = O_2 + 2Br^- + 2H^+$; $\Delta F°_{298} = -18697$ cals.

(3)—(1) + (2) $2H_2O_2 = 2H_2O + O_2$; $\Delta F°_{298} = -50180$ cals.

The large negative values of ΔF show that these reactions have a great tendency to take place in acid solution and, therefore, that the bromine-bromide catalysis is possible.

We do not wish to imply that these calculations have proved that the presence of bromide and bromine will cause the decomposition of hydrogen peroxide in acid solution. The experimental test is still necessary, since thermodynamics cannot furnish evidence that Reactions 1 and 2 are more rapid than the uncatalyzed reaction, 3. Also Reactions 1 and 2 do not constitute the only series of reactions involving bromine that may be assumed to account for the catalysis. These reactions may take place in steps, for example through hypobromous acid; or an altogether different pair of compensating reactions may be assumed, involving, for example, bromine and bromate ion.

The following calculations were made before the experimental work was begun.

$$5H_2O_2 + Br_2 = 2BrO_3^- + 2H^+ + 4H_2O;\ \Delta F°_{298} = -65267 \text{ cals.} \quad (4)$$

$$5H_2O_2 + 2BrO_3^- + 2H^+ = 5O_2 + Br_2 + 6H_2O;\ \Delta F°_{298} = -185633 \text{ cals.} \quad (5)$$

By dividing these results by 5, we obtain for the free energies of these reactions per mole of hydrogen peroxide consumed, —15053 and —37127 cals., respectively. These values of ΔF are of the same order of magnitude as those obtained for Reactions 1 and 2; Reactions 4 and 5, also, have a great tendency to take place, and on the basis of the thermodynamic calculations there is no more reason for expecting the bromine-bromide catalysis than the bromic acid-bromine catalysis. However, other experiments have failed to find any evidence in favor of the latter, at least in acid concentration up to *N*.

When bromine is treated with hydrogen peroxide in the presence of nitric or sulfuric acid at room temperature or at 50–60°, Reaction 2 takes place and not Reaction 4. The absence of bromate at any time during the reaction was proved by cooling the solution, extracting the bromine rapidly with carbon tetrachloride, adding excess of alkali, and boiling until all the peroxide was decomposed; the resulting solution contained bromide but no bromate. This procedure has been shown by Bray and Miller, working in this Laboratory, to be a satisfactory method of determining iodate in the presence of iodine and hydrogen peroxide.

On the other hand, bromate in acid solution after a short induction period rapidly oxidizes hydrogen peroxide with evolution of oxygen. When excess peroxide is used the bromine concentration rapidly reaches a maximum and then gradually decreases to a constant value. These qualitative results show that the formation of bromine by Reaction 5 and by the reaction between bromate, bromide and hydrogen ions is more rapid than the transformation of bromine into bromide ion by Reaction 2.

We shall now consider what oxidation-reduction couples are possible catalysts for the decomposition of hydrogen peroxide. Corresponding to any couple, O-R, a pair of compensating reactions may be written in which hydrogen peroxide oxidizes R to O and reduces O to R, respectively. Both of these reactions will have a tendency to take place (and ΔF will be negative) only when the couple O-R is neither too weak nor too powerful an oxidizing agent. Thus, if we consider weaker and weaker oxidizing couples, the tendency of O to oxidize hydrogen peroxide will steadily decrease, and the concentration of R at the steady state will approach such a small value that its rate of reaction with hydrogen peroxide becomes negligible. Similarly, with more and more powerful oxidizing couples an upper limit is approached where the oxidation of hydrogen peroxide is possible, but not its reduction. Accordingly, if at a given concentration of hydrogen ion all possible couples were arranged in order in an oxidation-reduction series, we should expect the catalysts to lie within a range which can be approximately designated in advance;[6] beyond this range there would be at one end of the series many reducing agents and at the other a few powerful oxidizing agents which react quantitatively with hydrogen peroxide without accompanying catalytic decomposition.

The failure to act as a catalyst of a couple whose oxidation potential lies within this range is to be attributed to the slowness of the reactions. Therefore, the test of this method and of the chemical theory of catalysis upon which it is based is to be made by examining whether there are any catalysts for the decomposition of hydrogen peroxide which lie outside the indicated range. As far as homogeneous catalysts are concerned, we do not know of such an exception.

The possibility that the chemical theory may be extended to include contact catalysts is worth serious consideration. Examples of a close relationship between catalysis and ordinary chemical reactions are not difficult to find. Thus, hydrogen peroxide reduces manganese dioxide to manganous ion and lead dioxide to plumbous ion in acid solution, oxidizes manganous hydroxide to the dioxide and plumbite ion to plumbate ion or lead dioxide in alkaline solution, and is catalytically decomposed by manganese dioxide and lead dioxide under intermediate conditions. Such a relationship seems to be more than a mere coincidence.

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[6] The electrometric force of half cells corresponding to the various couples furnishes a convenient method of arranging the couples in order in an oxidation-reduction series, and is directly related to the decrease in free energy of the reaction O + hydrogen = R + water. The range in which hydrogen peroxide catalysts may be expected to be found is approximately 0.5 volts above and below the oxygen potential, that is, 1.2 ± 0.5 volts at molal concentration of hydrogen ion, and correspondingly lower values at lower acid concentrations.

This method of choosing catalysts can, of course, be used for any reactions for which the necessary free-energy data are even approximately known. For the present, it is likely to be most useful in oxidation-reduction reactions, since in this field there is little difficulty in selecting two possible forms of the catalyst, and the necessary free-energy data are usually available or can be determined. As an illustration it may be mentioned that several years ago the suggestion was made by one of the authors that reactions involving chlorine were most likely to be catalyzed by couples whose potentials were not too far removed from that of the chlorine electrode. The reaction $ClO_3^- + 5Cl^- + 6H^+ = 3Cl_2 + 3H_2O$ and the reverse reaction are very slow in dilute solution even at 90°, as shown by Olson in his investigation of this equilibrium.[7] To hasten the approach to equilibrium the following couples were selected for trial: manganic-manganous, cobaltic-cobaltous, and nickelic-nickelous. Olson found that the reactions were accelerated by the introduction of a small amount of a manganous, cobaltous or nickelous salt, and used the manganous catalyst in his experiments. In this case some solid manganese dioxide separated, but it is certain that the homogeneous cobalt or nickel catalyst would also have been satisfactory.

Methods of Analysis

The concentrations of the various stock solutions were determined as follows. Bromide solutions were analyzed gravimetrically by weighing silver bromide. Sodium carbonate was the reference substance for acids and alkali solutions, and sodium oxalate for permanganate. Hydrogen peroxide solutions were determined by titration with permanganate. The permanganate solution was also used in standardizing thiosulfate; this iodimetric method gave results reproducible within 0.1%. Bromine in the absence of peroxide was determined iodimetrically with thiosulfate. The potassium iodide used was free from alkali and iodate.

The initial concentrations of the various substances in a reaction mixture were determined from the volumes and concentrations of the stock solutions taken and the total volume of the reaction mixture. The later concentrations of bromide and acid during the reaction were calculated from the change in the bromine content by means of either Reaction 1 or 2.

The concentration of bromine in each sample withdrawn for analysis was determined by extracting it completely and as rapidly as possible with carbon tetrachloride, adding the extracts to a solution (preferably faintly acid) of potassium iodide in a glass-stoppered flask, and titrating the liberated iodine with thiosulfate (0.02 *N* or 0.10 *N*). Loss of bromine during the transfer was inappreciable, provided that the short stem of the separat-

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[7] Olson, THIS JOURNAL, **42**, 896 (1920). On p. 899 in the 6th last line the word *chloride* is a misprint for *chlorine*.

ing funnel, which was ground at any angle just below the stopcock, was washed out at once with a jet of carbon tetrachloride. Two to four extractions with small portions of carbon tetrachloride were usually sufficient, but when the concentrations of bromide and bromine were high, as many as 8 or 10 extractions were necessary.

The success of this method depends on the fact that the liberation of bromine by Reaction 1 is slow in dilute solutions at low temperatures. This error was found to be in general negligible or small when the portion of solution taken for analysis was diluted two or three fold by adding it to ice-cold distilled water in the separating funnel. The most rapid reactions studied were encountered in the few experiments on Reaction 2 at low concentrations of acid and bromide; in this case the sample was added to cold dil. sulfuric acid, since the speed of this reaction is not altered by dilution alone, but is decreased by the acid.

Immediately after removal of the bromine the hydrogen peroxide was determined in the same sample. The presence of bromide interferes with the usual permanganate titration. In dilute acid solution the peroxide-permanganate reaction is much faster than the bromide-permanganate reaction, but only an approximate result can be obtained by direct titration. Towards the end of the titration bromine is liberated and the pink permanganate color finally obtained fades quickly. The following method of analysis, however, was found to give satisfactory results. It consists in the use of excess of permanganate and the iodimetric determination of the excess oxidizing agent,—permanganate and bromine.

Procedure for the Determination of Peroxide in the Presence of Bromide.—To the aqueous solution, free from bromine, add enough water and sulfuric acid to make the volume about 150 cc. and the acid concentration 0.3 to 0.5 *N*; than add immediately, and rather rapidly, potassium permanganate until a distinct pink color remains for 2 or 3 seconds. (An excess of 1 to 3 cc. of 0.1 *N* potassium permanganate solution is recommended.) Stir the solution vigorously, add a moderate excess of potassium iodide, and after waiting for a short time (but not longer than 1 minute) titrate the liberated iodine with thiosulfate solution.

If acid is not already present it must be added before the permanganate since, otherwise, the mixture would become alkaline during the reaction, manganese dioxide would be formed instead of manganous ion, and some hydrogen peroxide might be catalytically decomposed. The solution is stirred in order to facilitate the escape of oxygen.

The results of a series of consecutive analyses of known hydrogen peroxide solutions are given in Table I. In each experiment 15 cc. of hydrogen peroxide solution was used; the equivalent volume of 0.1 *N* potassium permanganate, obtained by direct titration (in the absence of bromide), is shown in the second column. The corresponding volume determined by the new method is shown in the second last column, and the percentage difference in the final column.

TABLE I

DETERMINATION OF PEROXIDE IN THE PRESENCE OF BROMIDE

No.	Volumes used		Analytical data			
	H_2O_2 = cc. of 0.1 *N* $KMnO_4$	Cc. of *N* KBr	0.1 *N* $KMnO_4$ Cc.	0.1 *N* Thio. Cc.	Result Cc.	Difference %
1	24.51	0.0	26.71	2.13	24.58	+0.28
2		0.0	27.73	3.29	24.44	— .28
3		0.0	28.04	3.47	24.57	+ .24
4		0.0	29.82	5.21	24.61	+ .41
5	24.84	0.0	25.34	0.58	24.76	— .32
6		0.3	25.86	1.05	24.81	— .12
7		0.5	25.88	1.00	24.88	+ .16
8		1.0	25.84	0.98	24.86	+ .08
9		2.0	25.76	0.98	24.78	— .23
10		5.0	25.85	0.96	24.89	+ .20

From these results and others not recorded we have concluded that the method is accurate to within 0.2 or 0.3%.

The results would be low if the dissolved oxygen, which supersaturates the solution, oxidized iodide to iodine. This reaction is slow and the error is negligible when the thiosulfate titration is completed within 2 or 3 minutes after the addition of the potassium iodide. The titration was not begun at once since some thiosulfate might be oxidized to sulfate if any oxidizing agent other than iodine were still present, thus giving rise to a positive error. In some of the experiments in which a large excess of potassium permanganate was used high results were obtained, as in No. 4.

In a number of other analyses the order of mixing the reagents was changed and the sample was added to the acidified potassium permanganate solution: the results were practically the same as in the regular procedure.

Any error in the bromine determination which is due to either formation of bromine by Reaction 1 or disappearance of bromine by Reaction 2 (during the analysis) would cause a corresponding negative error in the peroxide determination. Catalytic decomposition of hydrogen peroxide during this analysis would produce an additional error in the same direction.

Rate Measurements at the Steady State

In a number of experiments similar to those represented in Fig. 1, the specific reaction rate, k, in the rate equation

$$\frac{-\mathrm{d}(H_2O_2)}{\mathrm{d}t} = k(H_2O_2) \tag{6}$$

corresponding to a first order reaction with respect to hydrogen peroxide, was calculated. During the formation of bromine, Reaction 1, k increased gradually, and during Reaction 2, k decreased rapidly; but in each case k approached a definite value at the steady state.

The experiments presented in Table III were performed at 25° in a thermostat in a dark-room to test the validity of Equation 6 at the steady state. In order to allow the steady state to be practically attained no measurements were made until 2 or 3 hours had elapsed. The constancy or lack of constancy of the bromine analyses in the first samples withdrawn then served as a measure of the distance from the steady state. Values of k were usually computed by substituting in the integrated equation, $k = \frac{2.30}{t-t_0} \log C_0/C$, where C_0 was taken as the first of the series of concentrations measured after the steady state had been approximately reached. The value of k may also be determined by plotting $\log C$ against t, and multiplying the slope $\left(\frac{\mathrm{d} \log C}{\mathrm{d}t}\right)$ of the resulting straight line by 2.30.

Blank experiments under similar conditions with solutions of hydrogen peroxide in dilute solutions of sulfuric acid showed that the rate of decomposition was negligible in comparison with the catalyzed reaction. Thus in 5 days there was not more than 2% decomposition in a 0.08 M hydrogen peroxide solution in 0.1 N sulfuric acid.

The detailed results of one experiment are given below, to illustrate the method of computing the specific reaction rate, and to demonstrate that the reaction is first order in respect to hydrogen peroxide.

Table II

A Rate Experiment at the Steady State

Measurements were begun 120 minutes after mixing solutions.

Steady-state concentrations: Bromine, 2.8×10^{-5} M; Potassium Bromide, 0.070 M; Sulfuric Acid, 0.0835 N; Hydrogen Peroxide, See Table.

$t-t_0$	Vol. of 0.0966 N $KMnO_4$	(H_2O_2)	$k \times 10^4$
0	16.68	0.0805	..
237	16.12	.0780	1.44
295	16.09	.0770	1.22
1420	14.00	.0676	1.23
2615	12.12	.0586	1.22
2745	11.92	.0576	1.22
4300	9.82	.0475	1.23

The average of the values of k given in the fourth column, excluding the first one, is 1.22×10^{-4}. This agrees exactly with the value obtained from a $\log C-t$ plot. The constancy of the first order constant, observed in this case and in all other similar experiments (which need not be given in detail), demonstrates that the reaction is accurately first order in respect to hydrogen peroxide. Since the two methods of calculation give the same results, they were used interchangeably in the following determinations.

The results of a number of determinations of the steady-state rate are summarized in the first 10 columns of Table III. The initial concentrations of acid and bromide are given in Cols. 2 and 3. The initial concentration of bromine was in all cases zero. In Cols. 4 and 5, are listed the acid and bromide concentrations, corrected for the formation of bromine measured at the steady state. The first order constants, recorded in the tenth column, were computed by one or the other of the two methods described in the preceding paragraphs. The ninth column gives the concentrations of peroxide at which the steady-state measurements were begun and ended. Experiments in which pure peroxide was used are marked with an asterisk, in all others a 3% commercial solution was used. Low concentrations of peroxide, as in Expts. 4, 7, 12 and 13 rendered the peroxide determinations, and therefore the rate constants, inaccurate. The experiments are arranged in order of increasing acid. All concentrations listed are molal; the acid concentration is molal in respect to hydrogen

TABLE III

RATE MEASUREMENTS AT THE STEADY STATE

	Initial concns.		Steady-state concns.								
No.	Acid	Bromide	Acid	Bromide	Bromine found	Tribromide calc.	Bromine calc.	Peroxide	$k \times 10^4$	$K = \frac{k}{(H^+)\ (Br^-)}$	$R = \frac{(Br_2)}{(H^+)^2\ (Br^-)^2}$
1	0.130	0.100	0.129	0.099	0.00008	0.00005	0.00003	0.16–0.06	2.30	0.0180	0.20
2	0.1465	.1472	0.1462	.1469	.00018	.000127	.000053	.14–0.08*	3.75	.0174	.12
3	0.168	.199	0.166	.197	.00086	.00046	.00020	.08–0.02	5.26	.0159	.193
4	0.167	.050	0.167	.050	.000029	.000013	.000016	.02–0.01*	1.67	.0200	.23
5	0.257	.050	0.257	.050	.000112	.000050	.000062	.17–0.09	2.10	.0163	.38
6	0.257	.100	0.256	.099	.000354	.000218	.000135	.16–0.06	4.20	.0164	.210
7	0.417	.020	0.417	.020	.000020	.000005	.000015	.02–0.01*	1.41	.0169	.22
8	0.527	.100	0.526	.099	.00140	.00087	.00053	.34–0.04	7.42	.0143	.196
9	0.835	.010	0.835	.010	.000028	.000004	.000024	.08–0.05	1.17	.0140	.35
10	0.835	.020	0.835	.020	.000086	.000021	.000065	.16–0.05*	2.41	.0144	.23
11	0.977	.1962	0.947	.1559	.0148	.0106	.0042	.14–0.05*	21.5	.0146	.191
12	1.670	.050	1.664	.044	.00323	.00133	.00190	.10–0.00*	9.96	.0140	.364
13	2.820	.050	2.805	.033	.00735	.00256	.00479	.01–0.00*	13.3	.0144	.565

ion, normal in respect to sulfuric acid. In the calculation of K (second last column) the acid and bromide were assumed to be completely ionized. It was determined by trial and by plotting that the rate of disappearance of peroxide could be expressed by the following differential equation.

$$\frac{-d(H_2O_2)}{dt} = K(H_2O_2)(H^+)(Br^-) \qquad (7)$$

There is no deviation from this law produced by a 30-fold variation of the bromide concentration. The relation holds with reasonable accuracy for changes in acid concentration between 3.0 N and 0.2 M. Below 0.2 N acid the value of K increases as the acid concentration decreases, as may be noticed in the first few values in Table III.[7a] This effect will be discussed in a later paper. The average value of K, taken from Col. 11, neglecting experiments in which the acid concentration was less than 0.2 N, is 0.0140.

The simplest theory for this bromine-bromide catalysis is that there is a single pair of compensating reactions, related to Reactions 1 and 2, the rates of which are equal at the steady state. Since hydrogen peroxide is used up in both of these reactions, the absolute rate of disappearance of peroxide will be twice that calculated for either of the compensating reactions. From the kinetic results summarized by Equation 7 it is accordingly to be expected that the rate of one of these reactions will be represented by the differential equation

$$\frac{-d(H_2O_2)}{dt} = K_1(H_2O_2)(H^+)(Br)^- \qquad (8)$$

where $K_1 = \frac{1}{2}K$ of Equation 7, $= 0.007$.

The most probable product of this third order reaction is believed to be hypobromous acid. If this assumption is made, then the two compensating reactions are,

$$H_2O_2 + H^+ + Br^- = HBrO + H_2O \qquad (9)$$

and

$$H_2O_2 + HBrO = O_2 + H^+ + Br^- \qquad (10)$$

This "kinetic mechanism" for the catalysis (Reactions 9 and 10) is not inconsistent with the "gross mechanism," represented by Reactions 1 and 2. Since the hydrolysis of bromine,

$$Br_2 + H_2O = HBrO + H^+ + Br^- \qquad (11)$$

is a reversible reaction, and equilibrium is reached very rapidly, the concentration of hypobromous acid at any instant may be expressed in terms of bromine, hydrogen ion and bromide ion, and the rate equation for Reaction 10 (and 2) may be given the form:

$$\frac{-d(H_2O_2)}{dt} = \frac{K_2(Br_2)(H_2O_2)}{(H^+)(Br^-)} \qquad (12)$$

At the steady state the absolute rates of Reactions 9 and 10 are equal,

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[7a] The experiment shown in Table II is at even lower acid concentration than that in Expt. 1, Table III. The value of K is 0.0208: that of R 0.280.

and it therefore follows that Equations 8 and 12 may be equated. Then if the ratio of K_I to K_2 be denoted by R,

$$R = K_1/K_2 = \frac{(Br_2)}{(H^+)^2(Br^-)^2} \qquad (13)$$

Expressed in words, this relation requires that the concentration of bromine at the steady state shall be proportional to the square of the product of the concentrations of hydrogen ion and bromide ion, and independent of the peroxide concentration. It should be noted that Equation 13 is not peculiar to the hypobromite mechanism, but may be derived from any assumed mechanism which postulates two and only two slow hydrogen peroxide reactions, one of which is the reverse of the other in respect to hydrogen-ion and the bromine terms. For example, if Reactions 1 and 2 were assumed to be the kinetic mechanism, the same relation would be obtained.

The Determination of the Steady-State Function

When the initial concentrations in a reaction mixture are known and the bromine concentration at the steady state has been determined, the value of the function R, Equation 13, can be calculated. Values of the bromine concentrations, determined after 2 or 3 days, are given in Table III, Col. 6 and Table IV, Col. 7. The necessary corrections for tribromide in equilibrium with the bromine and bromide were made by means of the equilibrium relation at 25° given by Lewis and Randall,[8] which however has not been demonstrated to hold for concentrations of bromide ion above 0.1 M.

$$Br_2 + Br^-; = Br_3^- \quad (Br_3^-) = 16.2\,(Br_2)(Br^-) \qquad (14)$$

The calculated concentrations of tribromide and bromine are given in Tables III and IV. The change in the bromide concentration due to tribromide formation is usually negligible, but the correction has been made wherever necessary, before tabulating the bromide concentrations at the steady state. No attempt was made to correct for the degree of ionization; in other words, the strong electrolytes are considered to be completely ionized.

The calculated values of R = (bromine)/(acid)^2(bromide)^2 are given in the last columns of Tables III and IV. In the latter table, Expts. 1 to 8 belong to a preliminary series at room temperature (about 20°); the mixtures were shielded from the light, though not as carefully as in the later experiments at 25°, and the bromine concentrations were measured after a shorter time—about 20 hours.

For concentrations of sulfuric acid between 0.1 N and N the values of R are practically constant, within the experimental errors. When the bromine concentration is very small, the error in its determination may be large. An examination of the original experimental data showed that

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[8] Lewis and Randall, THIS JOURNAL, **38**, 2348 (1916).

this error was most likely to have been very great in Expts. 1, 2, 4, 5, 7, 9 and 10 of Table III, and the only serious discrepancies are the high values of *R* in 5 and 9 and the low value in 2. Omitting these three results, the average value of *R* at 25° for acid concentrations between 0.1 *N* and 1.0 *N* and bromide concentrations between 0.02 *M* and 0.3 *M* (8 experiments in Table III and No. 10 in Table IV) is 0.208.

TABLE IV

CONCENTRATION MEASUREMENTS AT THE STEADY STATE

	Initial concentrations			Steady-state concentrations					
No.	Bromine	Acid	Bromide	Acid	Bromide	Bromine found	Tri-bromide calc.	Bromine calc.	$R = (Br_2)/(H^+)^2(Br^-)^2$
1	...	0.48	0.10	0.478	0.098	0.000089	0.00055	0.00034	0.156
2	0.037	0.48	.026	0.552	.097	.00139	.00085	.00054	.189
3	...	0.48	.20	0.469	.185	.00545	.0042	.0013	.173
4	0.045	0.48	.110	0.554	.180	.00760	.0057	.0019	.194
5	...	0.48	.240	0.462	.215	.00895	.0070	.0020	.154
6	0.052	0.48	.136	0.559	.205	.01260	.0097	.0029	.217
7	...	0.48	.30	0.441	.252	.01715	.0138	.0034	.182
8	0.042	0.48	.196	0.531	.252	.01845	.0149	.0036	.195
9	...	0.244	.50	0.218	.463	.01303	.01149	.00154	.151
10	...	0.976	.0982	0.968	.0880	.00390	.00229	.00161	.202
11	...	1.464	.0982	1.448	.0773	.00820	.00455	.00365	.290
12	...	1.951	.0491	1.943	.0398	.00390	.00152	.00238	.397
13	...	2.440	.0491	2.428	.0352	.00587	.00212	.00375	.513
14	...	2.928	.0491	2.912	.0302	.00812	.00267	.00545	.702
15	...	3.175	.0245	3.169	.0184	.00302	.00070	.00232	.682
16	...	3.550	.0245	3.543	.0171	.00371	.00080	.00291	.790

The alternately low and high values of *R* in the first 8 experiments of Table IV seem to be due to the fact that the steady state was approached from opposite sides in the odd-numbered and even-numbered experiments, and was not quite reached at 20° in the time allowed—about 20 hours. A temperature correction to 25° would lower the values of *R* a little, while a correction for the possible action of light might raise them a great deal. The average value 0.183 is, therefore, considered to be too low. We have chosen, for the range of acid and bromide concentrations stated above, the value at 25°: $R = 0.20$.

The effect of greatly increasing the bromide concentration seems to be the lowering of the value of *R*: compare the single experiment at 0.5 *M* bromide, No. 9, Table IV. However, in this case the calculated bromine concentration is only 0.116 of the measured concentration, and the low value of *R* may be due to an error in the correction for tribromide.

When the sulfuric acid concentration is greater than normal the values of *R* increase rapidly with increasing acid concentration: compare Expts. 11 to 16, Table IV, and 12 and 13, Table III. It seems likely that this increase is due to some specific effect of hydrogen ion or sulfate ion and not to a general "salt effect," since the presence of potassium bromide does not tend to increase R. In case the relation $R = K_1/K_2$ still holds in this region, then the increase of R is due to a decrease of K_2, Equation 12, since K and therefore presumably K_1 remain constant at these high acid concentrations (cf. Expts. 12 and 13, Table III). On the other hand, the assumption upon which the derivation of Equation 13 was based may not hold at high acid concentrations, and some reactions other than the single pair of compensating reactions may be responsible for the increase of the bromine concentration and the consequent increase of R. For example, by analogy with the iodine-iodate reaction it is not improbable that the rate of formation of bromate, Reaction 4, becomes appreciable at high acid concentration, and that bromate, bromide and acid then react rapidly to form bromine; the result would produce a distinct increase in the concentration of bromine at the steady state, but only a very small change in the rate of disappearance of hydrogen peroxide, Equation 7. The experimental material in the remainder of the paper presents results obtained in the range of sulfuric acid and bromide concentrations in which both R and K have been shown to be practically constant.

That exposure to *light* produced a great decrease in the value of R was noticed in the preliminary work. The results of a few experiments at room temperature (about 20°) are given in Table V. The conditions in Expts. 1 to 8, Table IV, were more nearly like those in No. 2 than those in Nos. 3, 4 or 1a.

TABLE V

EFFECT OF LIGHT

Initial concentrations: H_2SO_4, 0.75 N: KBr, 0.15 M: Br_2, 0.0 M

	Steady-state concentrations					
No.	Bromine found	Bromine calc.	Bromide	Acid	R	Experimental conditions
1	0.0005	0.00015	0.149	0.749	0.016	Direct light (not sunlight) for 6 hours
2	.0065	.00202	.137	.737	.195	Almost completely shielded, 24 hours
3	.0073	.00227	.135	.735	.232	In dark, 24 hours
4	.0070	.00218	.136	.736	.220	In dark, 24 hours
1a	.0070	.00218	.136	.736	.220	After (1), in dark 24 hours
2a	.0003	.00009	.149	.750	.008	After (2), in sunlight, 6 hours

From the relation $R = K_1/K_2$ it follows that the chief effect of the light is to increase greatly the speed of Reaction 2 relative to that of Reaction 1. For any given constant illumination a steady state will be reached, which depends on the intensity of the light. If the speed of Reaction 1 is not appreciably altered by light, then in a given reaction mixture at the steady state the specific reaction rate, Equation 6 (or 7), will be independent of the intensity of the illumination (provided that this remains constant) and therefore the same as in the dark. This point has not been tested experimentally.

To determine the *effect of temperature*, the experiments shown in Table VI were performed in the dark at 39.4° (Expts. 1–3) and at 0° (Expts.

4–6) and the values of *R* calculated. The values of $(Br_3^-)/(Br_2)(Br^-)$ used in correcting for tribromide, 15.1 at 39.4° and 19.6 at 0°, were based on the data given by Linhart[9] for the temperature range 0° to 32.6°.

TABLE VI

EFFECT OF TEMPERATURE

No.	Initial concentrations Acid	Bromide	Steady-state concentrations Acid	Bromide	Bromine found	Tribromide calc.	Bromine calc.	$R = (Br_2)/(H^+)^2(Br^-)^2$
1	0.977	0.0982	0.972	0.0920	0.00242	0.00141	0.00101	0.126
2	0.732	.1963	0.717	.1760	.00743	.00540	.00203	.127
3	0.488	.245	0.475	.227	.00649	.00502	.00147	.126
4	1.22	.1228	1.19	.0825	.0154	.0095	.00590	.610
5	0.732	.1963	0.695	.1461	.0183	.0136	.00471	.454
6	0.488	.2452	0.455	.1991	.0165	.0131	.00337	.410

At the higher temperature the values of *R* do not vary when the acid concentration at the steady state is increased from approximately 0.5 *N* to 1 *N*, while at 0° the increase of *R* is rapid, in this range. As already pointed out, the values of *R* show a similar increase at 25° only when the acid concentration is above normal. The decrease of *R* with increasing temperature is less rapid above 25° than at lower temperatures.

Rate Measurements at a Distance From the Steady State

The remaining experiments described in this paper were undertaken to determine whether the rate of formation of bromine (Reaction 1) is represented by the differential equation (8), where $K_1 = 0.0070$ at 25°; and also whether the rate of disappearance of bromine (Reaction 2) is represented by Equation 12, where $K_2 = K_1/R = 0.007/0.20 = 0.035$ at 25°.

In the case of Reaction 1 (when no bromine is present) the initial rate of disappearance of peroxide is exactly equal to the initial rate of formation of bromine. In other words the effect of Reaction 2 is negligible. The rate of formation of bromine at $t = 0$ may be determined graphically from a plot of bromine concentration against time, and the first order constant k_1 may then be calculated when the initial concentration of hydrogen peroxide is known. Instead of using this method we found it more convenient to plot log $[(H_2O_2)\text{initial} - (Br_2)]$ against time and determine k_1 directly from the tangent at $t = 0$. Values of K_1 were then calculated from the relation $K_1 = k_1/(\text{acid})(\text{bromide})$. The results are shown in Table VIII.

In the first three experiments, which were probably not very accurate, the values of K_1, 0.0054 to 0.0085, did not differ greatly from the predicted value, 0.0070. This method, used in determining k_1, is open to the objection that it provides no way of detecting an error due to any initial disturbance.

Accordingly, a second method was developed and tested in two more

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[9] Linhart, THIS JOURNAL, **40**, 158 (1918).

accurate experiments. It requires the measurements of both the peroxide and bromine concentrations and the careful construction of the two concentration-time plots.[10] Equations 15 and 16 follow from the assumption of a single pair of compensating reactions.

$$-\mathrm{d}(H_2O_2)/\mathrm{d}t = K_1(H_2O_2)(H^+)(Br^-) + K_2(H_2O_2)(Br_2)/(H^+)(Br^-) \qquad (15)$$

$$\mathrm{d}(Br_2)/\mathrm{d}t = K_1(H_2O_2)(H^+)(Br^-) - K_2(H_2O_2)(Br_2)/(H^+)(Br^-) \qquad (16)$$

By addition $-\mathrm{d}(H_2O_2)/\mathrm{d}t + \mathrm{d}(Br_2)/\mathrm{d}t = 2K_1(H_2O_2)(H^+)(Br^-)$ (17)

It is evident that K_1 may be determined[11] directly from Equation 17 when, at any instant, the two rates and the concentrations of peroxide, acid and bromide are known. The rates were determined by drawing tangents to the concentration-time plots. The final results in two experiments are shown in the last column of Table VIII.

TABLE VII

DETAILS OF EXPERIMENT 5, TABLE VIII

	Concentrations					Rates × 10^4			
$t-t_0$ min.	Bromine	H_2O_2	½H_2SO_4	Bromide	Bromide Corr.	$\frac{-\mathrm{d}(H_2O_2)}{\mathrm{d}t}$	$\frac{\mathrm{d}(Br_2)}{\mathrm{d}t}$	$\frac{-\mathrm{d}(H_2O_2)}{\mathrm{d}t} + \frac{\mathrm{d}(Br_2)}{\mathrm{d}t}$	$2K_1$
0	0	0.1377	0.977	0.196	0.196	2.0	2.0	4.0	0.0151
10	0.0020	.1354	.972	.191	.190	2.1	1.7	3.8	.0152
20	.0038	.1333	.969	.188	.185	2.2	1.4	3.6	.0150
50	.0071	.1266	.963	.182	.177	2.2	1.0	3.2	.0148
100	.0105	.1156	.956	.175	.167	2.2	0.3	2.5	.0136
150	.0122	.1142	.953	.172	.163	2.1	0.3	2.4	.0148
200	.0132	.0932	.951	.170	.160	2.0	0.2	2.2	.0154

TABLE VIII

SUMMARY OF DETERMINATIONS OF K_1

	Initial concentrations					
No.	H_2O_2	½H_2SO_4	Bromide	k_1	K_1 Method I	K_1 Method II
1	0.0420	2.12	0.10	0.00115	0.0054	....
2	.0418	1.06	.10	.00071	.0067	....
3	.0837	1.13	.69	.0067	.0085	....
4	.0757	1.50	.372	.00372	.0067	0.0071
5	.1377	0.977	.1962	.00146	.0076	0.0074

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[10] The following method was used to detect any serious error in one of the measurements of bromine or hydrogen peroxide in samples from the reaction mixture. The measured concentrations of Br_2 and H_2O_2 in moles per liter were plotted as ordinates against time as abscissas. Then the sum, S = concentration of $H_2O_2 + \Delta Br_2$ (the change in the bromine concentration from zero time), was calculated, plotted against time, and a smooth curve drawn. At small values of time this curve approached a horizontal straight line, and an accurate determination of the initial H_2O_2 concentration was therefore possible. Since errors in the determination of Br_2 and H_2O_2 (due to the progress of Reaction 1) tend to compensate each other when this sum is taken, the S curve can be drawn more accurately than either the Br_2 or the H_2O_2 curve considered by itself. Finally, smooth Br_2 and H_2O_2 curves were drawn, which were consistent with the S curve and its departure from the horizontal line corresponding to the initial peroxide concentration.

[11] Compare Bray, *J. Phys. Chem.*, 9, 573 (1905).

The detailed results in the case of Expt. 5 are given in Table VII. The concentrations of bromine (total) and peroxide in the second and third columns were taken from smooth curves constructed as explained in detail in Ref. 10 (see p. 1266). The difference between the bromide concentration in Cols. 5 and 6 is the tribromide concentration. It is to be noted that the measurements were continued until the ratio of the rates of the two compensating reactions had decreased from infinity at $t = 0$ to 1.1/0.9 at $t = 200$ minutes. The average value of K_1 from this experiment, 0.0074, is given in the last column of Table VIII. The initial value of K_1, obtained either by Method I or from the first values in Table VII, is only slightly higher, 0.0076. In a similar experiment, No. 4, the average value of K_1 is 0.0071, while the initial value is slightly lower, 0.0067.

The following conclusions may, therefore, be drawn. There is no initial disturbance in this reaction and no trend in the values of K_1 as the reaction proceeds. In sulfuric acid solutions at 25° the rate of Reaction 1 is represented by the differential equation, $-\mathrm{d}(H_2O_2)/\mathrm{d}t = K_1(H_2O_2)(H^+)(Br^-)$, where $K_1 = 0.0070$ (when the acid and bromide are assumed to be completely ionized). Finally, this reaction accounts for half the peroxide decomposed at the steady state.

The initial rate of Reaction 2 is so rapid that no attempt was made to measure it. However, a method similar to the second one used in studying Reaction 1 was found to be satisfactory. As before, both bromine and peroxide measurements were made, and their rates of disappearance determined graphically. The differential equations corresponding to Nos. 15, 16 and 17 are

$$-\mathrm{d}(H_2O_2)/\mathrm{d}t = K_2(H_2O_2)(Br_2)/(H^+)(Br^-) + K_1(H_2O_2)(H^+)(Br^-) \qquad (18)$$

$$-\mathrm{d}(Br_2)/\mathrm{d}t = K_2(H_2O_2)(Br_2)/(H^+)(Br^-) - K_1(H_2O_2)(H^+)(Br^-) \qquad (19)$$

By addition, $-\mathrm{d}(H_2O_2)/\mathrm{d}t - \mathrm{d}(Br_2)/\mathrm{d}t = 2K_2(H_2O_2)(Br_2)/(H^+)(Br^-)$ (20)

From the two rates and the corresponding concentrations at a given time, $2K_2$ was calculated by means of Equation 20. It is to be noted that the rate term, $\mathrm{d}(Br_2)/\mathrm{d}t$, should be written $\mathrm{d}(\Sigma Br_2)/\mathrm{d}t$ in the above and all earlier equations, and that in determining its value no correction was made for tribromide. On the other hand this correction was made in determining the concentrations of bromine and bromide to be substituted in the right hand member of Equation 20.

A preliminary experiment yielded values of K_2 of the right order of magnitude, but on account of the low concentration of acid used the rate was too great to permit of accurate measurements. Two other experiments at higher acid concentration were then carefully performed. The detailed results are shown in Tables IX and X, respectively, and the method of constructing the concentration-time plots is shown for the first experiment in Fig. 2.

The points in the upper part of the figure represent the sum, measured hydrogen peroxide concentration + decrease in measured bromine concentration. Curve *S* is seen to be nearly linear, and its extrapolation to zero time was used to determine the initial concentration of hydrogen peroxide. If Reaction 2 had taken place alone, *S* would have been a horizontal line, and its observed departure from this horizontal line is due to Reaction 1. Curves I and II in the lower part of the figure represent the decrease in hydrogen peroxide and total bromine, respectively. These two curves are initially coincident, and the later differences correspond exactly to the departure of Curve *S* from the horizontal line. The smooth curves agree well with the experimental data except in the first 10 minutes, when the high speed of reaction (and accompanying evolution of oxygen gas) prevented accurate measurements.

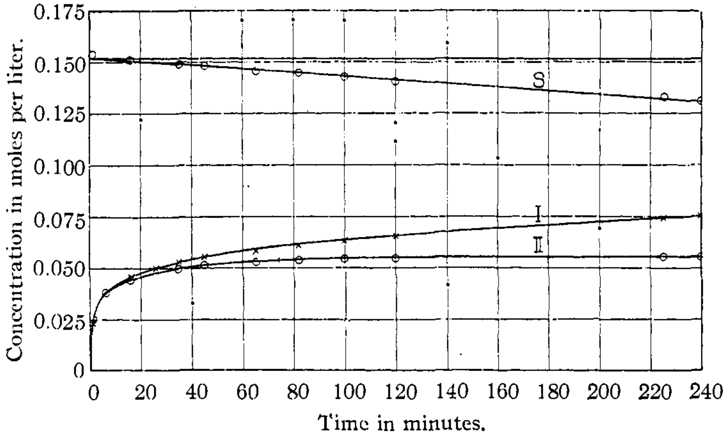

Fig. 2.—Cf. Table IX.

An exactly similar figure was obtained when the experimental data in the second experiment (Table X) were plotted. In this case it was necessary to decrease the calculated initial bromine concentration, as shown in

TABLE IX

DETERMINATION OF K_2, EXPT. 1

COMPARE FIG. 2

	Concentrations						Rates × 10^4			
$t-t_0$	Bromine	H_2O_2	½H_2SO_4	Bromide	Bromine calc.	Bromide corr.	$\frac{-d(H_2O_2)}{dt}$	$\frac{-d(Br_2)}{dt}$	$\frac{-d(H_2O_2)/dt}{-d(Br_2)/dt}$	$2K_2$
0	0.0572	0.152	0.380	0.00955	0.0528	0.0051	...	....	...	...
5	.0204	.114	.454	.0833	.0144	.0673	15.5	14.5	30.0	0.056
10	.0160	.109	.462	.0911	.0073	.0832	6.5	6.4	12.9	.062
15	.0129	.106	.469	.0981	.0054	.0904	4.6	4.4	9.0	.067
25	.0096	.102	.475	.1047	.0037	.988	3.75	2.55	6.3	.072
50	.0055	.096	.483	.1129	.0020	.1094	1.75	0.90	2.65	.073
75	.0040	.092	.486	.1159	.0014	.1133	1.50	0.49	1.99	.085
100	.0032	.088	.488	.1175	.00112	.1153	1.20	0.20	1.40	.080
150	.0023	.084	.490	.1193	.00078	.1178	0.80	0.062	0.86	.076

TABLE X

DETERMINATION OF K_2, EXPT. 2

	Concentrations								Rates × 10^4			
$t - t_0$	Bromine measured	H_2O_2 measured	H_2O_2	Bromine	Bromide	Bromine calc.	Bromide corr.	$\frac{1}{2}H_2SO_4$	$-d(H_2O_2)/dt$	$-d(Br_2)/dt$	$-d(H_2O_2)dt$ $-d(Br_2)/dt$	$2K_2$
0	(0.0804)	0.1137	0.1137	0.0740	0.0098	....	....	0.585	...	....	....	...
1	.0542	.0889	....	....	....	....	....	...	...	....	....	...
8	.0408	.0846	.0783	.0380	.0818	0.0188	0.0626	.643	10.3	(10.3)	(21)	(0.057)
18	.0320	.0703	.0707	.0320	.0938	.0144	.0756	.672	6.1	6.0	12.1	.060
27	.0287	.0658	.0659	.0287	.1004	.0124	.0830	.676	4.6	4.2	8.8	.061
35	.0260	.0621	.0627	.0259	.106	.105	.0910	.681	3.6	3.0	6.6	.062
45	.0236	.0603	....	....	....	....	....	...	...	....	....	...
61	.0209	.0553	.0554	.0209	.116	.0080	.0980	.691	2.1	1.4	3.5	.056
78	.0190	.0532	....	....	....	....	....	...	...	...	....	...
97	.0174	.0494	.0497	.0174	.123	.0062	.112	.698	1.32	0.72	2.04	.052
134	.0149	.0452	.0455	.0147	.128	.0050	.118	.703	1.14	0.49	1.63	.061
146	.0142	.0443	....	....	....	....	....	...	...	...	....	....
171	.0134	.0406	.0412	.0134	.131	.0045	.122	.706	1.08	0.26	1.34	.062

Table X, since otherwise the ΔBr_2 curve would have been above the ΔH_2O_2 curve for the first 70 minutes, which was impossible. This correction is in the direction corresponding to loss of bromine from the reaction vessel by volatilization, but the discrepancy was probably mainly due to experimental error in the initial bromine determination. If any attempt had been made in the first experiment to correct for volatilization, the result would have been a lowering of the ΔBr_2 curve in Fig. 2, but this would have caused only a small increase in the value of K_2.

In Table X the experimental data actually obtained are shown in the second and third columns, while the corresponding data obtained from a plot similar to Fig. 2 are given in the next two columns.

Each of the values of the rates $-d(H_2O_2)/dt$ and $-d(Br_2)/dt$ shown in these tables is the average of several independent estimates of the slope of the tangent to the corresponding curve. The values tabulated were chosen before any calculation of $2K_2$ was undertaken and no attempt was made to smooth out the results, as by plotting the rates or their ratio against time. Consequently, the possible error in any one value of $2K_2$ may be as great as 15 or 20%. (The corresponding error in the determination of $2K_1$, Table VII, was much smaller, owing to the slower rate.) Since the ratio of the two rates does not differ from unity by more than a few per cent. in the first 15 minutes, it is evident that the correction due to Reaction 1 is very small in this time interval. Later this correction increases rapidly, especially in the first experiment; and the rate of Reaction 1 is approximately half that of Reaction 2 at 75 minutes, in the first experiment, and 150 minutes in the second.

During this progress from Reaction 2 towards the steady state there is no evidence of a trend in the values of $2K_2$ shown in the last column of the tables. K_2 was estimated to be 0.035 and 0.030, respectively, in the two experiments. These results are in good agreement with the predicted value, 0.035.

The experimental results presented in this section are not sufficient in themselves to demonstrate the validity of differential equations 8 to 12; but when considered in connection with the rate measurements at the steady state and the constancy of the steady-state function in sulfuric acid solutions between 0.1 N and N at 25°, there can be no doubt that the rates of Reactions 1 and 2 are represented by these equations. It may also be concluded that the catalysis is completely accounted for by the assumption that Reactions 1 and 2 are taking place independently at the steady state.

The fact that this simple result is obtained is an argument in favor of the hypobromous acid mechanism represented by Equations 9 and 10. Moreover, the concentration of hypobromous acid at any instant may be calculated from the concentrations of bromine, bromide and acid by means of the equilibrium function[12] $(H^+)(Br^-)(HBrO)/(Br_2) = 5.2 \times 10^{-9}$ at 25°. The complicated equation (12) for Reaction 2 can, therefore, be replaced by the simple bimolecular expression, $-d(H_2O_2)/dt = K_3(H_2O_2)(HBrO)$, where, at 25°, $K_3 = K_2/5.2 \times 10^{-9} = 6.7 \times 10^6$. This specific reaction rate is very large, and the concentration of hypobromous acid at any instant is correspondingly very small. For example, in Expt. 6, Table III, at the steady state it is 2.8×10^{-11} moles per liter; while in the rapid-rate experiment presented in Table IX it is 1.4×10^{-7} M at $t = 20°$, and decreases rapidly as the reaction proceeds.

Our use of sulfuric acid and the assumption that it is completely ionized are open to criticism. The product $(H^+)(Br^-)$ is present in each of the four functions investigated, and in our mixtures containing sulfuric acid it is impossible to estimate from existing data either the concentration or the activity-product. For this reason we are now using as acid hydrobromic acid or perchloric acid, and are extending the measurements to more dilute solutions. We expect to determine the extent to which "activities" rather than concentrations must be used in interpreting the results.[13] Experiments not included in this paper indicate that the activity product $a_{H^+} \times a_{Br^-}$ is preferable to the concentration product.

Summary

1. We have shown that in acid solution hydrogen peroxide oxidizes bromide to bromine, and reduces bromine to bromide, and that these two reactions can take place independently in the same solution. When the rates of these two compensating reactions are equal, the net result is the catalytic decomposition of hydrogen peroxide. This constitutes a "steady

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[12] Bray and Connolly, THIS JOURNAL, **33**, 1487 (1911).

[13] Compare Brönsted, *Z. physik. Chem.*, **102**, 187 (1922).

state," in which the concentrations of bromine, bromide, and acid remain constant in a single experiment.

2. At the steady state the rate of decomposition of the peroxide in the dark at 25° in sulfuric acid solutions above 0.2 N is represented by (Equation 7), $-d(H_2O_2)/dt = 0.0140 (H_2O_2)(\text{acid})(\text{bromide})$.

3. At the steady state the following functional relation has been demonstrated to hold for sulfuric acid concentrations below normal (Equation 13): $R = (Br_2)/(\text{acid})^2(\text{bromide})^2 = 0.20$. The value of R increases slightly with decreasing temperature, but decreases to a very small value when the reaction mixture is exposed to sunlight.

4. Definite evidence that the catalysis is completely accounted for by the two compensating reactions is obtained by measuring the rate of each at a distance from the steady state. The results obtained agree closely with those predicted from the steady-state data and the assumption of a kinetic (or rate-determining) mechanism involving hypobromous acid (Equations 8 to 12). The ratio of the specific reaction rates of the two reactions is equal to R, and at the steady state each reaction accounts for half the peroxide decomposed.

5. The possibility of choosing catalysts by means of free-energy data is discussed and some examples are given.

6. A method is described for the volumetric determination of hydrogen peroxide in the presence of bromide.

BERKELEY, CALIFORNIA

NOTES

The Collodion Membrane for Liquid Junctions.—Investigators in the measurement of hydrogen-ion concentrations by the electromotive-force method have greatly felt the need of an effective simple device which will prevent the mechanical intermixing of one liquid into another at the liquid junctions in the system being measured. In this respect, the authors believe that they have made an improvement by the use of a collodion membrane. It should be borne in mind, however, that this type of junction is applicable only to those solutions to whose ions the collodion membrane is equally permeable, because if the membrane is not equally permeable, then, as shown by the work of Loeb,[1] the effect known as the Donnan equilibrium leads to high potential values at the membrane.

The collodion membrane is made simply by dipping the siphon tube of the electrode vessel several times into a small test-tube of collodion (18 g. of ether per oz. (31 g.); 27% alcohol, U. S. P. IX) and exposing it to the air until a solid membrane is formed at the end of the siphon tube. It is best to expose the collodion solution at first to the air for a short

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[1] Loeb, "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., New York. 1922. Chap. VIII.