[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RATE OF OXIDATION OF HYDROGEN PEROXIDE BY BROMINE AND ITS RELATION TO THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN A BROMINE-BROMIDE SOLUTION

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Introduction

The catalytic decomposition of hydrogen peroxide in a hydrobromic acid solution has been shown to be due to the simultaneous oxidation and reduction of hydrogen peroxide by bromine and by bromide ion, respectively.[1] The rate of decomposition, at constant ionic strength, is given by the following equation

$$-d(H_2O_2)/dt = K(H_2O_2)(Br^-)(H^+) \qquad (1)$$

Similarly, the steady-state bromine concentration may be written as

$$(Br_2) = R/(H^+)^2(Br^-)^2 \qquad (2)$$

The simplest kinetic mechanism consistent with these facts postulates the occurrence of two rate determining reactions, the formation and reduction of hypobromous acid

$$H_2O_2 + Br^- + H^+ = HBrO + H_2O \qquad (3)$$
$$H_2O_2 + HBrO = H^+ + Br^- + O_2 \qquad (4)$$

and a rapid reversible equilibrium, the hydrolysis of bromine.

In agreement with this mechanism it was found[2] that the rate of oxidation of bromide ion by hydrogen peroxide (at a distance from the steady state) can be represented by an equation having the same form as the law of catalysis (Equation 1), but with a constant half as great, $K_1 = K/2$.

It seems probable, therefore, that the rate of reduction of bromine by hydrogen peroxide can be represented, in agreement with the mechanism, by the following equation

$$-d(H_2O_2)/dt = K_2(Br_2)(H_2O_2)/(Br^-)(H^+) \qquad (5)$$

where $K_2 = K/2R$. It is difficult to obtain an accurate measure of this rate. When the bromide and hydrogen ion concentrations are low enough to render the catalytic rate negligible, the rate of the reduction is so rapid at 25° that it practically cannot be measured by any ordinary method. Two measurements were made[3] in an intermediate range, where the rate is fast but measurable, and the catalytic rate is not negligible but can be corrected for by a method involving a series of approximations. Although the results of these two measurements are in agreement with the predic-

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[1] Bray and Livingston, THIS JOURNAL, **45**, 1251 (1923).

[2] (a) Ref. 1, pp. 1265–7, Tables VII and VIII (5 experiments); (b) Livingston and Bray, THIS JOURNAL, **45**, 2052 (1923), Table IV (1 experiment).

[3] Ref. 1, pp. 1268–9, Tables IX and X.

tions based upon the mechanism, they do not constitute a satisfactory *independent* proof of the validity of Equation 5. The purpose of the present paper is to furnish such a proof.

The rate measurements of Balint[4] at 0°, which furnish strong evidence in favor of Equation 5 but were overlooked until after our work was completed, will be discussed later. The objections of Christiansen[5] to our conclusions will also be considered.

Methods

A method for measuring reaction velocities can only be applied when the half time of the reaction is large compared to the time required for mixing the component solutions. The time required for mixing moderately large volumes by simple hand shaking may be as great as one minute. By the use of very small volumes and special apparatus the time can be reduced to less than a second.[6]

Probably the simplest way of obtaining rapid mixing is by means of a flow method. Stewart and Edlund[7] used a flow method of mixing in their study of a bimolecular gas reaction. They estimate that with their apparatus mixing was complete in less than a second. Hartridge and Roughton[8] have made an extensive study of the application of flow methods to the determination of rapid reaction velocities in aqueous solutions. In their apparatus the mixing occurs in a small cylindrical, or conical, chamber into which tangential jets of the component solutions are forced. They followed the course of the reaction either by measuring the absorption spectra of the solution, or by determining the change in its temperature due to the heat of the reaction. They estimate[8b] that their perfected apparatus is capable of measuring the rate of a reaction having a half time as small as one thousandth of a second.

The apparatus described here was designed to measure the rates of reactions having half times of from one-half to six seconds. It is represented schematically in Fig. 1.

The three-liter flasks, A and A', serve as reservoirs for the component solutions. C is the mixing chamber and D the reaction tube. E, E' and E'' are outlets, controlled by the large two-way stopcocks, P and P'. F is a second mixing chamber, which can be placed beneath either outlet E or E'. H is a Bunsen stirrer, driven by an 1800 r.p.m. motor. I is an overflow tube, leading to a collecting vessel; this tube can be converted into a siphon by closing stopcock O. A nitrogen cylinder was connected to tube J through a reducing valve. The nitrogen pressure was further controlled by the mercury

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[4] Balint, *Thesis* (in Hungarian), University of Budapest, **1910**.

[5] Christiansen, (a) *Z. physik. Chem.*, **117**, 453 (1925); (b) *ibid.*, **128**, 430 (1927).

[6] See C. Benedicks, *ibid.*, **70**, 12 (1910).

[7] Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923).

[8] Hartridge and Roughton, (a) *Proc. Roy. Soc. (London)*, **104A**, 376 (1923); (b) *Proc. Camb. Phil. Soc.*, **22**, 426 (1924); (c) see also the recent work of Saal, *Rec. trav. chim.*, **47**, 73 (1928).

regulator, K, and was measured by the open manometer, L The apparatus was constructed entirely of Pyrex glass.

The mixing chamber, C (see detail C, Fig. 1), consists of a "Y" tube made from *flattened* capillary tubing. It is 4.5 cm. long, and has a volume of 0.12 cc. As is indicated in the figure, the flattened capillaries are so arranged that the surface of contact between the two component solutions is as large as possible. This type of mixing chamber, which was suggested by Professor Branch of this department, has the advantage of producing complete mixing at slow as well as at rapid rates of flow, and of having a very small volume. It has the disadvantage of offering a considerable resistance to the flow, and thereby limiting the range of reaction rates which can be measured.[9]

The reaction tube D was made of 0.70 cm. tubing. The volumes of the tube to the ends of E and E′ are 18.04 and 30.9 cc., respectively. The large two-way stopcocks were bored to 0.70 cc. and did not produce a constriction in the tube.

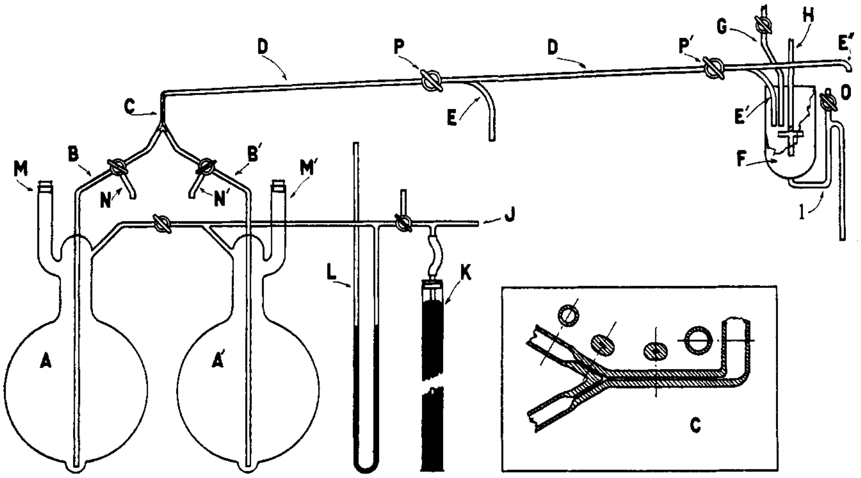

Fig. 1.—Apparatus.

Temperature control was obtained by submerging the reservoir flasks, A and A′, in a thermostat and wrapping tubes B, B′, C and D with asbestos and friction tape. This wrapping also protected the reacting mixture from light. To test the effectiveness of the temperature control, measurements were made of the temperature of the solution emerging at E or E′, when the apparatus was operating under the conditions of an actual experiment. With room temperature about 20° and the temperature of the thermostat at 25.0° and at 35.2°, the temperature of the emergent solution was 25.0 and 34.8°, respectively.

In principle the flow method is identical with the customary methods of determining reaction velocities; it consists of the determination of the concentration of the reactants before and after a known interval of time. In the method presented here, this interval begins when the reactants are brought together in some element of volume, and ends when the reaction,

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[9] For a discussion of the general problem of rapidly mixing solutions by flow methods and of following the progress of the reaction (by physical methods) in the resulting solution, see Hartridge and Roughton, ref. 8.

occurring in that volume, is stopped by mixing with a third solution. We may take this as equal to the time, τ, required for an element of volume to pass from the mixing chamber, C, through the reaction tube, D, to the end of the outlet, E or E′. Therefore

$$\tau = Ut/V \tag{6}$$

where U is the volume of the reaction tube and V the volume of solution delivered in time t. The results of a series of calibrations, using pure water at 25°, can be represented with fair accuracy for pressures between 20 and 38 cm. of mercury by the following equation

$$\tau = U/(11.0P + 174) \tag{7}$$

τ is expressed in minutes, U in cc., and P (the pressure) in cm. of mercury. The value of τ is also slightly affected by the level of the solutions in the reservoir flasks; this correction never exceeds 3%, and for pressures above 30 cm. is negligible. τ is, of course, dependent on the viscosity of the solution; however, the rate of flow of the dilute solutions used in these experiments never differed from that of water by 1%. The flow was the same regardless of which outlet was used. The calibrations would have been useless if oxygen gas had been evolved in the reaction tube, but bubble formation was not observed in any experiment until after the mixture had emerged at outlet E or E′.

To determine the initial concentrations of the reactants it is necessary to know the concentrations of the stock solutions (in the reservoir flasks) and the relative amounts of these two solutions brought together in the mixing chamber C. Since the mixing chamber used was not exactly symmetrical, the volumes flowing from the two reservoirs were not equal. The relative amounts delivered were determined, under a variety of conditions, by introducing distilled water into one reservoir and 0.10 N tri-iodide solution into the other, and then analyzing the resultant mixture. A number of such experiments showed that, for pressures greater than 22 cm., 0.552 part of the total volume delivered came from flask A. For lower pressures, the value of this ratio increases gradually to 0.558, when the pressure is decreased to 18 cm. It is not affected by interchanging the water and tri-iodide solution. A small departure occurs when the levels of the two solutions in the reservoirs are not the same; thus a difference in level of 9 cm. caused the ratio to change by only 5%. The making of a correction was avoided by wasting (through outlet N or N′) the solution which was in excess until the levels were equal at the beginning of each experiment.

To determine the velocity of a rapid reaction by *chemical* means it is necessary not only to mix the component solutions rapidly but also, after a known short time, to stop the reaction by mixing the reacting solution with some appropriate solution. In general this third solution must contain some substance capable of reacting with (and thereby removing) one of the reaction components with extreme rapidity. In the experiments presented here we have utilized the reduction of bromine by iodide ion

$$Br_2 + 2I^- = 2Br^- + I_2 \qquad (8)$$

which Saal[8c] has recently shown to be completed in less than 0.004 sec. This reaction is followed by a comparatively slow one between hydrogen peroxide and iodide ion, since the solution used to stop the reaction always contained an excess of iodide, and sufficient acid to prevent the catalytic decomposition of the peroxide. The reacting mixture was delivered directly into a vessel, F, containing the iodide solution, which was stirred rapidly (see the description of Fig. 1). To maintain the iodide concentration, fresh iodide solution was added continuously and the mixture was allowed to overflow into a collecting vessel.

An iodimetric method of analysis was used in *determining hydrogen peroxide*, as well as bromine, the iodine liberated in acid solution being titrated with thiosulfate. The peroxide solution was pipetted into a solution which contained 2 g. of potassium iodide, 20 milli-equivalents of sulfuric acid and enough water to make the final volume 100 cc. The mixture, in a glass-stoppered vessel, was set aside in the dark for about forty minutes. After the titration with thiosulfate the mixture was again set aside for about twenty minutes; the absence of "after-bluing" was evidence that the reaction between H_2O_2, I^- and H^+ was complete under these conditions. It was found that no error was introduced by beginning the titration before the reaction was complete.[10] The low concentration of acid, 0.2 *N*, was used in order to minimize the oxygen error[11] due to reaction between O_2, I^- and H^+.

To check the accuracy of our method a solution of hydrogen peroxide was titrated with the potassium permanganate solution which had been used in standardizing the thiosulfate solution.[12] A small excess of potassium permanganate was added and this excess was determined iodimetrically. A 25.03cc. portion of the hydrogen peroxide solution was found to be equivalent to 20.90 and 20.92 cc. of thiosulfate by the potassium permanganate method, and to 20.93 and 20.93 cc. of thiosulfate by our iodimetric method.

In employing this method it is important that acid be present when the iodide and peroxide are mixed, since iodide alone catalyzes the decomposition of the peroxide into water and oxygen. Thus in two experiments in which the acid was added one minute and five minutes after the

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[10] Harcourt and Esson, *J. Chem. Soc.*, **20**, 476 (1867); Bell, *J. Phys. Chem.*, **7**, 61 (1903).

[11] This error seems unavoidable in the rapid method recommended by Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, **1924**, Vol. II, p. 576, since the acid concentration is 2.25 *N*.

[12] Bray and Miller, THIS JOURNAL, **46**, 2204 (1924).

peroxide and iodide were mixed, it was found that 12.5 and 45% of the peroxide had decomposed.[13]

The experimental procedure probably can be best explained by giving the details of an actual experiment (Table I, No. 8). The stock hydrogen peroxide solution was 0.04295 *M;* the stock bromine solution 0.02622 *M.* Both of them were 0.00063 *M* in respect to perchloric acid. One liter of acid–iodide solution was used; it contained 10 cc. of concentrated sulfuric acid and 25 g. of potassium iodide. The nitrogen pressure was 20.8 cm. The volume of the reaction tube was 30.9 cc. since outlet E′ was used. Immediately before the experiment about one liter of solution was wasted through E″. The experiment lasted 104 sec. (measured with a calibrated stop watch). The mixing chamber, F, overflowed into and was drained into a 2-liter graduated flask. About 245 cc. of water was required to make up the mixture (reaction mixture + acid–iodide solution) to two liters. The resulting solution contained 0.01908 oxidizing equivalent per liter. From these data and the calibrations we may compute the duration of the reaction and the concentrations of the reactants and products before and after this time interval.

At 20.8 cm. pressure, 0.554 part of the reaction mixture was made up from the hydrogen peroxide stock solution. Therefore

$$(H_2O_2)_0 = 0.554 \times 0.04361\ M = 0.02416\ M$$
$$(Br_2)_0 = B = 0.446 \times 0.02664\ M = 0.01188\ M$$
$$(H^+)_0 = C = 0.00063\ M$$

Referring to the calibrations again (see Equation 7), we find the reaction time, τ, is 0.00770 minute and the rate of flow is 6.70 cc./sec. With this flow 764 cc. should be delivered in 104 seconds. To obtain a check of this value we subtract the volume of the acid–iodide solution and the water used from two liters (2000 cc. − 1245 cc. = 755 cc.). This check was used to detect any gross error and in the experiments at 25° the volume calculated from the calibrations was used.[14] Knowing the volume of the

[13] It is possible that this source of error may account for the low results of Wagner, *Ind. Eng. Chem.*, **17**, 973 (1925), in analyzing barium peroxide, since the order of mixing seems to have been peroxide, water, iodide, acid.

[14] The calculated and measured volumes differed by more than 1.2% in only four experiments. Nos. 4, 7, 13 and 14. The results based on the calculated volumes are shown in Table I, and those based on the measured volumes are given in the following table.

Expt.	Diff. in vol., %	K_2, Table I	$10^3 x$	τ (min.)	K_2
4	4.3	0.0238	3.805	0.0807	0.0163
7	1.6	.0178	4.785	.0448	.0213
13	1.6	.0258	3.675	.0457	.0217
14	3.3	.0268	4.32	.0791	.0193

The new values of K_2 in the sixth column are in better agreement than the old ones with the values of K_2 in the remaining experiments (Table I).

In the two experiments at 35°, Nos. 20 and 21, the calculations were based on the measured volumes.

solution delivered, as well as the concentration of oxidizing equivalents in the 2-liter sample, we may compute the sum of the concentrations of hydrogen peroxide and bromine in the solution delivered.

$$(H_2O_2) + (Br_2) = A + B - 2x = (2000/764)(0.01908/2) = 0.02500\ M$$

Combining this with the values of A and B we can obtain x, the loss in bromine (or peroxide) in moles per liter.

$$A + B = 0.02416 + 0.01188 = 0.03604\ M$$
$$x = {}^1/_2(0.03604 - 0.02500) = 0.00552\ M$$

To determine the rate constant from these data it is necessary to obtain the integrated form of Equation 5. Using the symbols already defined and letting $(Br^-)_0 = D$, we may write Equation 5 in the following form

$$dx/dt = K_2(A-x)(B-x)/(C + 2x)(D + 2x) \qquad (9)$$

By integrating and eliminating the constant we obtain

$$\tau K_2 = 4x + \frac{(2B + C)\,(2B + D)}{(A - B)} \ln \frac{B}{(B - x)} - \frac{(2A + C)\,(2A + D)}{(A - B)} \ln \frac{A}{(A - x)} \qquad (10)$$

It should be noted that in the derivation of this formula no allowance was made for the formation of tribromide, from bromine and bromide ion; however, this effect is negligible in the experiments presented here.[15]

Results and Conclusions

The experimental data are summarized in Table I. Three recent experiments, Nos. 15–17, made with our apparatus by H. A. Bois and B. Makower, are included; also the first point in each of our earlier experiments,[3] Nos. 18 and 19. The second to fifth columns give the initial concentrations of hydrogen peroxide, bromine, acid and bromide, respectively. The acid added was perchloric, except in Expts. 18 and 19; the bromide in Expts. 16–19 was potassium bromide.

The values of K_2 given in the eighth column of Table I do not show any marked trend with the initial concentrations of hydrogen peroxide, bromine or acid, nor with the duration of the reaction: we may conclude, therefore, that Equation 5 correctly represents the rate of the reaction. It is interesting to compare the values of K_2 in Expts. 18 and 19 (0.037 and 0.030) with the published values[3] (0.035 and 0.030), which were computed by a method involving successive approximations, and were based upon a series of analyses extending over an hour. The computing method then used allowed corrections to be made for the catalytic rate and for the formation of tribromide ion.

The values of K_2, however, do show a small trend, namely, an increase with the ionic strength, Col. 9. This is not surprising when it is remem-

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[15] The effect of tribromide is largest when the bromide concentration is small, and therefore would have been most serious in Expts. 3 and 12. In these cases it was estimated, by a method of approximations, that a correction for tribromide would have decreased the values of K_2 by not more than 10%.

Table I

Experimental Data and Calculations

Temp., 25°, in Expts. 1–19, 35° in Expts. 20 and 21

Expt. no.	Initial concn., (moles per liter) × 10^3 H_2O_2	Br_2	H^+	Br^-	10^3x	τ, min.	K_2	μ, ionic strength	γ^2, (HBr)	$\chi_2 = K_2\gamma^2$
1_A	22.66	11.63	0.28	0	4.865	0.0630	0.0171	0.0052	0.90	0.0154
2_A	22.74	11.57	.28	0	5.405	.0773	.0205	.0057	.89	.0183
3_B	7.61	15.78	.35	0	3.455	.0447	.0205	.0038	.91	.0187
4_B[a]	7.61	15.78	.35	0	4.145	.0772	.0238	.0045	.91	.0216
5_B	7.61	15.78	.35	0	4.080	.0778	.0223	.0044	.91	.0202
6_C	24.16	11.88	.63	0	4.685	.0453	.0196	.0053	.90	.0176
7_C	24.16	11.88	.63	0	4.575	.0456	.0178	.0052	.90	.0160
8_C	24.16	11.88	.63	0	5.52	.0770	.0208	.0062	.89	.0185
9_D	19.69	17.10	.63	0	5.14	.0435	.0210	.0057	.89	.0187
10_D	19.69	17.10	.63	0	6.01	.0752	.0214	.0066	.88	.0189
11_D	19.69	17.10	.63	0	6.03	.0759	.0217	.0067	.88	.0192
12_E	23.86	13.86	12.6	0	3.31	.0309	.0242	.0159	.82	.0198
13_E	23.90	13.83	12.6	0	3.92	.0450	.0258	.0165	.82	.0210
14_E[a]	23.90	13.83	12.6	0	4.795	.0765	.0268	.0174	.81	.0217
15_F	18.85	11.15	0.60	0	4.566	.0609	.0195	.0052	.90	.0176
16_G	20.12	11.88	.20	2.25	4.497	.0605	.0200	.0070	.88	.0176
17_G	20.12	11.88	.20	2.25	3.819	.0351	.0203	.0063	.89	.0180
18_H[b]	152.0	57.2	380	9.55	36.8	5.0	.0372	.60	.34	.0127
19_K[b]	113.7	74.0	585	9.80	36.0	8.0	.0297	.91	.33	.0098
20_L	18.89	9.89	0.63	0	5.31	0.0543	.0473	.0059	(.89)	(.0420)
21_L	18.89	9.89	0.63	0	4.645	.0315	.0484	.0053	(.90)	(.0430)

[a] Rejected, see ref. 14.

[b] Ref. 3.

bered that no allowance is made for the activities in Equation 5.[16] If we assume that the activity coefficients of the neutral molecules involved are equal to unity, we may write Equation 5 as follows

$$-d(H_2O_2)/dt = \chi_2(H_2O_2)(Br_2)/(H^+)(Br^-)\gamma^2_{HBr} \qquad (11)$$

where χ_2 is a true constant equal to $K_2\gamma^2_{HBr}$. This equation may be derived either by assuming that the rate is proportional to the activities of the components (in this case practically identical with the concentrations) or by assuming the correctness of Brönsted's[17] reaction velocity hypothesis. In all of the experiments except numbers 18 and 19, the ionic strength changed considerably during the reaction. Because of this it is impossible to determine accurately the value of χ_2. An approximate set of values can be obtained by assuming that for each experiment the ionic strength is constant and has a value equal to that for the solution when χ has a value half as great as its final value. Using the activity coefficients

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[16] See (a) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); (b) Livingston, This Journal, **48**, 53 (1926).

[17] (a) Brönsted, ref. 16a; (b) *Z. physik. Chem.*, **115**, 337 (1925); (c) Brönsted and Livingston, This Journal, **49**, 435 (1927); (d) Brönsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, **1927**.

of hydrobromic acid corresponding to these ionic strengths,[18] a series of values of χ_2, Col. 9, has been computed. The average value is 0.018. The results of Expts. 18 and 19 are not included in the average, but do not differ greatly from it. The discrepancy may possibly be due to experimental inaccuracies, but is more probably evidence that Equation 11 does not hold exactly at high ionic strength.[19] Otherwise, the variations in χ_2 are no greater than the experimental error.

We may combine the value of χ_2 with the average value of χ_1, 0.043/2,[19a] to obtain a value for the steady-state function, ρ.

$$\rho = \chi_1/\chi_2 = 0.043/2 \div 0.018 = 1.2 \qquad (12)$$

This value lies well within the range of values (0.9 to 2.6)[20] calculated from steady-state concentration measurements by means of the equation

$$\rho = R/\gamma^4 \qquad (13)$$

but is somewhat smaller than the mean value, 1.7, previously chosen. However, it seems probable that too great weight was then given to the larger values of ρ, which were based upon measurements made in the presence of sulfates and at high ionic strengths.

Balint's Results.—Equations 5 and 9 and the hypobromous acid mechanism were also obtained (in 1910) by Balint,[4] who measured the rate of reduction of bromine by hydrogen peroxide in aqueous solution at 0°. He followed the course of the reaction by measuring the change in volume or pressure due to the oxygen gas evolved, from 5 to 10 readings being taken during each run. His experiments appear to have been extremely well planned and accurate. He proved that the reaction corresponds quantitatively with the equation

$$H_2O_2 + Br_2 = O_2 + 2H^+ + 2Br^- \qquad (14)$$

but the stoichiometry was studied only in the absence of added hydrobromic acid, and he was apparently unaware of the reaction which occurs between H_2O_2, Br^- and H^+. Fortunately, we have been able to calculate, by means of an estimated value of K_1 at 0°, that the error introduced by this reaction is negligible in all his experiments, with the possible exception of No. 23. The initial concentrations and the results are summarized in Table II.

Balint calculated K_2 in Expts. 6–15 by a formula equivalent to Equation 10, and in Expts. 16–23 by assuming that the concentration of all substances except hydrogen peroxide remained constant during the reaction. All of the results were corrected (approximately) for tribromide formation, and in the second group of experiments a further correction was applied for the apparent degree of ionization of the electrolytes present. Since we

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[18] Livingston, THIS JOURNAL, **48**, 45 (1926).

[19] Cf. (a) Livingston, *ibid.*, **48**, 56 (1926); also (b) Livingston and Bray, *ibid.*, **47**, 2076 (1925).

[20] See Table III, ref. 19a, p. 57.

TABLE II

BALINT'S EXPERIMENTS AT 0°

	Nos. 6 to 15	Nos. 16 to 23	Final
Init. concn. (molal), H_2O_2	0.00023–0.0049	0.0011–0.0068	
Init. concn. (molal), Br_2	.00014– .0079	.043– .079	
Init. concn. (molal), H^+ (total acid)	.00075– .0426	.072– .534	
Init. concn. (molal), Br^- (total bromide)	.00219– .0120	.058– .623	
K_2, Balint, average	.000749	.000741	0.000745
K_2, without Balint's correction for ionization	.000749±2.7%	.000936±12%	
$\chi_2 = K_2\gamma^2$	.000635±9%	.000605±11%	.00062

believe that this latter correction is scarcely an admissible one, we have recalculated K_2 in these experiments (Nos. 16–23) using the stoichiometric concentrations. We have also applied the activity correction by the method already discussed (see Equation 11), with the assumption that the activity coefficient of hydrobromic acid has the same values at 0° as at 25°; the resulting values of χ_2 are shown in the last line of Table II, the final average being 0.00062.

Comparison of this value of χ_2 at 0° with our values at 25 and 35°, 0.018 and 0.043, leads to the conclusion that the temperature coefficient of the reaction (Equation 14) decreases with increasing temperature. This result and the temperature coefficient of the bimolecular reaction between hydrogen peroxide and hypobromous acid (Equation 4) will be discussed in another paper.

The Hypobromite Ion Mechanism Suggested by Christiansen.—From certain theoretical considerations, Christiansen[5] has concluded that hypobromite ion rather than hypobromous acid is involved in the reduction of bromine by hydrogen peroxide. An error in logic in his first theoretical treatment[5a] is corrected[21] in his recent paper.[5b] His general treatment covers the various possible special cases and includes those we have considered. Thus the conclusion that hydrogen peroxide reacts more rapidly with hypobromous acid than with hypobromite ion may be shown to follow from his general equation if the steady-state function is assumed to have the form shown in Equation 2. Christiansen, by basing his decision entirely on those measurements of the steady-state concentrations which were made with sulfuric acid at high concentration,[22] concludes that the steady-state function contains the concentration of hydrogen ion to the inverse third power and that, therefore, the reduction of bromine involves hypobromite ion rather than hypobromous acid. The experimental result that he cites is true only for concentrations of sulfuric acid greater than 1 *N* and we believe that it is not possible to draw from this

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[21] Cf. ref. 5 b, p. 434, lines 17–22.

[22] See Fig. 1, ref. 5 a, p. 434; and contrast the general agreement in Table III ref. 14 a, p. 57.

result any conclusion in regard to the mechanism of the simple reaction. It seems probable that this effect is due to the occurrence of side reactions, such as the formation of bromate ion.[23] However, since the question has been raised, it seems worth while to test the hypobromite mechanism with the data presented in this paper.

If we replace Equation 4 by the following expression

$$H_2O_2 + BrO^- = Br^- + O_2 + H_2O \qquad (15)$$

and assume, as before, that the bromine hydrolysis equilibrium is maintained during the reaction, we may write for the rate of reaction

$$dx/dt = K_2'(A - x)(B - x)/(C + 2x)^2(D + 2x) \qquad (16)$$

Integrating this expression and eliminating the constant, we obtain

$$\tau K_2' = 4x^2 + Ex + F\ln\frac{B}{(B - x)} - G\ln\frac{A}{(A - x)} \qquad (17)$$

where $E = 8(A + B + C + D/2)$,
$F = (B^2E - 8AB^2 + 4BCD + 2BC^2 + C^2D)/(A - B)$, and
$G = (A^2E - 8A^2B + 4ACD + 2AC^2 + C^2D)/(A - B)$

Four experiments at widely varying acid concentration were chosen to test this formula. The results of these computations are given in Table III.

TABLE III

COMPARISON OF SPECIFIC REACTION RATES BASED ON THE HYPOBROMITE ION AND HYPOBROMOUS ACID MECHANISMS

Expt. no., Table I	(H^+)	$K_2' \times 10^4$	$K_2 \times 10^2$
8	0.00063	1.8	2.1
12	.0126	4.2	2.4
18	.380	140	3.7
19	.585	188	3.0

The second column lists the initial acid concentrations; the third the values of K_2' (Equation 17); and the fourth the values of the constant of Equation 10 (or 9) taken from Table I. These data demonstrate clearly that Equation 17 (and therefore Equation 15) does not fit the facts.

Summary

1. A convenient method is presented for measuring reaction velocities having half times of the order of magnitude of one second.

2. The rate of reduction of bromine by hydrogen peroxide is shown to conform to the equation

$$-d(H_2O_2)/dt = \chi_2(H_2O_2)(Br_2)/(H^+)(Br^-)\gamma^2_{HBr}$$

even in solutions in which the concentrations of acid and bromide are very small. At 25 and 35° the values of χ_2 are 0.018 and 0.043, respectively, when concentrations are expressed in moles per liter and times in minutes.

3. This equation and the value of χ_2 at 25° are concordant with, and

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[23] Cf. ref. 1, p. 1264. In several of the rate experiments performed at high acid concentration, analytical evidence was obtained for the existence of small quantities of an oxidizing agent having the properties of bromate ion.

were predicted from, experimental data on the catalytic decomposition of hydrogen peroxide.

4. Balint's earlier measurements at 0°, which hitherto have been overlooked, are summarized. When the activity correction is applied χ_2 is equal to 0.00062.

5. The hypobromite ion mechanism suggested by Christiansen is shown to be unsatisfactory.

6. The hypobromous acid mechanism for the reaction between hydrogen peroxide and bromine and for the catalytic decomposition of hydrogen peroxide is in excellent agreement with the known experimental facts.

7. A satisfactory iodimetric method of determining hydrogen peroxide is described.

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THE REDUCTION POTENTIAL OF SELENOUS ACID AND THE FREE ENERGY OF AQUEOUS SELENIC ACID

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Introduction

It is well known that selenic acid may be prepared by oxidizing an aqueous solution of selenous acid with chlorine, and that selenic acid may be reduced to selenous acid by treatment with concentrated hydrochloric acid. This at once leads to the conclusion that, for the reaction $Cl_2 + H_2SeO_3 + H_2O = H_2SeO_4 + 2HCl$, there should be a concentration of hydrochloric acid at which a measurable amount of both selenic and selenous acids would be present when the pressure of chlorine is approximately one atmosphere.

The equilibrium conditions of this reaction were investigated for the purpose of determining, with the aid of the known chloride–chlorine potential, the reduction potential of the reaction H_2SeO_3 (1 m.) + H_2O = $HSeO_4^-$ (1 m.) + $3H^+$ (1 m.) + $2E^-$. The thermodynamic relations involved are indicated below.

The reaction, written in the ionic form $Cl_2\ (g) + H_2O + H_2SeO_3 = 3H^+ + HSeO_4^- + 2Cl^-$ takes place in the hypothetical voltaic cell

$$\mathrm{Pt}\left\{\begin{matrix} \mathrm{H_2SeO_3} & (1\ \mathrm{m.}) \\ \mathrm{HSeO_4^-} & (1\ \mathrm{m.}) \\ \mathrm{H^+} & (1\ \mathrm{m.}) \end{matrix}\right. \,\|\, \mathrm{Cl^-}\ (1\ \mathrm{m.}),\ \mathrm{Cl_2}\ (1\ \mathrm{atm.}) + \mathrm{Pt}$$

The free energy decrease $(-\Delta F)$ attending the change in state in this cell, corresponding to the passage of two faradays, may be calculated either from the electromotive force E of the cell, or from the equilibrium constant K of the reaction by the following well-known equations

$$-\Delta F = 2\mathrm{E}F = RT \ln K$$