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

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN A BROMINE-BROMIDE SOLUTION. II. RATE MEASUREMENTS IN DILUTE SOLUTIONS AND IN THE ABSENCE OF SULFATE, AND THEIR INTERPRETATION AS A FUNCTION OF THE ACTIVITY PRODUCT OF HYDROBROMIC ACID

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Introduction

In a previous paper on the catalytic decomposition of hydrogen peroxide in a bromine-bromide solution,[1] a series of rate measurements were given for the steady-state condition, and the following kinetic equation was determined.

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

where K is approximately equal to 0.0144 for acid concentrations between 0.2 N and 3.0 N. The concentrations used were expressed in moles per liter, and were computed on the assumption that all the electrolytes were completely ionized. It was pointed out at that time that the value of K, obtained from measurements in solutions of potassium bromide and sulfuric acid, increased as the acid concentration was decreased below 0.2 N. To determine the nature of this effect, steady-state rate measurements have now been made in still more dilute solutions of sulfuric acid and potassium bromide, and in various acid-bromide solutions that do not contain sulfate.

Experimental Measurements

As before, the reactions were conducted at 25° in the dark. The experimental conditions, methods, and method of computing used were the same as those explained in detail in the earlier paper.

At low acid concentration the decomposition of hydrogen peroxide in the absence of the catalyst introduces a fairly important error. To determine what concentration of acid was necessary to render this effect negligible, three blank solutions were prepared. Each blank contained 0.12 M hydrogen peroxide. To two of them sulfuric acid was added to make them 0.0098 N and 0.073 N, respectively. The first order constant (k) for the neutral solution was 0.176×10^{-4}, a more rapid rate than that at 0.0147 N acid, Expt. 7, Table I. No appreciable loss occurred during a 3-day

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[1] Bray and Livingston, THIS JOURNAL, **45**, 1251 (1923). On p. 1253, fifth from the last line, $F_{298°}$ is a misprint for $\Delta F_{298°}$.

Recently our attention has been called to a paper by Trifonow: "Eigenschaften und Struktur der Persalpetersäure" (Trifonow, *Z. anorg. Chem.*, **124**, 123 (1922)). He mentions the oxidation of bromide and the reduction of bromine by hydrogen peroxide, and states that the former reaction may be retarded by dilution and the latter by the addition of a fairly large quantity of KBr and H_2SO_4.

period, in either of the acidified solutions, although these experiments were made in ordinary glass containers. To reduce this effect, wax-lined bottles were used in several of the experiments conducted at low acid concentration (Expts. 7, 8 and 9 of Table II, and 3 and 6, of Table VI).

Steady-State Measurements in the Presence of Dilute Sulfuric Acid

The results of 7 determinations of the steady-state rate in the presence of dil. sulfuric acid are summarized in Table I. The arrangement and conventions adopted are the same as those used in the third table in the preceding paper. In this table (I) the peroxide concentrations marked with an asterisk were made up from "Superoxol," the others from a 3% commercial solution. Since the interest of this table is primarily in the rate constants, the values of "bromine-calculated" and "tribromide-calculated" have been omitted; the "calculated" bromine concentrations were used, however, in computing the values of R listed. The last three columns will be explained later.

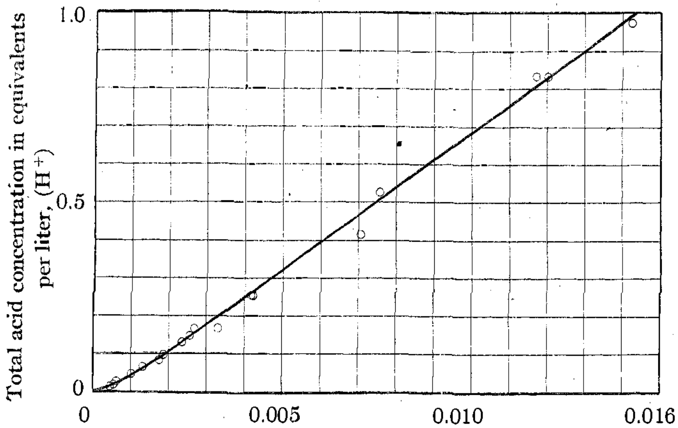
TABLE I

STEADY-STATE RATE MEASUREMENTS IN THE PRESENCE OF DILUTE SULFURIC ACID

	Initial concn.		Steady-state concn.					
Expt.	Acid	Bromide	Acid	Bromide meas.	Bromine	Peroxide	$k \times 10^4$	R
1	0.0976	0.0982	0.0973	0.0979	0.00014	0.03–0.01*	1.80	0.59
2	.0835	.070	.0835	.070	.000028	.09– .05	1.22	.26
3	.0645	.100	.0644	.100	.000053	.16– .08	1.30	.49
4	.0465	.0935	.0465	.0935	.....	.02– .01*	0.937	..
5	.0257	.103	.0257	.103	.....	.03– .01*	.615	..
6	.01965	.0342	.01965	.0342	.....	.21– .18*	.1826	..
7	.01473	.0244	.01473	.0244	.....	.21– .19	.1081	..

Expt.	K	μ	γ	χ
1	0.0189	0.244	0.774	0.0315
2	.0208	.195	.784	.0335
3	.0202	.197	.784	.0325
4	.0216	.164	.792	.0344
5	.0232	.142	.798	.0364
6	.0272	.0537	.827	.0398
7	.0301	.0465	.854	.0413

The value of K is seen to increase as the acid concentration is decreased. It is apparently approaching a limiting finite value, and is not increasing indefinitely, as it would if there were any appreciable catalysis in a neutral bromide solution. To demonstrate this, the ratio of the first order constant to the bromide concentration, $k/(\mathrm{Br}^-)$, has been plotted against the hydrogen-ion concentration, (H^+), Fig. 1. Results from Table III of the first paper,[1] as well as those from Table I, are represented. It is apparent that when this curve is extrapolated to $(\mathrm{H}^+) = 0$ (practically identical with neutral solution on this scale) it will pass through or very near the origin; that is, the absolute rate of the catalytic decomposition will be negligibly small. Since the rate of the reaction between bromine and peroxide is very rapid in neutral solution, it follows that the rate of oxidation of bromide by peroxide is negligible under these conditions, for any bromine formed by this reaction would be rapidly reduced with the resultant decomposition of hydrogen peroxide. This is in marked contrast to the iodide-peroxide reaction, the rate equation for which has the following form:[2]



The ratio of the first-order rate constant to the total bromide concentration, $k/(\mathrm{Br}-)$

Fig. 1

$$d(I_2)/dt = (I^-)\,(H_2O_2)\,[K' + K(H^+)] \qquad (2)$$

Our results demonstrate that the constant term (K') is unnecessary in the rate equation of the bromide oxidation.

Since the possibility of an independent reaction not involving acid has been eliminated, the most plausible explanation of the increase of K with a decrease in acid concentration is the assumption that the sulfuric acid is not completely ionized. It will be recalled that all values of K and R were computed upon the assumption that sulfuric acid was completely ionized. The assumption of incomplete ionization is in agreement with a series of measurements by Noyes and Stewart,[3] who state that singly-ionized sulfuric acid (HSO_4^-) may be considered as a weak acid, with an ionization constant of 3×10^{-2} in the range 0.1 M to 0.025 M sulfuric acid. It should also be noted that when sulfuric acid is treated as a strong electrolyte the values of the activity coefficients for dilute solutions are very low.[4]

Steady-State Measurements in Hydrobromic Acid Solutions

To discover to what extent the observed increase of the constant in dilute solution was due to the presence of sulfuric acid, a series of steady-state

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[2] Bray, *Z. physik. Chem.*, **54**, 486 (1906).

[3] Noyes and Stewart, THIS JOURNAL, **32**, 1133 (1910).

[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 357.

rate measurements were made in which the only electrolyte was hydrobromic acid. The results of 9 such measurements are summarized in Table II. In all the experiments listed the initial peroxide concentrations were made up to 0.16 *M* or greater, from a "Superoxol" solution.

Table II

Steady-State Rate Measurements in Hydrobromic Acid Solution

	Initial concn.	Steady-state concn.								
Expt.	HBr	Acid	Bromide	Bromine meas.	$k \times 10^4$	K	R	μ	γ	x
1	0.429	0.346	0.311	0.0417	26.8	0.0250	0.60	0.346	...	....
2	.286	.256	.244	.0150	17.0	.0271	.76	.256	...	....
3	.214	.206	.203	.0042	11.2	.0268	.57	.206	0.782	0.0438
4	.147	.146	.146	.00051	5.96	.0279	.33	.146	.796	.0440
5	.0945	.0945	.0945	....	2.58	.0289	..	.0945	.817	.0433
6	.0677	.0677	.0677	....	1.36	.0297	..	.0677	.834	.0427
7	.0432	.0432	.0432	....	0.593	.0318	..	.0432	.858	.0432
8	.0338	.0338	.0338	....	0.384	.0337	..	.0338	.870	.0445
9	.0217	.0217	.0217	....	0.164	.0348	..	.0217	.889	.0440

The average value of *K* obtained from these measurements is about twice as great as the average value (0.0144) obtained in sulfuric acid solutions above 0.2 *N*, but is only slightly greater than the average value obtained from measurements in dil. sulfuric acid solution, Table I. Below 0.3 *N* acid the value of *K* increases regularly as the hydrobromic acid concentration is decreased. At higher concentrations, for which the rate is very rapid, the values obtained for *K* were not always concordant and there is some evidence for the existence of a small amount of bromate at the steady state.

Two additional experiments were performed to discover what factor was responsible for the low rates observed in the sulfuric acid-potassium bromide solutions.

	Initial concns.		Steady-state concns.			
Expt.	HBr	Na_2SO_4	Bromide	Acid	R	K
A.....	0.1881 *M*	0.492 *M* = 0.964 *N*	0.1880 *M*	0.1880 *N*	0.0080	0.0042
		H_2SO_4				
B.....	.113 *M*	.976 *N*	.100 *M*	1.08 *N*	.445	.0239

These experiments show that the effect is due to the sulfate ion. Taken in conjunction with the results with solutions of sulfuric acid and potassium bromide and with hydrobromic acid solutions, they show that the value of *K* increases towards a definite value when the ratio, $\Sigma SO_4/\Sigma$acid, is decreased without limit, and that it decreases indefinitely when the ratio is increased. The approximate constancy of *K* in the third table of the preceding paper was due to the constant ratio of sulfate to acid, and therefore the average value of the constant (0.0144) is not fundamental.

The values of *R*, $(Br_2)/(H^+)^2\,(Br^-)^2$ vary with the ratio of sulfate to acid in the same direction but more rapidly than the values of *K*, as is shown in Table III.

TABLE III

THE SPECIFIC EFFECT OF THE SULFATE ION

Expt.	$\Sigma SO_4/\Sigma_{acid}$	K	R
A	2.6	0.0042	0.008
Av. of Table III, Ref. 1	0.5	.0144	.22
B	.45	.0239	.45
Av. of Table II	..	.03	.60

It is evident that these results are in agreement with the assumption that singly-ionized sulfuric acid is a weak acid.

The Rate of Appearance of Bromine in Hydrobromic Acid Solution

As an additional check on the mechanism,[5] an experiment was performed on the rate of appearance of bromine in hydrobromic acid solution. The results were computed by the second method, explained in the preceding paper.[6] The smoothed out data and computations are given in Table IV.

TABLE IV

RATE OF APPEARANCE OF BROMINE IN A HYDROBROMIC ACID SOLUTION

$t-t_0$	Concentrations			Rates × 10^4			
Min.	Bromine	Peroxide	HBr	$-d(H_2O_2)/dt$	$d(Br_2)/dt$	Sum.	$2K_1$
0	0	0.0292	0.294	...	...	...	...
5	0.00020	.0290	.294	4.0	3.4	7.4	0.029
10	.00038	.0288	.293	4.0	3.1	7.1	.029
20	.00069	.0284	.293	4.0	2.8	6.8	.028
30	.00099	.0280	.292	4.0	2.4	6.4	.027
40	.00122	.0276	.292	4.0	2.4	6.4	.027
60	.00170	.0268	.291	3.8	2.2	6.0	.026
80	.00216	.0261	.290	3.6	1.8	5.4	.025
100	.00233	.0254	.289	3.1	1.6	4.8	.023

The average value of 2 K_1 is 0.0273. This is in excellent agreement with the value of K (0.0271) obtained from steady-state measurements, with an initial hydrobromic-acid concentration of 0.286 M. It is not known whether the observed small decrease of 2 K_1 with time has any theoretical significance or is due to experimental error.

Steady-State Measurements in Solutions of Perchloric and Hydrobromic Acids

Since perchloric acid is a strong non-reactive acid, it was chosen as a substitute for sulfuric acid. A series of experiments, which were performed in relatively dilute solutions containing perchloric and hydrobromic acids, are summarized in Table V.

In only three of these experiments was the bromine concentration measurable; 0.00089 M in 1, 0.000016 M in 2, and 0.00008 M in 5. The corresponding values of R are 0.35, 0.43 and 0.27, respectively. The values of K obtained are of the same order of magnitude as those obtained in pure hy-

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[5] Ref. 1, pp. 1261, 1270.

[6] Ref. 1, p. 1266.

drobromic acid solution, and like the latter, they increase as the concentration of electrolyte is decreased.

TABLE V

STEADY-STATE RATE MEASUREMENTS IN SOLUTIONS CONTAINING PERCHLORIC ACID

	Initial concn.		Steady-state concn.						
Expt.	$HClO_4$	HBr	Acid	Bromide	$k \times 10^4$	K	μ	γ	x
1	0.370	0.0719	0.4405	0.0766	7.52	0.0223	0.442	...	....
2	.2778	.0180	.2958	.0180	1.353	.0254	.296	...	....
3	.222	.0144	.236	.0144	8.94	.0262	.236	0.775	0.0436
4	.148	.0540	.202	.0539	2.91	.0267	.202	.782	.0432
5	.185	.0144	.199	.0144	0.752	.0267	.199	.783	.0426
6	.0924	.0720	.164	.0719	3.18	.0269	.164	.792	.0429
7	.0924	.0288	.121	.0288	1.00	.0[illegible]7	.121	.805	.0443
8	.0462	.0540	.100	.0540	1.59	.0293	.100	.814	.0442
9	.0370	.0144	.0514	.0144	0.240	.0324	.0514	.849	.0449

The Steady State in Solutions Containing Metallic Bromides

Several experiments were performed in solutions containing barium or potassium bromide. The results of these experiments are summarized in Table VI.

TABLE VI

STEADY-STATE RATE MEASUREMENTS IN SOLUTIONS CONTAINING METALLIC BROMIDES

	Initial conc.		Steady-state conc.								
No.	HBr	KBr	Acid	Bromide	Bromine meas.	$k \times 10^4$	K	R	μ	γ	x
1	0.113	0.196	0.107	0.306	0.00286	7.83	0.0239	0.45	0.306	...	....
2	.0540	.1464	.0537	.2001	.00014	2.854	.0264	.28	.200	0.782	0.0430
3	.0719	.0732	.0716	.1448	.00013	2.880	.0278	.36	.145	.797	.0437
4	.0360	.0732	.0359	.1090	.000024	1.123	.0286	.54	.109	.810	.0435
5	.0134	.0736	.0134	.0870	....	0.378	.0322	..	.0870	.821	.0477
6	.0268	.0245	.0268	.0514	....	.459	.0333	..	.0514	.837	.0475
7	.0216	.0146	.0216	.0363	....	.277	.0352	..	.0363	.868	.0469
	HBr	$^1/_2BaBr_2$									
8	.0719	.0528	.0717	.1245	.000094	2.44	.0272	.39	.151	.795	.0431
9	.0540	.0264	.0540	.0804	....	1.30	.0299	..	.0936	.817	.0447
10	.0176	.0176	.0360	.0352	....	0.613	.0318	..	.0624	.838	.0453
	$HClO_4$	KBr									
11	.0924	.0491	.0924	.0491	....	1.29	.0283	..	.141	.798	.0445
12	.0462	.0491	.0462	.0491	....	0.688	.0294	..	.0953	.816	.0442

The values of K obtained from measurements in these solutions have the same magnitude and trend as those obtained in hydrobromic acid solutions.

Theoretical Discussion

Substitution of Activities for Concentrations in the Rate Equation

The gradual increase in the specific reaction rate with a decrease in the concentration of the catalyst,[7] at low concentrations, suggests that activi-

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[7] For convenience, the term catalyst has been used to refer to that unit of the catalytic pair, the concentration of which occurs in the steady-state rate equation, in this case hydrobromic acid.

It should be noted that it is not illogical to use steady-state data in determining the effect of activities upon rates. In the present case the steady-state rate (rate of decomposition of peroxide) is exactly twice the rate of Reaction 1 (oxidation of bromide), and the two-rate equations differ only by a factor of 2 in the constant.

ties rather than concentrations should be used in the rate equation. Recently several cases of catalytic-rate measurements have been reported for which fairly accurate constants could be obtained by substituting activities for the concentrations of the reacting ions, in the rate equations. Fales and Morrell[8] applied this correction to the acid hydrolysis of cane sugar. Harned and Pfanstiel[9] have used a similar method in studying the acid hydrolysis of ethyl acetate. In both cases the use of activities improved the constancy of the specific reaction rate, but still left much to be desired. A more satisfactory example is the rearrangement of acetylchloro-aminobenzene to *p*-chloro-acetanilide in the presence of hydrochloric acid, which was investigated by Harned and Seltz.[10] This case differs from the other two cited in that it involves the activity of hydrochloric acid rather than the individual ion activity of hydrogen ion.

The reaction discussed here, like the rearrangement of acetyl-chloroaminobenzene, involves the activity of the halide acid, and not the activity of any individual ion. Assuming that the rate is determined by the product of the activities of the ions of the catalyst, and the concentration of the non-electrolyte (hydrogen peroxide), the rate may be expressed by the following equation.

$$-d(H_2O_2)/dt = \chi(H_2O_2)a_{H^+}a_{Br^-} = \chi(H_2O_2)\ (H^+)\ (Br^-)\gamma^2_{HBr} \qquad (3)$$

It follows from Equation 1 that the relation of the "activity-rate" constant (χ) to the "concentration-rate" constant (K) is given by the following expression.

$$K/\gamma^2_{HBr} = \chi \qquad (4)$$

Data on the activity of hydrobromic acid solutions are rather meager, but the electromotive-force measurements of Storch[11] tend to show that below 0.10 N the activities of hydrobromic and hydrochloric acids are identical.[12]

To correlate the observations in the various solutions used, which involved mixed electrolytes of various valence types, it is necessary to introduce the concept of ionic strength.[13] Since it has been demonstrated empirically that, in dilute solutions, the activity of a solute is a function of the total ionic strength and is independent of the nature of the other solutes,

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[8] Fales and Morrell, This Journal, **44**, 2072 (1921).

[9] Harned and Pfanstiel, *ibid.*, **44**, 2193 (1922).

[10] Harned and Seltz, *ibid.*, **44**, 1480 (1922).

[11] Lewis and Storch, *ibid.*, **39**, 2544 (1917).

[12] Ref. 4, pp. 335, 336.

[13] The ionic strength may be defined as half the sum of the products of the stoichiometrical molalities of the ions and the squares of their valences. Thus, for sulfuric acid the ionic strength is 3 times the molal concentration. Compare Ref. 4, p. 373. In the present paper the concentrations in moles per liter have been used instead of molalities, but the resulting numerical difference is not appreciable except in the more concentrated solutions.

we may assume that in the various mixed solutions used the activity coefficient of hydrobromic acid, γ_{HBr}, is a function of the ionic strength, μ, only.

In the last columns of Tables I, II, IV and V, the values of the ionic strength, μ, the mean activity coefficient, γ_{HBr}, and the rate constant corrected for the activity effect, χ, are listed. Values of the corrected constant have been computed for ionic strengths below 0.25, although it is hardly to be expected that either the assumption of the identity of the activities of hydrobromic and hydrochloric acids or the ionic-strength principle can be applied over this entire range. With the exception of the measurements in sulfuric acid solutions in Table I, the values of the corrected constants (χ) do not show any marked trend. The average value for pure hydrobromic acid solutions (Table II) is 0.0437 ± 0.0005. For perchloric-hydrobromic acid solutions (Table IV) the average value is 0.0437 ± 0.0006. On the other hand, the uncorrected constant (K) for the same experiments varies from 0.0348 to 0.0260, a decrease of 25.3%.

Taking 0.0437 as the average value of χ, values of K for a series of ionic strengths may be computed by Equation 4, from the values of γ_{HCl} given by Lewis and Randall.[12] Table VII lists the values so obtained.

TABLE VII

THE CALCULATION OF K FROM $\chi = 0.0437$ AND γ

μ	γ_{HCl}	K (Computed)	μ	γ_{HCl}	K (Computed)
0	1.000	(0.0437)	0.100	0.814	0.0289
0.005	0.947	.0392	.200	.783	.0268
.010	.924	.0373	.300	.768	.0258
.020	.894	.0349	.500	.762	.0254
.050	(.850)	.0316	....	....	.....

In Fig. 2, K (computed) has been plotted against μ. The experimental values of K, Tables I, II, V and VI and the first 6 values of Table III (Ref. 1), have also been plotted. At ionic strengths below 0.25, the values of K obtained in pure hydrobromic acid solutions and in perchloric-hydrobromic acid solutions are in remarkable agreement with the theoretical curve.

Although rate measurements cannot be used very generally for the determination of activity coefficients, they may be useful in certain limited cases. The data presented here have been used to obtain an estimate of the activity of hydrobromic acid, in solutions containing various electrolytes, relative to its activity in pure aqueous solutions. The results of such considerations are summarized as follows.

1. The activity of hydrobromic acid in perchloric acid solutions (less than 0.25μ) is almost identical with that of pure hydrobromic acid solutions of the same ionic strength. At higher concentrations there is apparently a small negative departure.

2. In all solutions containing metallic bromides the activity seems to be slightly greater below 0.15μ and slightly less above 0.15μ than the activity in pure hydrobromic acid solutions of the same ionic strength.

3. If it be assumed, and it is not an improbable assumption, that the presence of sulfuric acid does not depress the specific rate of the catalyzed decomposition, we may use the data given in Table I and in Table III of the preceding paper (Ref. 1) to obtain an approximate estimate of the activity coefficient of hydrobromic acid in potassium bromide-sulfuric acid solutions over a wide range of concentrations. The activity coefficient so obtained is practically independent of variations in the ratio (KBr)/(H_2SO_4) from 2.0 to 0.035. A few averaged values are given in the following table.

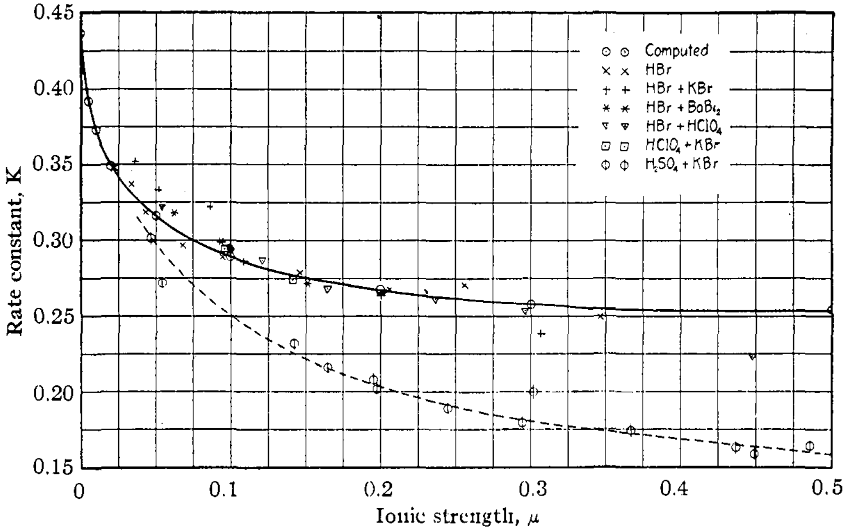

Fig. 2

TABLE VIII

THE ACTIVITY COEFFICIENT OF HYDROBROMIC ACID IN SOLUTIONS OF SULFURIC ACID AND POTASSIUM BROMIDE

μ	0.05	0.10	0.20	0.40	0.60	1.00	2.00	3.00	5.00
γ_{HBr}	.83	.73	.67	.62	.58	0.57	0.57	0.57	0.57

Although the general idea, that activities or "active mass" should be substituted for concentrations in the rate equations, has been discussed for years, one of the first attempts at an experimental test of this principle was made by Bugarsky[14] in 1910. He measured the rate of reaction between alcohol and bromine in 4 different solvents and attempted to estimate the activities by means of partition coefficients. In 1920, Jones and W. C. McC. Lewis[15]

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[14] Bugarsky, *Z. physik. Chem.*, **71**, 705 (1910).

[15] Jones and W. C. McC. Lewis, *J. Chem. Soc.*, **117**, 1123 (1920).

studied the acid hydrolysis of sucrose. They obtained their hydrogen-ion activities from cell measurements in the presence of the sugar, but their results are rendered somewhat uncertain by the presence of a diffusion boundary in their cell. This is also true for the results of Fales and Morrell.[8] The type of equation, used by Jones and Lewis[15] and the more recent workers[8,9,10] is one in which activities are substituted for the corresponding concentration terms. Following this convention, the rate equation for the bromine-bromide catalysis would be

$$—d(H_2O_2)/dt = K'a_{H_2O_2}a_{H^+}a_{Br^-} = K'(H_2O_2)\ (H^+)\ (Br^-)\gamma_{H_2O_2}\,\gamma^2{}_{HBr} \qquad (5)$$

To bring this equation into agreement with the experimental data it is necessary to assume that $\gamma_{H_2O_2}$ is constant in electrolyte solutions whose ionic strengths vary from 0.25 to 0.02. Although there is no definite evidence on this point, it seems an improbable assumption.

Recently Brönsted[16] has pointed out that the substitution of activities for concentrations in rate equations cannot be generally used to obviate "reaction anomalies," for in dilute solutions the activity coefficients of all electrolytes decrease as the total electrolyte concentration is increased, while under these same conditions the rate constants decrease, increase, or are unaffected by a change in the electrolyte concentration. He assumes that all reactions proceed through the formation and decomposition of an unstable intermediate, the valence of which is the algebraic sum of the valences of its components. From these assumptions he shows that it is consistent with thermodynamics and in good agreement with experimental results to represent the rate of any actual reaction as proportional to the product of the activities of the component molecular species divided by the activity coefficient of the intermediate complex. In agreement with this system the law of the bromine-bromide catalysis would be

$$—d(H_2O_2)/dt = \frac{K''}{\gamma_{H_2O_2\cdot HBr}}\,a_{H_2O_2}\,a_{H^+}\,a_{Br^-} = K''(H_2O_2)(H^+)(Br^-)\gamma^2{}_{HBr}\,\frac{\gamma_{H_2O_2}}{\gamma_{H_2O_2\cdot HBr}} \qquad (6)$$

In order that this equation shall represent the experimental data it is necessary for the ratio of the activity coefficients of hydrogen peroxide and the neutral complex ($H_2O_2.HBr$) to be constant over the range of concentrations studied. There is no reason to believe this assumption improbable.

The evidence presented here, as well as that presented by Harned and Seltz,[10] demonstrates that the rate of a catalytic process involving neutral molecules is proportional to a function of the activity of the catalyst rather than of the concentration. If the activity coefficient of the substance undergoing transformation is constant, as Harned assumes, the facts may be expressed equally well by the "activity-rate" theory or by Brönsted's theory.[17] If this assumption proves to be false, these results may be taken

[16] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[17] For a discussion of these theories and additional references, see the paper by Scatchard, THIS JOURNAL, **45**, 1580 (1923), which appeared while this article was in proof.

as a definite confirmation of a special case of Brönsted's theory. We shall continue this investigation by direct measurement of the activities involved and by further rate measurements.

Summary

1. The steady-state rate of the bromine-bromide catalysis of hydrogen peroxide has been measured in dil. solutions of sulfuric acid and potassium bromide, and it has been shown that the rate constant approaches a definite finite value as the sulfuric acid is indefinitely decreased.

2. The steady-state rate has also been measured in the following solutions: hydrobromic acid, hydrobromic-perchloric acid, hydrobromic acid-potassium bromide, hydrobromic acid-barium bromide, and perchloric acid-potassium bromide. The rate constants obtained from measurements in these various solutions are all slightly larger than those obtained from measurements in dil. sulfuric acid solutions, and are about twice as great as those obtained in sulfuric acid solutions above 0.2 *N*.

3. At the steady state, in hydrobromic acid and hydrobromic-perchloric acid solutions of ionic strength less than 0.25 and in 8 out of the 12 remaining experiments in the absence of sulfate, the rate of decomposition of peroxide is represented by the following expression within the limits of experimental error, 1% to 2% (the discrepancy in the 4 excepted experiments lies between 4% and 9%):

$$-d(H_2O_2)/dt = 0.0437\ (H_2O_2)\ (H^+)\ (Br^-)\gamma^2_{HBr} \qquad (7)$$

4. The activity coefficient of hydrobromic acid in solutions containing sulfuric acid and potassium bromide has been estimated from the rate measurements in these solutions, by the assumption that Equation 7 holds.

5. The application of the "activity-rate" theory and of Brönsted's theory to the experiments presented here has been briefly discussed.

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LUMINESCENCE OF ORGANO-MAGNESIUM HALIDES

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Apparently the first notice of luminescence associated with a Grignard reagent dates from 1906, when Wedekind[1] found that phenylmagnesium bromide and phenylmagnesium iodide give a bright light when reacting with chloropicrin. This reaction has become widely known as the "Wedekind Reaction."

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[1] Wedekind, *Ber.*, **4**, 417 (1906); *Physik. Z.*, **7**, 805 (1906); *Chem. Zentr.*, **30**, 921 (1906); *Z. wiss. Phot.*, **5**, 29 (1907).