2. The activity of hydrobromic acid has been determined in a variety of solutions containing sulfates, and these results have been compared with those of Livingston and Bray,[4b] which were based upon reaction-rate measurements.

3. A method for the prediction of the mean activity of strong electrolytes in the presence of weak electrolytes has been suggested, and has been tested with certain data presented here.

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

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN A BROMINE-BROMIDE SOLUTION. III. THE INTERPRETATION OF RATE MEASUREMENTS AS A FUNCTION OF THE ACTIVITY PRODUCT OF HYDROBROMIC ACID

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That the steady-state rate of decomposition of hydrogen peroxide in a bromine-bromide solution is proportional to the activity product of the hydrobromic acid, has already been demonstrated by Livingston and Bray.[1] The evidence presented by them applies only to reaction mixtures of ionic strength less than 0.25, which do not contain sulfate. Because of the lack of activity data, they found it necessary to make the somewhat uncertain assumption that the activities of hydrobromic and hydrochloric acids are identical at identical concentrations.

Recently published values of the activity of hydrobromic acid in pure aqueous solutions, and in solutions containing sulfates,[2] make it possible to correct these computations, of Livingston and Bray, and to extend them to include solutions of higher ionic strength as well as to solutions containing sulfates.[3]

The Steady-State Rate in Terms of the Activity Product of Hydrobromic Acid

The existing rate data,[1,3] for solutions of hydrobromic acid and of potassium bromide and sulfuric acid, have been interpreted in terms of the recently published activity data, in Tables I and II. The steady-state concentrations of acid and bromide are given in the second and third columns, respectively; the first-order rate constant (k) in the third; and the "concentration" rate constant (K), as defined by Equation 1, in the fourth.

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

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[1] Livingston and Bray, THIS JOURNAL, **45**, 2048 (1923).

[2] Livingston, *ibid.*, **48**, 45 (1926).

[3] Compare Bray and Livingston, *ibid.*, **45**, 1251 (1923).

The ionic strength (μ) is given in the fifth column; the activity coefficient of hydrobromic acid (γ) in the sixth; and the rate constant, in terms of the activity of hydrobromic acid (χ), as defined by Equation 2, in the seventh.

$$-d(H_2O_2)/dt = \chi(H_2O_2)(H^+)(Br^-)\gamma^2 \qquad (2)$$

For a more detailed summary of the experimental measurements, see Refs. 1, 2 and 3. Expts. 1, 2, 4 and 5 of Table I are new results, but are based on experimental measurements similar to those already described.[1] Expts. 13 and 15 are also new, and are based on oxygen evolution measurements. This method of measurement was undertaken in the hope that experiments might be performed in more concentrated solutions, the loss of bromine by volatilization being negligible in these experiments, since the total volume of oxygen evolved was less than 0.1 liter. It proved difficult to obtain the required accuracy in concentrated solutions, and there was some evidence of the formation of bromate.[4]

The rate measurements[1] for solutions containing perchloric acid and for solutions containing metallic bromides have not been included in these tables, since the necessary accurate activity data are still unavailable, and since approximate computations based on these data have already been published.[5]

TABLE I

THE STEADY-STATE RATE IN HYDROBROMIC ACID SOLUTIONS

No.	Concentrations		$k \times 10^4$	K	μ	γ	χ
	Acid	Bromide					
1	0.0098	0.0098	0.0340	0.0356	0.010	0.924	0.042
2	.0135	.0135	.0674	.0377	.014	.912	.045
3	.0217	.0217	.1640	.0348	.022	.894	.044
4	.0220	.0220	.1680	.0347	.022	.894	.043
5	.0288	.0288	.2800	.0338	.029	.882	.043
6	.0338	.0338	.384	.0337	.034	.874	.044
7	.0432	.0432	.593	.0318	.043	.861	.043
8	.0677	.0677	1.360	.0297	.068	.840	.042
9	.0945	.0945	2.580	.0289	.095	.822	.043
10	.1460	.1460	5.96	.0279	.146	.804	.043
11	.2060	.2030	11.20	.0268	.206	.791	.043
12	.2560	.2440	17.00	.0271	.256	.787	.044
13	.3300	.3010	25.85	.0261	.330	.786	.042
14	.3460	.3110	26.80	.0250	.346	.785	.041
15	.3790	.3250	31.20	.0255	.379	.787	.041

In Table I the values of χ are independent of the ionic strength from 0.010 to 0.38; and in Table II, from 0.05 to 1.0. In these same concentration ranges the values of K increase 30% (Table I) and 100% (Table II). The average values of K and χ are 0.031 ± 0.004 and 0.043 ± 0.001 for Table I, and 0.019 ± 0.003 and 0.048 ± 0.001 for the first 15 experi-

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[4] Compare Ref. 1, p. 2051; also W. C. Bray, THIS JOURNAL, **43**, 1262 (1921).

[5] Ref. 1, Tables V and VI, p. 2053.

TABLE II

THE STEADY-STATE RATE IN SOLUTIONS CONTAINING POTASSIUM BROMIDE AND SULFURIC ACID

No.	Concentrations Acid[a]	Bromide	$k \times 10^4$	K	μ	γ	χ[b]
1	0.0147	0.0244	0.1081	0.0301	0.047	0.78	0.050
2	.0197	.0342	.1826	.0272	.054	.76	.047
3	.0257	.0103	.615	.0232	.142	.68	.050
4	.0465	.0935	.937	.0216	.164	.67	.048
5	.0644	.1000	1.300	.0202	.197	.65	.048
6	.0835	.0700	1.220	.0208	.195	.65	.048
7	.0973	.0980	1.800	.0189	.244	.63	.048
8	.1290	.0990	2.300	.0180	.285	.62	.047
9	.1462	.1469	3.75	.0174	.367	.61	.047
10	.1660	.1970	5.26	.0159	.451	.59	.046
11	.1670	.0500	1.67	.0200	.300	.62	.052
12	.2570	.0500	2.10	.0163	.435	.59	.047
13	.2560	.0990	4.20	.0164	.485	.59	.047
14	.417	.0200	1.41	.0169	.646	.57	.052
15	.526	.0990	7.42	.0143	.891	.56	.046
16	.835	.0100	1.17	.0140	1.265	.56	.045
17	.835	.0200	2.41	.0144	1.275	.56	.047
18	.947	.1557	21.50	.0146	1.660	.57	.045
19	1.664	.0430	9.96	.0140	2.560	.61	.038
20	2.805	.0330	13.30	.0144	4.280	.68	.031

[a] Molal with respect to hydrogen ion.

[b] There is a slight inconsistency inherent in our calculations of the values of χ, inasmuch as the concentrations for the rate measurements are recorded as moles per liter while the activity data are expressed in terms of molalities (moles per 1000 g. of water). This difference is negligible for dilute solutions, but increases with the concentration; for example, it would introduce an error of about 1.5% in the value of the ionic strength computed for a solution 0.25 *M* in respect to sulfuric acid and 0.10 *M* in respect to potassium bromide.

ments ($\mu < 1.0$) of Table II. The fact that the average value of χ is 10% higher in Table II than in Table I may be without theoretical significance. This departure could be explained as due to a constant negative error, of about 4%, in the measured values of the activity coefficient; or as due to a constant positive error, of about 10%, in the measured values of the rate in these solutions, caused by impurities in the sulfuric acid or potassium bromide used. Neither of these suggestions, however, seems very probable.

These same data, as well as the approximate data of Tables V and VI of Ref. 1, have been represented graphically[6] in Fig. 1. The square root was substituted for the first power of the ionic strength in order that the plot might be more readily intelligible in the dilute range in which the most of the experiments were performed. Because of the abundance and

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[6] Compare (a) Ref. 1, Fig. 2. Also (b) Livingston and Bray, THIS JOURNAL, **47**, 2069 (1925), Fig. 2.

apparent accuracy of the data for dilute solutions, we can obtain a value for K at infinite dilution by direct extrapolation; we will take $K = 0.043$ as our standard value. It is apparent that the rate is not proportional to the product of the stoichiometrical concentrations of the components, for if this were true (that is, if Equation 1 were exact) all of the experimental points should lie along a straight horizontal line passing through 0.043. On the other hand, if Equation 2 were true, then

$$K = 0.043\ \gamma^2 \tag{3}$$

We have used this expression to obtain the two curves of Fig. 1. If Equation 3 were exact and there were no experimental errors involved in either the rate or activity measurements, the experimental points for hydrobromic acid solutions should fall on Curve I, and the points for sulfuric acid—potassium bromide solutions should fall on Curve II, and in so far as the ionic strength principle holds, the remaining points should fall on Curve I.

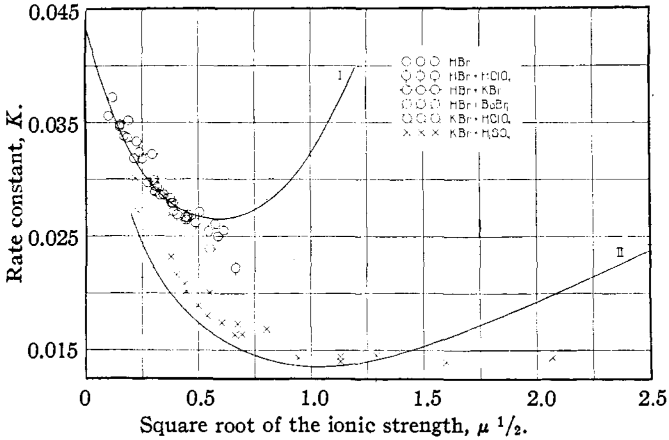

Fig. 1.—Analysis of the rate data.

We may conclude from these facts that Equation 2 is, and that Equation 1 is not, a satisfactory empirical equation for these data, at ionic strengths less than unity. At higher ionic strength there is apparently a negative departure from the predictions of Equation 2.

The Steady-State Function in Terms of the Activity Product of Hydrobromic Acid[6b]

The complete analysis of a simple case of chemical catalysis of this type involves a knowledge of two empirically determined quantities, the reaction-rate coefficient K, and the steady-state function[3] R. Since the former has proved to be a function of the activity rather than of the concentration of the "catalyst," it would appear quite probable that the latter should also involve activities, and indeed it follows from the mechanism of the reaction[3] that it must involve activities. As a first approximation, we shall assume that the concentration of bromine, corrected for tribromide formation, is equal to its activity. We may now define the steady-state function

$$\rho = R/\gamma^4 = (\mathrm{Br_2})/(\mathrm{H^+})^2(\mathrm{Br^-})^2\gamma^4 \qquad (4)$$

For the sake of brevity, we shall not quote all of the data in detail, but shall list only average values, corrected and uncorrected, for the several tables of Refs. 1 and 3. In the following table the first column gives reference to the source of the data, the second and third list the average values and the average percentage deviation, for the corrected and uncorrected steady-state functions.

TABLE III

RELATION OF THE STEADY-STATE FUNCTION TO THE ACTIVITY OF HYDROBROMIC ACID

Reference to data				
Ref.	Table	Expts.	$R = (\mathrm{Br_2})/(\mathrm{H^+})^2(\mathrm{Br^-})^2$	$\rho = R/\gamma^4$
3	III	1–12	0.21 ± 28%	2.0 ± 24%
3	IV	1–12	.21 ± 23%	1.6 ± 13%
1	I	1–3	.45 ± 31%	2.6 ± 32%
1	II	1–4[a]	.55 ± 16%	1.5 ± 15%
1	V	1, 2, 5	.35 ± 14%	0.9 ± 20%
1	VI	1, 4, 8	.40 ± 20%	1.0 ± 19%
1	No. A, p. 2051.		.0080	1.3

[a] Two additional measurements, corresponding to Expts. 13 and 15 of Table I, have been included in this average value. The values of R and ρ for Expt. 13 are 0.54 and 1.4, respectively; for Expt. 14, 0.53 and 1.4.

The first three lines refer to measurements in solutions containing sulfates; the fourth, fifth and sixth, to solutions of hydrobromic acid, hydrobromic and perchloric acids, and hydrogen and potassium bromides, respectively; the seventh to a solution 0.1881 M and 0.492 M in respect to hydrobromic acid and sodium sulfate. In the last-mentioned case, the value of the activity coefficient of hydrobromic acid, 0.281, was computed by means of the principle outlined in Ref. 2, p. 51. The values of R vary over a 74-fold range, those of ρ over a 2.9-fold range. The systematic variations observed within the various tables are largely eliminated by applying the activity correction. Probably the most accurate data are those given in Tables III and IV of Ref. 3, and Table II of Ref. 1. The weighted average of ρ for these three tables is 1.7 ± 0.2.

Summary

1. It has been shown that the steady-state rate of decomposition of hydrogen peroxide in a bromine-bromide solution can be represented by an empirical equation of the following form, for all solutions, including those containing sulfates, the ionic strength of which is less than unity.

$$-d(\mathrm{H_2O_2})/dt = 0.043\ (\mathrm{H_2O_2})(\mathrm{H^+})(\mathrm{Br^-})\gamma^2$$

At higher concentrations there is a negative departure from this law.

2. It has been shown that the constancy of the steady-state function for this catalytic reaction can be greatly improved by substituting activities for the concentrations of all electrolytes involved. The average value of the steady-state function, so corrected, is 1.7.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE SEPARATION OF THE ELEMENT CHLORINE INTO ISOTOPES. THE LIGHT FRACTION

BY WILLIAM D. HARKINS AND FRANCIS A. JENKINS

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1. Introduction

In January, 1920 Harkins and Broeker[1] *obtained the largest separation* of the isotopes of chlorine thus far reported. They obtained about 10 g. of chlorine of atomic weight 35.515, that is, with an atomic weight 0.058 higher than that of the ordinary element. Two other separations of the heavy fraction from chlorine[2] have been reported from this Laboratory. The present paper describes the results of a series of diffusions of hydrogen chloride through the stems of church-warden smoking pipes at atmospheric pressure. The diffusions were carried out in such a way as to obtain chlorine which has a lower atomic weight than the ordinary element. The decrease in atomic weight amounted to 0.039 unit. Thus the total extreme separation thus far obtained in this Laboratory amounts to 0.097 unit, *or one part in 365.* This is the greatest relative difference in atomic weight obtained by artificial means for any element.

2. *Experimental Part*

Construction and Operation of the Apparatus.—The tubes used to give a porous wall for the diffusion were the stems of church-warden pipes made in Scotland, since these had been found to have finer pores than any of the other porous porcelain available. They were carefully selected from the pipestems used in similar earlier work in this Laboratory. They had an average inside diameter of 2.0 mm. and a wall thickness of 2.2 mm. The small inside diameter aids in securing a thorough mixing of the gas.

Great care was taken in the selection of the tubes to insure absence of small leaks, and to obtain the proper degree of porosity. One end of the tube under investigation was first tightly closed with sealing wax and the other connected to an air pressure line and a manometer. The pipestem was then inserted in a glass jacket provided with an exit connected with a device for measuring the rate of efflux of the air. The air pressure was then regulated so that the manometer indicated an excess of 20 cm. inside the tube, and the velocity of diffusion of air into the jacket was measured, keeping the pressure

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[1] Harkins and Broeker, *Science*, **51**, 289 (1920); *Phys. Rev.*, **15**, 74 (1920); *Nature*, **105**, 230 (1920).

[2] Harkins and Hayes, THIS JOURNAL, **43**, 1803 (1921). Harkins and Liggett, *J. Phys. Chem.*, **28**, 74 (1924).