degree in the values of $(F^\circ - E_0^\circ)/T$, which is ample accuracy for most practical thermodynamic purposes.

Summary

The following form of expression is proposed for the approximate representation of heat capacities of solids and gases at high temperatures

$$C_p = a + bT + cT^{-1/2}$$

It is shown that for several typical substances for which accurate data are available, the heat capacity, heat content, and free energy may be represented with sufficient accuracy for thermodynamic computations by this expression and its integrated forms.

ANN ARBOR, MICH. RECEIVED OCTOBER 24, 1934

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

The Kinetic Salt Effect in the Fourth Order Reaction $BrO_3^- + Br^- + 2H^+ \longrightarrow$. Ionization Quotients for HSO_4^- at 25°

BY WILLIAM C. BRAY AND HERMAN A. LIEBHAFSKY

In the present investigation of the rate law, $-d(BrO_3^-)/dt = k(BrO_3^-)(Br^-)(H^+)^2$, initial rates of the reaction

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \quad \text{(I)}$$

have been measured at 25°, and in the presence of added perchlorate, in order to obtain values of k that may be compared directly with those obtained by Young and Bray[1] in their study of the reaction

$$BrO_3^- + 3H_2O_2 = 3O_2 + Br^- + 3H_2O \quad \text{(II)}$$

in perchloric acid solutions. One of the reasons for undertaking this work was to determine whether, at low ionic strength, the specific rate, k, increases rapidly in the manner required by the conclusions of Young and Bray. It also seemed desirable to re-examine the earlier results in sulfate solutions of Skrabal and Weberitsch[2] (Reaction I) and of Bray and Davis[3] (Reaction II), and to analyze them by a method which distinguishes between the change of k due to the presence of HSO_4^- and that due to variation in ionic strength.

In each experiment all the bromine liberated in the time allowed was determined iodimetrically in the reaction flask by means of an accurately standardized 0.02 M sodium thiosulfate solution. The reaction, I, was stopped by adding a solution which contained the necessary amount of phosphate buffer and a large excess of potassium iodide. This method of determining bromine in the presence of bromate is not new, and the precautions necessary for accurate iodimetric analysis need not be described in detail.

The volume of each mixture was usually 250 cc. and was smaller only when the concentrations of the reacting substances were rather high. The flasks used had closely fitting glass stoppers, which were sealed with paraffin in the long-time experiments with very dilute solutions. The gas space above the solution was not large. The stock solutions of sodium bromate, hydrobromic acid, sodium bromide and magnesium perchlorate and the distilled water were brought to the temperature of 25° before mixing. The perchlorate solution was prepared by neutralizing a measured quantity of very concentrated perchloric acid solution with magnesium oxide, diluting to a definite volume, and adjusting the concentration of hydrogen ion to a value equal to or slightly greater than 10^{-7} molal.

With the above procedure it was possible to determine accurately the quantity of bromine liberated before the concentration of any reactant had decreased by a large percentage amount, and, therefore, to calculate k by means of the fourth order differential equation. Average rather than initial concentrations were used, and all concentrations were expressed as moles per liter. This "method of constant rates" has been discussed by a number of investigators,[4] and methods of obtaining exact values of k have been described by De Lury[4b] and by Skrabal and Weberitsch.[2] Since in our experiments the product of the initial concentrations never exceeded the product of the average concentrations by more than 10.5%, the error in k due to our method of calculation never

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[1] Young and Bray, THIS JOURNAL, **54**, 4284 (1932).

[2] Skrabal and Weberitsch, *Monatsh.*, **36**, 211 (1915).

[3] Bray and Davis, THIS JOURNAL, **52**, 1427 (1930).

[4] See, for example, (a) Lash Miller and Bray, *J. Phys. Chem.*, **7**, 92 (1903); (b) De Lury, *ibid.*, **7**, 239 (1903); (c) **10**, 423 (1906); (d) Skrabal and Weberitsch, Ref. 2.

exceeded a few tenths of a per cent. It was clearly not worth while to estimate and add this small correction.

The results of Skrabal and Weberitsch[2] in sulfate solution, obtained by means of the method of constant rates, prove that there are no appreciable initial disturbances in Reaction I, and therefore justify the calculation of k from a single rate measurement.

The experimental data at ionic strengths less than $\mu = 1$ are presented in Fig. 1: values of ($^1/_4$) log k are plotted against $\mu^{1/2}$. The factor, $^1/_4$, corresponds to the exponent, 4, in the equation, k/γ^4 = a true constant, given by Young and Bray.[1] (They concluded that the activity coefficient, γ, is equal to γ_{HBr} when the ionic strength is less than 0.5.) This method of plotting was adopted because it furnishes an excellent representation of the actual experimental data, and enables k^0, the value of k at $\mu^{1/2} = 0$, to be estimated accurately by comparison with a family of log γ curves. The method is closely related to that used by Randall[5] in interpreting equilibrium and electromotive force data.

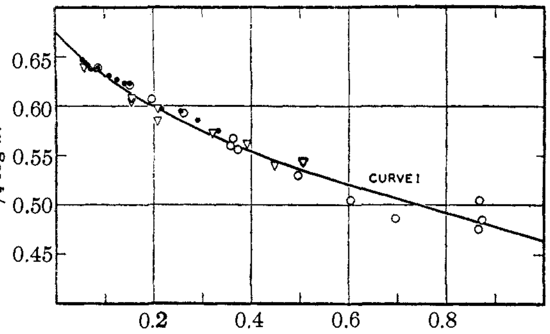

Fig. 1.—Variation of k with ionic strength. Reaction I: $BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$. The electrolyte is mainly HBr, ●; NaBr, ▽; $Mg(ClO_4)_2$, ○. *Cf.* Table I.

Three sets of experiments are shown, in which the ionic strength was due mainly to hydrobromic acid, sodium bromide and magnesium perchlorate, respectively. In the first two series the bromate concentration was varied from 3.74 to 9.58 (10^{-4}) M, and the lowest concentration of hydrogen ion or bromide ion was 2.16 (10^{-3}) M. In the perchlorate series the concentration of bromate was always in the neighborhood of 3.80 (10^{-4}) M, and that of hydrobromic acid was near 7.35 (10^{-3}) M for all ionic strengths at which only one experiment was carried out. Near $\mu^{1/2}$ = 0.35, and also near $\mu^{1/2}$ = 0.85, there are given in Fig. 1 the results of a group of three experiments, in which the concentrations of hydrobromic acid were near 0.00735, 0.0111 and 0.0184 M. An average of the spreads for these two groups probably gives a fair estimate of the accuracy of our measurements. In the group at the lower (higher) ionic strength, the intermediate value of k was obtained at the lowest (highest) acid concentration: the addition of magnesium perchlorate even in moderate amounts thus does not alter the manner in which hydrobromic acid enters into the rate law. There is in Fig. 1 little if any evidence of a difference in the kinetic salt effects of the three electrolytes up to $\mu^{1/2}$ = 0.5.

The points in the diagram are represented fairly well by a single curve, which corresponds closely to the ($^1/_2$) log $\gamma_{\mathrm{BaCl_2}}$ curve in a $\mu^{1/2}$ diagram. Extrapolation to $\mu^{1/2}$ = 0 by means of this curve yields the value k^0 = 506, which is only 6.3% less than the value, 540, selected by Young and Bray.

The results of Young and Bray[1] at 25° (Reaction II) are plotted in Fig. 2. In the range of the measurements, $\mu^{1/2}$ = 0.23 to 0.9, all the points are close to a single, rather flat curve. Extrapolation by means of the log γ curve for HCl or HBr confirms the value k^0 = 540. As the log γ curves for these acids are the highest in the family of log γ curves referred to above, a distinctly lower value of k^0 can be obtained from these data only by using another method of extrapolation. Examination of the data shows

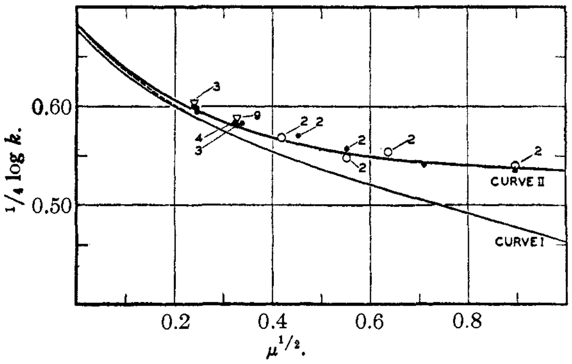

Fig. 2.—Variation of k with ionic strength. Data of Young and Bray. Reaction II: $BrO_3^- + 3H_2O_2 = 3O_2 + Br^- + 3H_2O$. The electrolyte is mainly $HClO_4$, ●; $HClO_4$ with some NaBr added initially, ▽; $NaClO_4$ and $HClO_4$, ○; $NaClO_4$, $HClO_4$ and some NaBr, ▲. ▽ 9 represents the average of 9 experiments. *Cf.* Table I.

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(5) (a) Randall and Vietti, THIS JOURNAL, **50**, 1526 (1928); (b) Randall, *J. Chem. Educ.*, **8**, 1062 (1931).

that the kinetic salt effects are nearly identical for perchloric acid and sodium perchlorate up to $\mu^{1/2} = 0.7$. This is a striking result, for these electrolytes, when added to 0.1 *M* hydrochloric acid, have widely different effects[6] on γ_{HCl}. It therefore seems probable that in this range of ionic strength the γ-function that measures the decrease in the specific rate of this reaction would not be altered if other uni-univalent electrolytes were added, or even magnesium perchlorate up to $\mu^{1/2} = 0.5$.

Data corresponding to the curves of Figs. 1 and 2 are summarized in Table I. The ionic strength is calculated from concentrations in moles per liter. Values of log γ may be obtained by subtracting ($^1/_4$) log k^0 from ($^1/_4$) log k.

TABLE I

VALUES OF *k* BASED ON RATE MEASUREMENTS OF REACTIONS I AND II (*cf.* FIGURES 1 AND 2)

		($^1/_4$) log k				
$\mu = \mu_c$	$\mu^{1/2}$	Reaction I	Reaction II	k(I)	k(II)	k(I) is less than k(II) by, %
0	0	(0.676)	(0.683)	(506)	(540)	6.3
0.0025	0.05	.652	(.659)	406	(433)	6.3
.01	.10	.632	(.639)	337	(360)	6.4−
.04	.20	.600	.607	251+	258−	6.3
.09	.30	.576	.585	201	219	8.2
.16	.40	.554	.569	165	189	12.8
.25	.50	.537	.558	141	171	17.5
.36	.60	.522	.550	122	159	23.2
.49	.70	.507	.545	107	151	29.1
.64	.80	.492	.541	93	146	36.3
.81	.90	.478	.538+	82	142+	42.2
1.00	1.00	.463	.536	71	139	48.9

The values of the specific rate based on Reaction I are always less than those based on Reaction II. The difference is large at high ionic strength, decreases rapidly to about 6% at $\mu^{1/2} = 0.2$, and therefore probably approaches zero at low ionic strength. The constant percentage difference below $\mu^{1/2} = 0.2$ shown in the table is due to the method of extrapolation, and is not to be regarded as an experimental result.

The very large divergence at high ionic strength may be due in part to a difference in the kinetic salt effects of sodium and magnesium perchlorates; but, as we have seen above, such specific differences seem in this case to be very small below $\mu^{1/2} = 0.5$ to 0.7. There remains in the range $\mu^{1/2} = 0.2$ to 0.6 a discrepancy of 6 to 20% in the values of k, which we believe to be too large to be accounted for by a systematic error of measurement in the one or other set of measurements.

A discrepancy of this kind would signify that there is a retarding effect in Reaction I which is absent (or at least smaller) in Reaction II. In the latter reaction, hydrogen peroxide (as well as bromide ion) is available for the removal of the various reactive compounds intermediate between bromate and bromine, so that these compounds probably accumulate to a greater extent in I than in II. The discrepancy in question may be explained by assuming that the rate-determining step of the fourth order reaction is reversible, since the maximum rate could then be obtained only when the intermediate product in this step is removed with sufficient rapidity. It may be noted that chlorine has a marked retarding effect in the complicated reaction[7] between chlorate and chloride ions in acid solution, and that in this case the simple fourth order reaction has been demonstrated only in the presence of a "chemical depolarizer,"[8] like iodide.[4a]

It would seem, therefore, that hydrogen peroxide is a better depolarizer for the bromate–bromide reaction than is hydrobromic acid at low concentration, and that this fact necessitates the use of two types of log γ curves in extrapolating the two sets of results in Fig. 2. We are consequently assuming that Curve I would extrapolate to the origin of Curve II, as indicated by the broken line in Fig. 2, if the retarding effect gradually disappeared in the region of very low concentrations, and that $k^0 = 540$ at 25°.

The analogous iodate–iodide reaction is ordinarily of the fifth order, but becomes fourth order at very low concentrations of iodide.[9] Bray and Liebhafsky[10] concluded that the fourth and fifth order reactions have independent rate-determining steps, and discussed possible intermediate compounds. Recently Skrabal[11] has published a comprehensive discussion of these and related reactions, and has considered the possibility that a fifth order bromate–bromide reaction might occur at high concentrations of bromide ion. We have found no evidence of such a reaction at ionic strengths below 0.7 (and concentrations of hydrobromic acid not greater than 0.1 *M*), but its existence is indicated by the results of some experiments at very high ionic strengths.

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[6] Murdock and Barton, THIS JOURNAL, **55**, 4077 (1933).

[7] Luther and MacDougall, *Z. physik. Chem.*, **62**, 199 (1908).

[8] Skrabal, *Z. Elektrochem.*, **30**, 124 (1924).

[9] Abel and Hilferding, *Z. physik. Chem.*, **136**, 186 (1928); *cf.* Skrabal, Ref. 8.

[10] (a) Bray, THIS JOURNAL, **52**, 3582 (1930); (b) Liebhafsky, *ibid.*, **53**, 2083 (1931).

[11] Skrabal, *Z. Elektrochem.*, **40**, 231 (1934).

The magnesium perchlorate series of Fig. 1 was extended to ionic strengths near 3, and the sodium bromide series to ionic strengths above 4. In the latter series, values of k as high as 800 were found at $C_{\text{NaBr}} = 4.2\ M$ and $C_{\text{H}^+} = 0.009\ M$; the results furnish at least qualitative evidence for the existence of the fifth order reaction corresponding to the differential equation $d(\text{BrO}_3^-)/dt = k'(\text{BrO}_3^-)(\text{Br}^-)^2(\text{H}^+)^2$. In the magnesium perchlorate series, so long as the concentration of hydrobromic acid did not exceed 0.007 M, the values of k were not far removed from Curve I produced. However, at $\mu = 3$, k was found to increase with increasing concentrations of hydrobromic acid, even at those concentrations for which no such effect had been observed at low ionic strength; and the increase was more rapid than had been indicated by the sodium bromide experiments. Such results are difficult to understand, and show further investigation to be necessary.

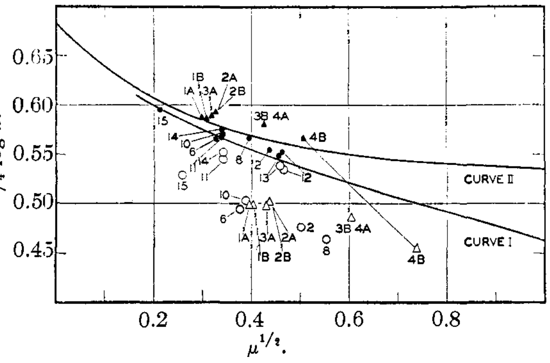

Fig. 3.—Variation of k with ionic strength in presence of sulfate. Reaction I: uncorrected, Table IIA, ○; corrected for HSO_4^-, Table V, ●. Reaction II: uncorrected, Table IIIA, △; corrected for HSO_4^-, Table V, ▲. Curves I and II are from Figures 1 and 2.

The results of the rate measurements in sulfate solutions,[2,3] and of our calculations, are presented in Fig. 3 and Tables II to VI. The original data, corresponding to complete ionization of sulfuric acid, are given in Tables II and III, and are represented by the lowest points in the diagram. The effect of the presence of HSO_4^- is illustrated by the slanting, nearly straight line drawn through one point, 4B: $(^1/_4)\log k$ increases and $\mu^{1/2}$ decreases as smaller and smaller values are assumed for the equilibrium quotient

$$K_{\text{HSO}_4^-} = C_{\text{H}^+}C_{\text{SO}_4^{--}}/C_{\text{HSO}_4^-}$$

A point on a line may be determined as follows. Assume any value of the specific rate, k, greater than the uncorrected value k', and calculate the concentration of hydrogen ion from the relation

$$k(C_{\text{H}^+})^2 = k'(2C)^2$$

where C is the concentration of sulfuric acid in moles per liter. The values of μ, $\mu^{1/2}$ and $K_{\text{HSO}_4^-}$ may then be determined, since $C_{\text{SO}_4^{--}} = C_{\text{H}^+} - C$ and $C_{\text{HSO}_4^-} = 2C - C_{\text{H}^+}$. It is evident that two sets of equilibrium quotients may be calculated from each set of kinetic data in sulfate solution, since each line cuts the two curves, I and II.

The values of $K_{\text{HSO}_4^-}$ shown in Tables II and III are obtained in this way. All the kinetic results[2,3] at 25° are included in IIA and IIIA. In Nos. 11, 12, 13 and 15, Table II, the values of (k) tabulated by Skrabal and Weberitsch were used (and should not have been changed by Young and Bray). It is important to note that a small error in (k) may alter greatly the calculated value of $K_{\text{HSO}_4^-}$; thus in No. 12, if the observed specific rate had been 132 instead of 137, $K_{\text{HSO}_4^-}$ would have been 0.073 instead of 0.110. It is therefore remarkable that only one result, No. 9, must be rejected; and that the two sets of $K_{\text{HSO}_4^-}$ values in Tables IIA and IIIA are in reasonably close agreement. This agreement, together with the divergence of the ionization quotients in Tables IIB and IIIB, leads us to conclude that the kinetic results in sulfuric acid solution are consistent with those in perchloric acid solution only when the over-all reaction is the same in the two sets of experiments. Therefore, the difference, whatever its cause, between Curves I and II in perchloric acid solutions in the range $\mu^{1/2} = 0.2$ to 0.6 appears in sulfuric acid solutions also.

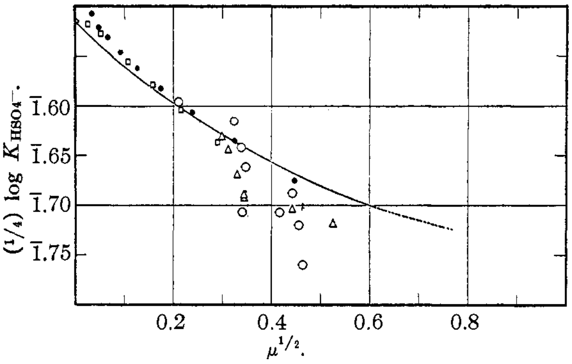

Fig. 4.—$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{--}$. Equilibrium data at 25°. Sherrill and Noyes, conductance measurements; □, H_2SO_4; ●, NaHSO_4; ⊳, limiting value at $\mu^{1/2} = 0$. Calculated from rate measurements; ○, Table IIA; △, Table IIIA.

TABLE II

VALUES OF $K_{HSO_4^-}$ CALCULATED FROM THE KINETIC DATA OF SKRABAL AND WEBERITSCH AT 25°. REACTION I: $BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$

A. By comparison with Curve I

Expt.	$C_{H_2SO_4}$	C_{KBrO_3}	C_{KBr}	(k)	$\mu^{1/2}$ Uncorrected	(1/4) log k Uncorrected	$\mu^{1/2}$ Curve I	(1/4) log k Curve I	C_{H^+} calcd.	$K_{HSO_4^-}$	(1/4) log $K_{HSO_4^-}$
15	0.02	0.001	0.005	130	0.257	0.529	0.210	0.598	0.0291	0.0243	$\bar{1}.596$
6	.03	.0005	.05	95	.375	.494	.324	.571	.0422	.0290	$\bar{1}.615$
9	.003	.001	.1	120?	.332	.520	.328	.569	.00478	.0069?	Reject
11	.005	.001	.1	151	.341	.545	.338	.567	.00902	.0370	$\bar{1}.642$
14	.005	.002	.1	162	.342	.552	.340	.566	.00939	.0675	$\bar{1}.707$
10	.03	.01	.05	103	.387	.503	.347	.565	.04514	.0443	$\bar{1}.662$
8	.10	.001	.005	72	.553	.464	.416	.552	.1336	.0675	$\bar{1}.707$
2	.05	.001	.1	80	.501	.476	.442	.547	.0720	.0566	$\bar{1}.688$
13	.0025	.001	.2	142	.457	.538	.456	.545	.00485	.0760	$\bar{1}.720$
12	.005	.001	.2	137	.465	.534	.464	.543	.00960	.110	$\bar{1}.760$

B. By comparison with Curve II

Expt.	Curve II				
15	0.205	0.606	0.0205	0.0189	$\bar{1}.569$
6	.317	.582	.0401	.0202	$\bar{1}.576$
8	.390	.570	.1229	.0364	$\bar{1}.640$
2	.429	.565	.0664	.0323	$\bar{1}.627$
12	.462	.562	.00880	.0277	$\bar{1}.610$

TABLE III

VALUES OF $K_{HSO_4^-}$ CALCULATED FROM THE KINETIC DATA OF BRAY AND DAVIS. REACTION II: $BrO_3^- + 3H_2O_2 = 3O_2 + Br^- + 3H_2O$

A. By comparison with Curve II

Expt.	$C_{H_2SO_4}$ moles/liter	C_{KBrO_3}	k_2	$\mu^{1/2}$ Uncorrected	(1/4) log k Uncorrected	$\mu^{1/2}$ Curve II	(1/4) log k Curve II	C_{H^+} calcd.	$K_{HSO_4^-}$	(1/4) log $K_{HSO_4^-}$
1A	0.05	0.00587	98	0.395	0.498	0.299	0.5855	0.06677	0.0336	$\bar{1}.632$
1B	.06	.01174	98	.402	.498	.312	.582	.06785	.0377	$\bar{1}.644$
3A	.06	.00489	97	.430	.497	.330	.579	.08213	.0480	$\bar{1}.670$
2A	.06	.00978	100	.436	.500	.344	.577	.08420	.0570	$\bar{1}.690$
2B	.06	.00978	101	.436	.501	.345	.5765	.08476	.0595	$\bar{1}.694$
3B	.12	.00489	76	.604	.470	.443	.564	.1558	.0654	$\bar{1}.704$
4A	.12	.00493	76	.604	.470	.443	.564	.1558	.0654	$\bar{1}.704$
4B	.18	.00493	65.6	.738	.454	.525	.556	.2253	.0754	$\bar{1}.719$

B. By comparison with Curve I

Expt.	Curve I				
1A	0.312	0.573	0.07072	0.0500	$\bar{1}.675$
2A	.362	.5615	.0904	.0926	$\bar{1}.742$
3B, 4A	.483	.540	.1740	.1420	$\bar{1}.788$
4B	.593	.522	.2635	.2240	$\bar{1}.840$

At low ionic strengths, the values of $K_{HSO_4^-}$ should increase rapidly with the ionic strength; and (1/4) log $K_{HSO_4^-}$ when plotted in a $\mu^{1/2}$ diagram should yield a curve similar to one of the family of log γ curves.[5] In Fig. 4 are represented the results from Tables IIA and IIIA, and those of Sherrill and Noyes[12] based on conductance measurements of sulfuric acid and sodium acid sulfate. The results are more concordant than was to be expected. We accepted the limiting value, $K^0_{HSO_4^-} = 0.0115$,[13] adopted by Sherrill and Noyes, and drew the curve in Fig. 4 to agree with the $\frac{1}{2}$ log $\gamma_{Na_2SO_4}$ curve.

TABLE IV

$HSO_4^- = H^+ + SO_4^{--}$ EQUILIBRIUM QUOTIENTS AT 25°
(*Cf.* FIG. 4)

$\mu^{1/2}$	$\log \frac{K_{HSO_4^-}}{K^0_{HSO_4^-}}$	$10^2 K_{HSO_4^-}$
0	0	1.15
0.05	0.024	1.43
.1	.045	1.74
.2	.0815	2.43
.3	.113	3.25
.4	.1405	4.19
.5	.165	5.25
.6	.185	6.31
.7	.200	7.28

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[12] Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926).

[13] This is nearly the same as the value 0.0120 recently found by Hamer, THIS JOURNAL, **56**, 860 (1934), in an extensive series of electromotive force measurements in dilute solutions, and temperatures ranging from 0 to 60°.

In Table IV are listed values of $K_{HSO_4^-}$ which correspond to the smooth curve in Fig. 4. It is believed that these results, in spite of their uncertainty at the higher ionic strengths, will prove useful in interpreting experimental data in dilute sulfuric acid solutions.

TABLE V

VALUES OF k, CORRECTED FOR PRESENCE OF HSO_4^-

Kinetic Data of Skrabal and Weberitsch, Table II

Expt.	$\mu^{1/2}$	$10^2 K_{HSO_4^-}$	$10^3 C_{H^+}$	k
15	0.212	2.51	29.4	241
6	.327	3.50	43.3	182
11	.339	3.60	9.0	186
14	.339	3.60	9.0	200
10	.342	3.63	43.6	191
8	.395	4.13	124.9	185
2	.437	4.58	69.8	164
13	.456	4.78	4.77	156
12	.463	4.84	9.2	162

Kinetic Data of Bray and Davis, Table III

Expt.	$\mu^{1/2}$	$10^2 K_{HSO_4^-}$	$10^3 C_{H^+}$	k
1A	0.298	3.25	66.4	222
1B	.308	3.31	66.6	221
3A	.319	3.42	78.3	228
2A	.327	3.48	78.4	234
2B	.327	3.48	78.4	236
3B, 4A	.425	4.45	147.8	210
4B	.506	5.32	215.6	183

By means of these values of $K_{HSO_4^-}$ we have calculated values of the specific rate, k, from the kinetic data in sulfuric acid solutions. The process is the reverse of that outlined above, and involves successive approximations. The results are listed in Table V and plotted in Fig. 3. As was to be expected from the method of evaluating $K_{HSO_4^-}$, the results of Skrabal and Weberitsch for Reaction I, are in general agreement with Curve I, and those of Bray and Davis for Reaction II with Curve II. The agreement would have been better if somewhat higher values had been assumed for $K_{HSO_4^-}$ above $\mu^{1/2} = 0.3$.

Summary

Initial rates of formation of bromine in the reaction, I, between bromate and bromide ions in acid solution were measured at 25° between ionic strengths as low as 0.003 and as high as 4.

Values of the specific rate, k, of this fourth order reaction were compared with those obtained by Young and Bray in their study of the reaction, II, in which bromate ion is reduced by hydrogen peroxide at ionic strengths between 0.06 and 0.8. These results were also compared with published kinetic data for the two reactions, I and II, in sulfuric acid solutions. The comparisons were made by plotting $^1/_4$ log k against $\mu^{1/2}$.

At low ionic strengths, k increases rapidly with decreasing ionic strength and the extrapolated value is in satisfactory agreement with the value, 540, calculated by Young and Bray. There is no evidence of specific salt effects when μ is below 0.3 to 0.5.

At ionic strengths above 0.02 the values of k from Reaction I are distinctly smaller than those from Reaction II, and the difference increases with increasing ionic strength. It is probable that the maximum rate of the fourth order reaction can be measured only when intermediate compounds are removed sufficiently rapidly by a chemical depolarizer, and that hydrogen peroxide is a better depolarizer than hydrobromic acid.

The large values of k obtained at high concentrations of sodium bromide furnish qualitative evidence for the existence of a fifth order bromate–bromide reaction. The results obtained in concentrated magnesium perchlorate solutions are difficult to understand, and indicate the need for further investigation.

Analysis of the kinetic data for sulfuric acid solutions yielded values of the ionization quotients, $K_{HSO_4^-}$, which are consistent with those calculated by Sherrill and Noyes from conductance measurements in more dilute solutions. It has been shown that the rapid increase to be expected in $K_{HSO_4^-}$ as the ionic strength is increased, which has been demonstrated by Sherrill and Noyes, continues into moderately concentrated solutions.

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