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

The Equilibrium Constant of the Bromine Hydrolysis and its Variation with Temperature

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Introduction

In 1910 Bray[1a] measured the conductivities of dilute aqueous bromine solutions in order to obtain therefrom the equilibrium constant for the bromine hydrolysis

$$Br_2 + H_2O \overset{K_1}{\rightleftharpoons} HBrO + H^+ + Br^- \quad (1)$$

This work was subsequently extended by Bray and Connolly,[1b] who gave the value $K_1 = (HBrO)(H^+)(Br^-)/(Br_2) = 5.2(10^{-9})$ at 25°. Some years later Jones and Hartmann,[2] as one result of a careful and thorough investigation, found that $K_1 = 0.57(10^{-9})$ at 0°.

Obviously it is generally desirable that an equilibrium constant be determined at more than two temperatures. That this is imperative for the hydrolysis of a halogen is evident from Jakowkin's[3] classic investigation of the chlorine hydrolysis. He found an anomalous variation with temperature for the K_1 of chlorine: $\log K_1$, when plotted against $1/T$, shows a curvature such that the corresponding ΔH becomes markedly larger as the temperature decreases. Accordingly, at the suggestion of Professor Bray, Mr. H. F. Galindo undertook to determine K_1 for bromine at several temperatures between 35 and 0°. His values[4] show a curvature in the $\log K_1$ *vs.* $1/T$ plot, but for 25 and 0° they are somewhat higher than those given above. The present investigation was undertaken to obtain another independent series of results in the same temperature range.

Dilute solutions of bromine were used because the proportion of tribromide (and polybromides) is decreased by dilution. The chief source of error in the conductance measurements is the presence of strong electrolytes introduced as impurities or formed in the reactions

$$3Br_2 + 3H_2O = 6H^+ + 5Br^- + BrO_3^-, \text{ and}$$
$$Br_2 + H_2O = 2H^+ + 2Br^- + {}^1/_2O_2$$

The second reaction does not occur if bright sunlight is avoided, and the first has now been shown to be negligible in dilute bromine solutions. In saturated solutions, however, this formation of hydrobromic and bromic acids is sufficiently rapid to cause a marked increase of the conductance with time,[5] and it is thus desirable to avoid bringing liquid bromine into contact with water in preparing solutions for conductance measurements; the dilute solutions employed in this investigation were therefore prepared by dissolving bromine vapor in water.

Materials.—Samples of bromine vapor were prepared as follows. The best quality of liquid bromine obtainable was allowed to stand overnight in contact with $BaBr_2 \cdot 2H_2O$ in order to remove traces of chlorine. It was then shaken vigorously with five successive portions of conductivity water and transferred to a separatory funnel. After half an hour, approximately half a dozen drops of liquid bromine were allowed to fall into each of several warm, dry, liter flasks. When vaporization was complete, the glass stoppers were placed in the flasks, which were later used as is described below. The hydrobromic acid solutions were prepared by diluting a 0.1 *N* stock solution, in turn prepared from redistilled hydrobromic acid and conductivity water.

One supply of water (sp. cond. at 25°, $1.0(10^{-6})$ reciprocal ohms), prepared by distilling first from alkaline permanganate and subsequently from barium hydroxide, was used for all measurements. The "water correction" was determined empirically as explained below.

Apparatus.—The cell (Cell II of Randall and Scott)[6] was of the Washburn type with dull platinum electrodes, and suited to acid concentrations below 0.004 *N*. A gallon Dewar vessel with Balsa wood cover, and provided with a stirrer, served as thermostat. A 1000-cycle vacuum tube oscillator in conjunction with a bridge of the type recently built by Leeds and Northrup according to the specifications of Jones and Josephs[7] was used for the conductivity measurements.

Procedure.—With everything else in readiness, a 200-cc. portion of conductivity water cooled to 0° was poured into a liter flask of bromine vapor. After shaking to dissolve the bromine, the solution was poured into the 250-cc. flask which served as the reservoir of the transfer apparatus. To this apparatus, designed to operate like a wash bottle, the cell, mounted in the Balsa wood cover of the Dewar vessel, was then connected. (Interchangeable glass joints were used throughout: at no time was the

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[1a] Bray, THIS JOURNAL, **32**, 932 (1910).

[1b] Bray and Connolly, *ibid.*, **33**, 1485 (1911).

[2] Jones and Hartmann, *Trans. Am. Electrochem. Soc.*, **30**, 295 (1916).

[3] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

[4] Galindo, Master's Thesis, University of California Library, 1931.

[5] The observed decrease in the rate of the reaction with dilution is in accord with the known experimental data on the rate of bromate formation; *cf.* Liebhafsky and Makower, *J. Phys. Chem.*, **31**, 1037 (1933).

[6] Randall and Scott, THIS JOURNAL, **49**, 636 (1927).

[7] Jones and Josephs, *ibid.*, **50**, 1049 (1928).

bromine employed ever in contact with organic matter.) By means of a two-way stopcock, air pressure was employed to fill transfer tube, cell and overflow tube with the solution; the stopcock was then turned to open the reservoir to the room, and approximately 100 cc. of solution was allowed to siphon out. At this point the flow was interrupted,[8] and approximately 10 g. of solution was siphoned into a flask containing an excess of slightly acid potassium iodide solution, care being taken to minimize volatilization of the halogens. (The flask was weighed before and after the sample was taken; the liberated iodine was titrated with standard thiosulfate solution.) The cell was then disconnected, stoppered, placed in the 0° Dewar vessel, and the conductivity measured. When constancy of the bridge reading showed that temperature equilibrium had been established, the cell was transferred to the Dewar vessel containing water at the next higher temperature to be investigated. By continuing this process, conductivity values for one sample of bromine could be obtained at five temperatures in less than two hours. After the measurement at the highest temperature (35°), the cell was returned to the ice-bath and another 0° value obtained. This second 0° value never differed appreciably from the first.[9]

Auxiliary Data.—For 25° the equivalent conductances of hydrobromic acid were obtained from

$$\Lambda_{25} = 427.8 - 132\sqrt{c} \qquad (2)$$

This equation represents an extrapolation of the results of Hlasko, as given in Landolt–Börnstein,[10] to the sum of 349.7 and 78.1, these being the equivalent conductances of hydrogen[11] and bromide[10] ions at infinite dilution and 25°. For any temperature and concentration, the equivalent conductances employed are calculable from

$$\Lambda_T = \Lambda_{25} \times \Lambda_T/\Lambda_{25} \qquad (3)$$

where Λ_{25} is the 25° conductance for the concentration in question, and the ratio Λ_T/Λ_{25} is the proper temperature coefficient, to be obtained from Table I, where are given the means of several series of measurements on hydrobromic acid solutions of approximately the concentrations encountered in the bromine work. Since these temperature coefficient determinations were carried out for the temperatures and in the cell used for the bromine measurements also, they provide an empirical means of evaluating K_1 at different temperatures from the latter. In the calculation of the temperature coefficients, the change of concentration due to thermal expansion was considered, the data for water being employed to evaluate it.

TABLE I

EQUIVALENT CONDUCTANCES OF DILUTE[a] HYDROBROMIC ACID SOLUTIONS AT VARIOUS TEMPERATURES

Temp., °C.	0.00	10.05	25.00	30.00	35.00
Λ_{25}/Λ_T	1.5992	1.2858	1	0.9315	0.8719
Λ_∞	266.6[b]	332.7	(427.8)	459.3	490.7

[a] Concentrations employed ranged from $2(10^{-4})$ to $6(10^{-4})M$. [b] The only datum that has been corrected for variation of cell constant with temperature.

At the close of the investigation, the values 3.642 at 25°, 3.641 at 18°, and 3.629 at 0° were determined for the cell constant, the 0.01 *D* potassium chloride solution recommended by Jones and Bradshaw[12] serving as standard; the results of a similar series, completed earlier, were somewhat higher, but showed the same unexpectedly large difference between the 18 and 0° values. In the evaluation of the bromine results, 3.642 was used throughout in calculating the specific conductances; any variation of cell constant with temperature is compensated by the empirically determined temperature coefficients.

The equivalent conductances of hydrobromic acid given in Table I for the different temperatures are each the product of 427.8 by the proper temperature coefficient. (For the dilute hydrobromic acid solutions employed, the temperature coefficient will differ but little from that for an infinitely dilute solution; these equivalent conductances may therefore be regarded as fairly accurate limiting values.) Correction for the variation of cell constant with temperature was made only for the 0° result; the data given above were used for this purpose. The new result for this temperature, 266.6, is in reasonable agreement with the sum of 222.5 and 43.1, the equivalent conductances of hydrogen and bromide ions at infinite dilution and 0° given in Landolt–Börnstein.[13]

The water employed in this investigation had a specific conductance × 10^6 of 0.5, 0.9 and 1.0 reciprocal ohms at 0, 18 and 25°, respectively, and proved sufficiently good for our purpose. Conductivity measurements on dilute hydrogen bro-

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[8] Since the surface bromine solution in the reservoir was never withdrawn during the filling of the cell, no great error could have been caused by volatilization of bromine within the reservoir. The short time required for the entire operation also tended to eliminate such an error, which would result from a difference of composition between the solution in the cell and the sample withdrawn for analysis.

[9] This evidence proves that the rate of the reaction $3Br_2 + 3H_2O = 6H^+ + 5Br^- + BrO_3^-$ is negligible in the dilute bromine solutions.

[10] Landolt–Börnstein, "Physikalische-chemische Tabellen," Verlag Julius Springer, Berlin, 1931, Ed. II, pp. 1049 and 1050.

[11] MacInnes, Shedlovksy and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

[12] Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

[13] Ref. 10, pp. 1061 and 1062.

mide solutions at 25° (ranging from $8(10^{-5})$ to $2(10^{-3})M$) gave concentrations usually somewhat higher than the true values, no "water correction" having been applied; subtracting three-fourths of the specific conductance of water satisfactorily eliminated the discrepancy, and this was therefore done for the data of Tables I and II. (Values for the specific conductance of water at other temperatures were found by interpolation and extrapolation of those given above.)

The effect of the tribromide equilibrium

$$Br_3^- \xrightleftharpoons{K_3} Br_2 + Br^- \qquad (4)$$

remains to be considered. In a dilute aqueous bromine solution, (H^+) and (HBrO) are equal; but, because of Br_3^- formation, (Br^-) is smaller by an amount easily calculable from $K_3 = (Br^-)(Br_2)/(Br_3^-)$. Throughout, the values of K_3 employed in the evaluation of (Br^-) were calculated from the general equation

$$\log K_3 = -(340/T) + 0.9100 - 1 \qquad (5)$$

which has been based principally upon the recent, accurate work of Griffith, McKeown and Winn.[14]

The addition of bromine to a moderately concentrated hydrobromic acid solution lowers not only (Br^-), but the conductivity of the solution as well. For example, Jones and Hartmann[2] found $23.5/43.7 = 0.54$ to be the ratio at 0° of the equivalent conductance of Br_3^- to that of Br^-. Assuming this ratio to be unchanged[15] at 25°, we find that converting hydrobromic acid completely to HBr_3 lowers the conductivity of a hydrobromic acid solution by 8.44% ($0.46 \times 78.1/427.8 = 0.0844$). Ordinarily, tribromide formation is far from complete, so that the percentage lowering of the conductance is given by $8.44 \times (Br_3^-)/\Sigma(Br^-)$. We shall assume this expression to be valid over the temperature range of our measurements.[15]

If a bromine solution has a specific conductance κ, it is convenient in actual practice to calculate first an uncorrected value for $(H^+) = (HBrO)$, thus

$$(H^+)_u = (HBrO)_u = \kappa/\Lambda \qquad (6)$$

$\Sigma(Br^-)/(Br_3^-)$ may then be evaluated, and the correct value of (H^+) obtained from

$$(H^+) = (H^+)_u/F_\Lambda, \text{ where } F_\Lambda = 1 - 0.0844\Big/\frac{\Sigma(Br^-)}{(Br_3^-)} \qquad (6a)$$

The equilibrium constants calculated in this manner from the experimental data are given in Table II.

Recalculation of Older Results.—In order to facilitate comparison, we shall recalculate results already in the literature before discussing those recorded in Table II.

Jones and Hartmann[2] took 240 to be the mobility of hydrogen ion at 0°; a better value[13] is 222.5. Also, they used $K_3 = 0.051$ for that temperature; Equation 5 gives 0.0462. Bray and Connolly[1b] mentioned the effect of Br_3^- formation on κ, but did not correct for it because the necessary data were not then available. For the value of K_3 at 25°, they employed 0.063, which is larger than 0.0588, given by Equation 5. For both investigations, the low value of K_3 affects the results primarily in that it lowers slightly the calculated (Br^-), and consequently tends to decrease the recalculated value of K_1; the other corrections, however, operate on the specific conductivities of the solutions and therefore affect, not only (Br^-), but (H^+) and (HBrO) as well and in such manner as to increase all three concentrations. Accordingly, we may expect a recalculation of these older results to yield for K_1 in dilute bromine solutions, higher values than those now given. Table III shows this expectation to be realized.

The lower values of K_1 from Tables II and III agree substantially among themselves although a trend, such that K_1 increases with (Br_2), persists in both sets of recalculated values. Recalculation has decreased this trend (from nearly 30% to, say, 20%) for the results of Bray and Connolly, to which no correction for Br_5^- formation has been applied, and for which original and recalculated values of K_1 may therefore be justifiably compared. The original values of Jones and Hart-

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(14) Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

(15) That $\Lambda_{Br_3^-}/\Lambda_{Br^-}$ is nearly independent of temperature appears highly probable as this is known to be true of $\Lambda_{I_3^-}/\Lambda_{I^-}$, for which Bray and MacKay [THIS JOURNAL, **32**, 914 (1910)] found $41.0/76.5 = 0.54$ at 25°, while Jones and Hartmann [*ibid.*, **37**, 241 (1915)] obtained $22.8/43.4 = 0.53$ at 0°; each ratio differs surprisingly little from that given in the text for $\Lambda_{Br_3^-}/\Lambda_{Br^-}$. The second assumption, that the equivalent conductance of HBr_3 is 8.44% lower than that of hydrobromic acid, could hold strictly only if the equivalent conductances of all ions concerned varied in the same way with temperature. Since this is not the case, the assumption represents a convenient approximation that is certainly sufficient for our purposes.

Although it is barely possible that the new value of K_1 at 0° (*cf.* Table IV) might affect slightly the value of $\Lambda_{Br_3^-}$ to be deduced from the data of Jones and Hartmann, no significant change in K_1 could result from the use of the revised value of this equivalent conductance.

Jones and Hartmann have shown that Br_5^- has a lower equivalent conductance than Br_3^-; the lowering of conductivity due to pentabromide formation, however, is usually negligible because the concentration of this complex ion is ordinarily very small.

TABLE II

SUMMARY OF CONDUCTIVITY EXPERIMENTS

Series	$\kappa \times 10^6$	$\Sigma(Br^-)/(Br_3^-)$	F_Λ	$(HBrO) = (H^+)$	(Br^-)	(Br_2)	(Br_3^-)	$K_1 \times 10^9$
				0.00°, K_3 = 0.0462				
4	55.6	5.40	0.984	0.212	0.173	10.48	0.039	0.74
5	82.2	2.68	.969	.320	.200	27.51	.119	.74
6	88.3	2.47	.966	.344	.204	31.54	.140	.77
7	60.5	4.35	.981	.231	.178	13.81	.053	.69
				10.05°, K_3 = 0.0502				
4	92.7	5.83	0.986	0.285	0.236	10.40	0.049	1.84
5	137.2	2.84	.970	.430	.278	27.37	.152	1.88
6	146.4	2.60	.968	.459	.282	31.39	.177	1.89
7	101.6	4.66	.982	.314	.247	13.71	.067	1.77
				25.00°, K_3 = 0.0588				
4	174.8	6.74	0.988	0.416	0.355	10.25	0.062	6.0
5	257.3	3.17	.973	.624	.427	27.13	.197	6.1
6	274.3	2.89	.971	.666	.435	31.13	.230	6.2
7	192.0	5.33	.984	.459	.373	13.54	.086	5.8
				30.00°, K_3 = 0.0614				
5	308.5	3.27	0.974	0.695	0.482	27.06	0.213	8.6
6	328.2	3.07	.972	.741	.499	31.04	.242	8.8
7	230.4	5.53	.985	.513	.420	13.57	.093	8.2
				35.00°, K_3 = 0.0641				
5	364.9	3.38	0.975	0.769	0.541	26.97	0.228	11.9
6	388.3	3.07	.973	.821	.554	30.96	.267	12.0
7	273.0	5.78	.985	.568	.470	13.42	.098	11.3

All concentrations are millimoles/liter, but values of K_1 are given in moles/liter. Values of $\Sigma(Br_2) = (HBrO) + (Br_2) + (Br_3^-)$ are 10.73, 27.95, 32.03 and 14.09 millimoles/liter for Series 4, 5, 6 and 7, respectively.

TABLE III

RECALCULATED RESULTS OF OLDER CONDUCTIVITY MEASUREMENTS

All concentrations are millimoles/liter, but values of K_1 are given in moles/liter; values of κ will serve to identify the results in Table III.

$\kappa \times 10^6$	Recalcd. $K_1 \times 10^9$	Original $K_1 \times 10^9$
286[b]	0.96	0.58[a]
177	.74	.54
144	.75	.57
124	.71	.55
67	.72	.59
57	.68	.56
Selected	.69	.57
b. Measurements at 25° by Bray and Connolly		
727[b]	6.7	5.7
549	6.6	5.7
545	6.7	5.8
506	6.0	5.2
503	5.9	5.2
398	5.7	5.1
287	5.6	5.2
291	5.8	5.4
261	5.5	5.2
Selected	5.6	5.2

[a] The only set of K_1 values in Table II or III that has been corrected for Br_5^- formation. [b] Measurement for saturated solution.

mann show no trend only because Br_5^- formation was assumed in their calculation; had this assumption not been made, the value of K_1 for the saturated solution would have been approximately 0.87(10^{-9}). Comparison of this value with, say, 0.56(10^{-9}) (*cf.* Table III) shows that recalculation has decreased the trend also in these results, pentabromide formation being neglected.

After consideration of all results in Tables II and III, 0.69(10^{-9}) at 0° and 5.7(10^{-9}) at 25° may be chosen as the best values of K_1. At the low ionic strengths employed, activity and concentration are identical for non-electrolytes; but for electrolytes a slight correction, tending to increase K_1, must be applied. Expressed in terms of activities, the equilibrium constant for the bromine hydrolysis thus becomes 0.70(10^{-9}) at 0° and 5.8(10^{-9}) at 25°.[16]

Table II contains all measurements made above 25°. The results of the three series first completed have been omitted; these were carried out with bromine solutions of concentrations lower

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[16] A trivial inconsistency remains to be considered. In analyzing for $\Sigma(Br_2)$, no correction was made for the density of the bromine solutions. As it happened, however, this density was more nearly 1 g./cc. than that of pure water; the correction is thus negligible.

than any recorded, and in an attempt to discover the limit of (Br_2) below which accurate results could not be obtained. (Low (Br_2) minimizes not only the tri-bromide corrections, but also the danger of bromate formation.) The inclusion of these higher and less concordant results would contribute nothing of value. A final summary of K_1 values is given in Table IV.

TABLE IV

SUMMARY OF BEST VALUES FOR $K_1 \times 10^{-9}$ AT DIFFERENT TEMPERATURES

Investigators	0°	10°	25°	30°	35°
J. and H. (recalcd.)	0.68				
B. and C. (recalcd.)			5.6		
Liebhafsky	0.69	1.76	5.8	8.2	11.3
Computed	.76	1.80	(5.8)[a]	8.4	(11.3)[a]
Selected[b]	.70	1.78	5.8	8.3	11.3

[a] Value assumed in deriving the equation $\log K_1 = 1.37804 - 2866.1/T$, from which computed values were obtained. [b] Only these finally selected values for K_1 are expressed in *activities*.

In order to determine whether $\log K_1$ is a linear function of $1/T$, slope and intercept for such a function were calculated from the 25 and 35° values of this constant. Corresponding values of K_1 for the other temperatures are easily computed from the resulting equation (*cf.* Table IV, footnote *a*). A comparison of the computed values with those in the row above them indicates that ΔH for Reaction 1 must be very nearly constant over the temperature interval from 10 to 35°. The computed 0° value, however, is some 10% higher than the observed, an amount considerably larger than the uncertainty in the latter; and this corresponds to an increase in ΔH as the temperature is lowered from 10 to 0°. We conclude, therefore, that the anomalous temperature variation observed by Jakowkin[3] for the K_1 of chlorine exists for bromine also, though to a much less degree.

The Existence of Pentabromide Ion.—The results of earlier investigations point to the existence of Br_5^- at appreciable concentrations even in unsaturated bromine solutions. Griffith, McKeown and Winn,[14] in their study of the tribromide equilibrium, obtained remarkable constancy of K_3 without applying a pentabromide correction, although (Br_2) varied from 0.001 to 0.02 *M* in their experiments; they concluded ". . . that for solutions of low bromine content . . pentabromide formation is not appreciable; further, it is likely that previous estimates of its extent (in stronger Br_2 solutions) are too high."

Guided by this conclusion we have made no allowance for Br_5^- formation in our calculation of K_1. While our results indicate this procedure to be justified at bromine concentrations below, say, 0.02 *M*, the unmistakable increase of K_1 with (Br_2) at high (Br_2) for both sets of recalculated values in Table III points qualitatively to Br_5^- formation. Further, the increases of K_1 over $0.69(10^{-9})$ and $5.7(10^{-9})$ are approximately proportional to the change in (Br_2),[2] as the establishment of the equilibrium

$$Br_5^- \overset{K_5}{\rightleftharpoons} 2Br_2 + Br^- \qquad (7)$$

would require. Consequently, the existence of pentabromide becomes very plausible, and we may calculate what value of K_5 will account for the increase in K_1 as recalculated for the saturated bromine solutions. We find[17] $(Br_2)^2(Br^-)/(Br_5^-) = 0.025$ at 0° and 0.055 at 25°. Jones and Hartmann, from a set of experiments designed especially to yield K_5 (*cf.* Ref. 2, Table IX), concluded that $K_5 = 0.0246$ at 0°. Linhart[18] gave $K_5 = 0.052$ at 26.5° based on the measurements of Worley.[19] From the composition of the saturated solution at 25°, as given by Bray and Connolly,[1b] we find $K_5 = 0.12$, which is probably too high. The values $K_5 = 0.025$ at 0° and 0.050 at 25° are probably accurate to ±10%; and it is very unlikely that Br_5^- formation in a solution where $(Br_2) = 0.02$ *M* reduces (Br^-) by more than 1%. The first conclusion (given above) drawn by Griffith, McKeown and Winn is thus substantiated, but the second does not follow as a necessary consequence—our calculations indicate that some of the earlier estimates[2,18] of pentabromide formation are substantially correct.

Summary

1. The conductivities of aqueous bromine solutions have been measured at five temperatures ranging from 0 to 35°, and the values of K_1, the equilibrium constant for the bromine hydrolysis, calculated for these temperatures.

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[17] At 0° we take (Br^-) to be 0.69/0.96 times the Table III value for the saturated solution, or $1.29\ (10^{-4})$. At this (Br^-) and $(Br_2) = 0.254$, $(Br_3^-) = 7.09\ (10^{-4})$, since $K_3 = 0.0462$. Now, $\Sigma\ (Br^-) = (H^+) = (HBrO) = (Br^-) + (Br_3^-) + (Br_6^-)$; whence $(Br_5^-) \times 10^4 = 11.68 - 1.29 - 7.09 = 3.30$ and $K_5 = 1.29/3.30\ (0.254)^2 = 0.025$. If these figures are correct, the true solubility of bromine is 0.2538 mole/liter at 0°. Similarly we find for the saturated solution at 25°: $(H^+) = (HBrO) = 18.41\ (10^{-4})$; $(Br^-) = 3.47\ (10^{-4})$; $(Br_3^-) = 12.22\ (10^{-4})$; $(Br_5^-) = 2.72\ (10^{-4})$; $(Br_2) = 0.2067$; $K_5 = 3.47/2.72\ (0.207)^2 = 0.055$. All concentrations are in moles/liter.

[18] Linhart, THIS JOURNAL, **40**, 158 (1918). $K_5 = 1/K'K''$; K' and K'' are defined by him.

[19] Worley, *J. Chem. Soc.*, **87**, 1107 (1905).

2. The conductance of hydrobromic acid has been measured over the same temperature range; limiting values for its equivalent conductance at five temperatures have been given.
3. The results of earlier investigations have been recalculated and shown to yield values of K_1 in substantial agreement with those newly determined.
4. The temperature variation of the K_1 for bromine becomes anomalous in the neighborhood of 0°; but the departure of $d(\log K_1)/d(1/T)$ from constancy is much less than that observed by Jakowkin in the case of chlorine.
5. The existence of pentabromide ion is highly probable; the values of $(Br^-)(Br_2)^2/(Br_5^-)$ are calculated to be 0.025 at 0° and 0.050 at 25°, in agreement with the results of earlier investigations.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Activity of Sodium in Concentrated Liquid Amalgams

BY E. S. GILFILLAN, JR., AND H. E. BENT

The purpose of this investigation of concentrated sodium amalgams is two-fold. In the first place it is desired to compare the activity of sodium in eighty-five atom per cent. amalgam, which is liquid at room temperature, with that of the pure metal. The use of this material in cleaving organic compounds is now so common as to make it desirable to discover the activity of this amalgam as compared with the pure metal and dilute amalgams. The second purpose of this investigation is to correlate the deviations from Raoult's law with those previously observed in experiments on dilute sodium amalgams. Sodium amalgams offer an extreme case of deviation from Raoult's law and hence are of particular interest from the standpoint of the theory of solutions.

Experimental Method

Most of the experimental detail has been described elsewhere.[1] The sodium was Kahlbaum material which had been filtered through a glass capillary in a vacuum to remove surface impurities. Unpublished work in this Laboratory by one of us with A. F. Forziati indicates that distillation of the sodium does not affect the e. m. f. of the cell. The amalgams were made up to approximately the correct composition and sealed in glass capsules. These were placed in the apparatus, the system evacuated and the tips of the capsules broken by means of magnetically controlled hammers. The composition of the liquid phase was determined by means of the data of Vanstone.[2] His excellent phase diagram permits one to read at each temperature the composition of the liquid phase with a probable error of something like 0.1% on the sodium side of the eutectic and perhaps 0.2 to 0.3% on the more dilute side of the eutectic. Sodium iodide in ethylamine served as the electrolyte. When first prepared the cell did not give constant values for the e. m. f. After agitating the electrolyte for some time the values became more reproducible. Some difficulty was experienced with amalgam "C" which at first gave rather erratic results. This was attributed to lack of homogeneity, for after repeated fusions and solidifications it gave good results. Difficulty was also experienced after a few days when two of the electrodes suddenly developed very high internal resistance. The platinum wire sealed into the cell was very fine (40 gage) and may have been broken by the expansion and contraction of the solid amalgams. After time had been allowed for equalization of concentration in the electrolyte the reproducibility was very good, the root-mean-square of the cross-checks being 0.03 mv.

Experimental Results

The observed e. m. f. data are given in Table I and represented graphically in Fig. 1. To relate these data to Raoult's law it is necessary to calculate the activity of solid sodium at the temperatures employed in our experiments referred to the supercooled liquid as the standard state. This may be accomplished if one knows the melting point, the heat of fusion and ΔC_p. Griffiths[3] has found the melting point to be 97.6° and the

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[1] Bent and Gilfillan, THIS JOURNAL, **55**, 3989 (1933).

[2] Vanstone, *Trans. Faraday Soc.*, **7**, 42 (1911).

[3] Griffiths, *Proc. Roy. Soc.* (London), **89**, 561 (1914).