case of thiophene an approximate combustion value for the liquid was obtained by subtracting the heat of vaporization of benzene (8100 cal./mole at 298°K.[16]) from Thomsen's result for the heat of combustion of gaseous thiophene as recently revised by Parks and Huffman.[16] The figures for the ΔH_{298} and ΔS_{298} of formation of each compound were then derived with the aid of the atomic heats of combustion and entropies used in the preceding paper of Parks and Light[2] together with the values S_{298} = 7.6 E. U.[10] per atom for rhombic sulfur and $\Delta H_{298} = -70{,}940$ cal.[17] for its combustion to $SO_2(g)$.

TABLE VI

THERMAL DATA AT 298.1°K.

The 15° cal. is used throughout and all weights have been reduced to a vacuum basis.

Substance	C_5H_{10}(l)	C_4H_4S(l)	$C_4H_8O_2$(l)
Heat of combustion at const. pressure	783,300	600,100	554,400
ΔH_{298}	−29,450	+16,400	−95,800
ΔS_{298} (in E. U.)	−113.5	−33.3	−132.4
ΔF°_{298}	+4,400	+26,300	−56,300

The molal free energies of formation of the three compounds from their elements appear in the last line of the table. These results, while they may easily involve absolute errors of the order of one or two thousand calories, show clearly that the ring compound, at least in some cases, possesses an appreciably higher free energy than comparable aliphatic substances. Thus the value for cyclopentane is 13,000 calories above that ($\Delta F^\circ_{298} = -8600$ cal.[18]) found previously for *n*-pentane. Similarly we may compare dioxane with butyric acid ($\Delta F^\circ_{298} = -91{,}500$ cal.[18]) and ethyl acetate ($\Delta F^\circ_{298} = -77{,}600$ cal.[18]), since these three compounds, though different in type, possess the same empirical formula; and again we find that the ring structure has definitely the highest free energy.

Summary

1. The specific heats of cyclopentane, thiophene, 1,4-dioxane, pyrene and graphite have been measured from the temperature of liquid air up to that of the room. Heats of fusion and of transition have also been determined for the first three substances.

2. The entropies of the four ring compounds and that of graphite have been calculated from these heat capacity data and the results have been correlated with entropy data found in previous investigations.

3. The free energies of cyclopentane, thiophene and dioxane have also been calculated.

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(16) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932, pp. 93, 207.

(17) Eckman and Rossini, *Bur. Standards J. Research*, **3**, 597 (1929).

(18) Reference 16, p. 232.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Equilibria in Aqueous Solutions of Bromine and Potassium Bromide

BY GRINNELL JONES AND SVEN BAECKSTRÖM

Introduction.—The evaluation of the standard potential of the bromine electrode from measurements of the potential of cells containing bromine and bromides requires a knowledge of the various equilibria present in such solutions. This paper records the results of an experimental investigation of these equilibria at 25° as a part of the determination of the standard potential of the bromine electrode.

A summary of the numerous earlier investigations of this problem is given in another paper.[1]

The equilibria which are generally believed to be present in aqueous bromine solutions (with or without added bromides) are hydrolysis, $Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HBrO$; and complex formation, $Br_2 + Br^- \rightleftharpoons Br_3^-$ and $2Br_2 + Br^- \rightleftharpoons Br_5^-$. For the first two reactions there is abundant evidence in the literature. Neither is there any doubt that a complex exists which is richer in bromine than the tribromide because the solubility of bromine in potassium bromide solutions of 0.1 *N* and above is greater than can be accounted for as Br_2, HBrO and Br_3^-. The evidence that this high complex has the formula, Br_5^-, as suggested by Jakowkin,[2] is, however, not conclusive. On the other hand, no one

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(1) Grinnell Jones and M. L. Hartmann, *Trans. Am. Electrochem. Soc.*, **30**, 295 (1916).

(2) A. A. Jakowkin, *Z. physik. Chem.*, **20**, 38 (1896).

has yet offered any better evidence in favor of any other formula for the higher complex.

Since the summary referred to above was published the problem has been studied by Lewis and Storch,[3] Linhart,[4] Sherrill and Izard,[5] and Griffith, McKeown and Winn.[6] All of the authors depend on the method first used by Jakowkin, which consists in distribution experiments in which bromine is distributed between carbon tetrachloride and water or an aqueous solution of a bromide. In general these later authors confirm and extend the earlier measurements of Jakowkin.

However, Jakowkin's method has serious difficulties. The distribution ratio is large, which is an unfavorable circumstance because it increases the analytical difficulties and because it results in a large error if there is even a slight emulsification of one phase in the other. The distribution ratio of molecular bromine between the two phases is furthermore not a constant but varies with the ionic strength of the aqueous phase, which was not adequately appreciated by many of the earlier investigators. Many also failed to make adequate allowance for hydrolysis and pentabromide formation.

The use of carbon tetrachloride as a solvent for bromine may now be avoided entirely by employing an instrument called an "equilibrator," invented by Grinnell Jones and B. B. Kaplan.[7] In the equilibrator the solvent may be replaced by water and the distribution of the volatile solute (bromine) between pure water and a solution of a bromide is achieved by automatic circulation of the vapor phase through the two miscible but separate liquid phases for as long as may be necessary for the equilibrium to be established.

Since there are three independent equilibria occurring simultaneously in the same solution, the experimental problem is to choose the conditions so that each of the three reactions in turn will be favored and the others repressed, and then to determine the concentration and activity of each ionic and molecular species in the solution by suitable analyses and other measurements. Solutions which are suitable for use in electromotive force measurements for the determination of the standard potential of the bromine electrode and which were actually used for this purpose have been included among the solutions studied.

Assuming the equilibria in a water solution of bromine to be those that correspond to the reactions

$$\mathrm{Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HBrO}$$
$$\mathrm{Br_2 + Br^- \rightleftharpoons Br_3^-}$$
$$\mathrm{2Br_2 + Br^- \rightleftharpoons Br_6^-}$$

it is possible to derive the following equations:

$$\frac{[\mathrm{H^+}]\,[\mathrm{Br^-}]\,[\mathrm{HBrO}]}{[\mathrm{Br_2}]}\,\frac{f_{\mathrm{H^+}}\,f_1\,f_{\mathrm{HBrO}}}{f_2} = K_{\mathrm{h}} \qquad (1)$$

$$\frac{[\mathrm{Br_3^-}]}{[\mathrm{Br_2}]\,[\mathrm{Br^-}]}\,\frac{f_3}{f_2 f_1} = K_3 \qquad (2)$$

$$\frac{[\mathrm{Br_5^-}]}{[\mathrm{Br_2}]^2\,[\mathrm{Br^-}]}\,\frac{f_5}{f_2^2 f_1} = K_5 \qquad (3)$$

$$[\mathrm{H^+}] = [\mathrm{HBrO}] \qquad (4)$$

$$[\mathrm{H^+}] = [\mathrm{Br^-}] + [\mathrm{Br_3^-}] + [\mathrm{Br_5^-}] \qquad (5)$$

$$[\mathrm{Br_2}] + [\mathrm{Br_3^-}] + [\mathrm{HBrO}] + 2[\mathrm{Br_5^-}] = S \qquad (6)$$

$$1000\,\kappa = \gamma([\mathrm{H^+}]\Lambda_{\mathrm{H^+}} + [\mathrm{Br^-}]\Lambda_1 + [\mathrm{Br_3^-}]\Lambda_3 + [\mathrm{Br_5^-}]\Lambda_5) \qquad (7)$$

In this system of equations brackets are used to designate concentrations, and the symbols have the following significance: S = the sum of all of the oxidizing constituents present, determined by iodimetric titration, expressed as moles of Br_2 per liter. κ = the specific conductance.

Λ_{H}, Λ_1, Λ_3, Λ_5 are the equivalent conductances at infinite dilution of the H^+, Br^-, Br_3^- and Br_5^- ions, respectively, $\gamma = \Lambda/\Lambda_0$, the conductance coefficient, formerly called the "degree of dissociation."

f_{H}, f_{HBrO}, f_1, f_2, f_3, f_5 are the activity coefficients of H^+, HBrO, Br^-, Br_2, Br_3^-, Br_5^-, respectively. If the solution used contained potassium bromide in addition to water and bromine, equation (5) must be replaced by

$$[\mathrm{K^+}] + [\mathrm{H^+}] = [\mathrm{Br^-}] + [\mathrm{Br_3^-}] + [\mathrm{Br_5^-}] \qquad (5')$$

and equation (7) by

$$1000\kappa = \gamma([\mathrm{K^+}]\Lambda_{\mathrm{K}} + [\mathrm{H^+}]\Lambda_{\mathrm{H}} + [\mathrm{Br^-}]\Lambda_1 + [\mathrm{Br_3^-}]\Lambda_3 + [\mathrm{Br_5^-}]\Lambda_5) \qquad (7')$$

The numerical values for S, κ, K^+ and the activity of the free bromine, $a_2 = f_2[\mathrm{Br_2}]$, can be determined for any particular solution by experiment and may therefore be regarded mathematically as known quantities and we may also assume that the activity coefficients, f, the conductance coefficients, γ, and the equivalent conductances, Λ, have been or can be determined independently and may therefore be regarded mathematically as known quantities. The purely

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(3) G. N. Lewis and H. Storch, THIS JOURNAL, **39**, 2544 (1917).

(4) G. A. Linhart, *ibid.*, **40**, 158 (1918).

(5) M. S. Sherrill and E. F. Izard, *ibid.*, **50**, 1671 (1928).

(6) R. O. Griffith, A. McKeown and A. G. Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

(7) Grinnell Jones and B. B. Kaplan, THIS JOURNAL, **50**, 1600, 1845 (1928).

mathematical difficulties of a general solution of these equations are so great that a solution by successive approximations seemed to be preferable.

Experimental

Bromine was purified by a method similar to that described by Baxter.[8] Potassium bromide was prepared by the procedure of Richards and Mueller.[9] Potassium nitrate was recrystallized three times with centrifugal drainage and dried for twenty-four hours at 180°.

All measurements were carried out at 25.00°.

The sampling and handling of all bromine solutions for analysis and for measurements of conductance, density, and electromotive force were carried out in closed all-glass systems (Fig. 1) designed so as to avoid errors due to loss of bromine by evaporation. The equilibrator and bottles, E, used for preparing the solutions were provided with capillary delivery tubes, D, which served to transfer the solutions to the analysis flasks, F, which already contained an excess of potassium iodide solution. The compressed air entering the equilibrator or bottles to replace the sample removed was given approximately the same bromine vapor tension as the air already present by passing it first through a bubbler, B, which was filled with some of the solution to be sampled by first tilting the container. The analysis flask was weighed with an excess of potassium iodide solution which wetted the glass beads in the side arm. The analyses were carried out by weight according to Washburn's method.[10] After adding a solution of disodium hydrogen phosphate as a buffer, the iodine which was equivalent to original bromine was titrated with sodium arsenite solution by means of weight burets.

After removing the samples for analysis, the conductance cells, pycnometers and electromotive force cells were attached at H and filled. The first portion of the solution which entered these receivers was forced out the other end and rejected because it must have been slightly weakened by loss of bromine.

The conductance increased slightly with time, but without reaching an upper limit for many hours. Since the change in conductance of the solution while stored in the original glass bottles was much slower, especially in the presence of bromides, we concluded that the effect was due to the catalytic effect of the platinum of the electrodes on some slow ion producing reaction.[1] Therefore the conductance measurements were taken as quickly as possible after filling the cells. The precision of these measurements is not high but it was adequate for our purpose.

The first step in the determination of the equilibrium constants was to prepare a series of solutions of bromine in water varying from 0.9% up to 29% of saturation and to determine the specific conductance, κ, and analysis, S, of each as recorded in Table I. Here the hydrolysis is the predominant reaction. The amounts of tribromide and pentabromide are at a minimum because the only bromide present is that formed by hydrolysis, and the bromine is much below saturation. These data therefore serve for the calculation of the hydrolysis constant after applying slight corrections for the tribromide and pentabromide present. This method was first used by Bray and Connolly,[11] who obtained the value $K_h = 5.2 \times 10^{-9}$. In the final round of the calculations by the method of successive approximations we used $K_3 = 16.0$ and $K_5 = 40$. Since the concentration of the H^+ does not exceed 0.001 N in even the most concentrated of these solutions, we may put the conductance coefficients, γ, and all of the activity coefficients, f, equal to unity, especially as the deviations of γ and f from unity tend to compensate each other. The following values of the equivalent conductances of the ions were used: $\Lambda_H = 350$, $\Lambda_1 = 77$, $\Lambda_3 = 43$, $\Lambda_5 = 30$ in these calculations. The values for the hydrolysis constant (Table I) show no systematic variation with the concentration in spite of a variation from 0.9 to 29% of saturation. The average result 5.8×10^{-9} is definitely higher than the value 5.2×10^{-9} obtained by Bray and Connolly. The great influence of temperature on the hydrolysis is shown by comparison with the value of 0.57×10^{-9} at 0° obtained by Jones and Hartmann.

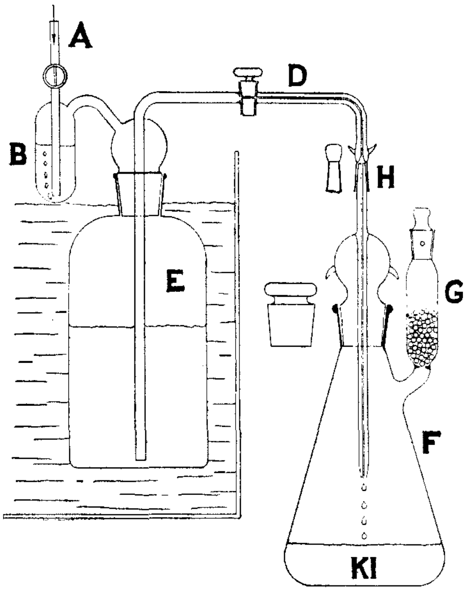

Fig. 1.

The activity coefficients of the ions in potassium bromide solutions have been determined with

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(8) G. P. Baxter, THIS JOURNAL, **28**, 1325 (1906).

(9) T. W. Richards and E. Mueller, *ibid.*, **29**, 639 (1907).

(10) E. W. Washburn, *ibid.*, **30**, 31 (1908). Arsenic trioxide was recrystallized until free from iron, dissolved in pure sodium carbonate to make an approximately 0.1 N solution. It was acidified with phosphoric acid (methyl red), boiled to free it from dissolved oxygen and stored under nitrogen. This solution was standardized at frequent intervals by the use of pure dry iodine. In some of the earlier analyses the sodium arsenite solution and a disodium hydrogen phosphate for a buffer were added to the analysis flask before the bromine solution was put into the flask. Erratic and grossly erroneous results were obtained by this procedure. These errors were traced to the formation of bromate by reaction between the free bromine and the alkaline disodium phosphate solution. The procedure described above avoids this difficulty completely.

(11) W. C. Bray and E. L. Connolly, *ibid.*, **32**, 932 (1910); **33**, 1485 (1911).

TABLE I

HYDROLYSIS OF BROMINE AT 25°

Experimental data			Computed concentrations based on $K_3 = 16.0$; $K_5 = 40$ and $\Lambda_H = 350$; $\Lambda_1 = 77$; $\Lambda_3 = 43$; $\Lambda_5 = 30$					
$\kappa \times 10^6$	$S \times 10^3$	% satd.	$H^+ \times 10^3$	$Br^- \times 10^3$	$Br_3^- \times 10^3$	$Br_5^- \times 10^3$	$Br_2 \times 10^3$	$K_h \times 10^9$
370.6	62.3	29.1	0.908	0.428	0.417	0.063	60.9	5.8
328.6	50.5	23.6	.801	.425	.335	.041	49.3	5.5
280.3	35.94	16.8	.678	.421	.236	.021	35.0	5.5
272.3	33.74	15.8	.657	.419	.220	.018	32.8	5.5
231.8	23.14	10.8	.555	.403	.144	.008	22.4	5.5
235.0	23.12	10.8	.563	.408	.146	.008	22.4	5.8
225.6	19.80	9.2	.539	.408	.125	.006	19.1	6.2
199.4	15.56	7.3	.475	.380	.091	.003	15.0	5.7
193.7	14.56	6.8	.461	.374	.084	.003	14.0	5.7
177.5	11.47	5.4	.421	.356	.063	.002	11.0	5.8
170.4	9.73	4.6	.403	.350	.052	.001	9.27	6.1
146.9	6.75	3.2	.347	.314	.032	.001	6.37	5.9
143.4	6.30	2.9	.338	.308	.029	.000	5.93	5.9
124.0	4.22	2.0	.292	.274	.017	.000	3.91	6.0
90.1	1.73	0.9	.211	.206	.005	.000	1.51	6.1
							Average	5.8

care by Harned[12] over a wide range of concentration. We have accepted these values as reliable and used them wherever necessary in the interpretation of our results. It has been necessary to assume that the activity coefficients of the tribromide ions and pentabromide ions are the same as that of the bromide ion in the same solution.

The next step was to determine the influence of the ionic strength on the activity coefficient of the free bromine. The activity coefficient of free bromine in potassium bromide solution cannot be determined directly owing to complex formation. The best way to estimate the "salting out effect" of ions on bromine, independently of the specific chemical affinities which result in the formation of complex ions, seems to be to assume that the activity coefficient of bromine in solutions of potassium bromide is the same as the activity coefficient of bromine in solutions of potassium nitrate of the same concentration, which can be determined easily by means of the equilibrator. Water was placed in one side of the equilibrator and a potassium nitrate solution (0.1 up to 1.0 *N*) was placed in the other side with bromine added to each. After rotating the equilibrator in the thermostat for a sufficient time (usually forty-eight hours) for the activity of the bromine to become identical in the two solutions, they were removed and analyzed. It was found, as was expected, that the concentration of the bromine in the water was greater than in the potassium nitrate solutions and that this ratio increased with the ionic strength. The results are recorded in Table II.

TABLE II

ACTIVITY COEFFICIENT OF BROMINE IN POTASSIUM NITRATE SOLUTIONS AT 25°

	Experimental data			Computed concentrations based on $K_h = 5.8 \times 10^{-9}$; $K_3 = 16.0$; $K_5 = 40$			
C KNO_3	$S \times 10^3$ KNO_3 side	$S \times 10^3$ H_2O side	% satd.	$Br_2 \times 10^3$ KNO_3 side	$Br_2 \times 10^3$ H_2O side	f_2	f_2 av. at round concns.
0.99812	8.254	9.221	4.3	7.674	8.784	1.145	1.14_2
.99812	19.91	22.30	10.4	18.97	21.59	1.138	
.50003	5.461	5.755	2.7	5.007	5.404	1.079	1.07_3
.50003	16.28	17.13	8.0	15.49	16.52	1.067	
.19997	8.087	8.252	3.8	7.575	7.838	1.035	1.03_0
.19997	18.92	19.24	9.0	18.11	18.59	1.026	
.09997	5.850	5.853	2.7	5.430	5.500	1.013	1.01_1
.09997	14.16	14.18	6.7	13.51	13.63	1.009	

The concentration of titratable bromine found by analysis in the water side of the equilibrator was then corrected for the effect of hydrolysis and for the presence of complex ions by computation using the values of the equilibrium constants which are known as a result of the patient

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(12) H. S. Harned, THIS JOURNAL, **51**, 424 (1929).

use of the method of successive approximations. This gives the concentration of the free bromine as such (Br_2) and since the ionic strength in these aqueous solutions is very low, this is equal to the activity of the free bromine in the water side and therefore also equal to the activity of the free bromine in the potassium nitrate side. The values of the concentration of each ion in each solution are omitted from Table II to save space in printing but they may be readily approximated by comparison with solutions of a similar degree of saturation recorded in Table I. The correction for hydrolysis and complex formation in the potassium nitrate solutions in the other side of the equilibrator was then computed in a similar manner except that the activity coefficients of the ions were assumed to depend on the ionic strength in accordance with Harned's measurements. The effect of making due allowance for the influence of ionic strength on the activity coefficients is to make the corrections come out slightly larger than they are in the aqueous solutions. The ratio of the concentration of the free bromine in the water to that in a potassium nitrate solution in equilibrium therewith gives the activity coefficient of the free bromine in the potassium nitrate solution. The "salting-out effect" of potassium nitrate on free bromine is clearly shown in Table II. As has been found in other similar cases the logarithm of the activity coefficient of an uncharged molecule is approximately a linear function of the ionic strength. The results give some indication that the activity coefficient of bromine is a decreasing function of the percentage of saturation but the data are not extensive enough to establish this trend definitely. It is assumed that $f_{\mathrm{HBrO}} = f_2$.

The next step was to choose experimental conditions so that the formation of tribromide is substantial and at the same time hydrolysis and pentabromide formation is minimized as much as is feasible. This was accomplished by adding potassium bromide (0.01 up to 1.0 *N*) and at the same time keeping the free bromine much below saturation (0.9 to 17.5% of saturation). The presence of bromide represses hydrolysis and the amount of pentabromide formed is small in the presence of such low concentrations of free bromine. By the use of the equilibrator the activity of the free bromine in these solutions of potassium bromide was determined in the manner already described for the potassium nitrate solutions. From the data on the potassium bromide solutions and the known values of K_h and K_5 and the activity coefficients shown in Table II, the concentration of the free bromine and of each of the ions present was computed and is shown in Table III. Then assuming that $f_1 = f_3$, the value of K_3 was readily computed. The values for K_3 show a slight tendency to decrease with increasing concentration of both the potassium bromide and free bromine. We have tried to cure this tendency by making other assumptions in regard to the formula of the

TABLE III

TRIBROMIDE EQUILIBRIUM CONSTANT FROM DATA ON DISTRIBUTION OF BROMINE BETWEEN WATER AND POTASSIUM BROMIDE SOLUTIONS AT 25°

Based on $K_h = 5.8 \times 10^{-9}$; $K_5 = 40$; f_2 from Table II

		Experimental data						KBr side of equilibrator						
Expt.	*C* KBr	$S \times 10^3$ KBr side	$1000\,\kappa'$ KBr + Br_2	$S_w \times 10^3$ water	% satd.	$[a_2] \times 10^3$	$Br_2 \times 10^3$	$H^+ \times 10^3$	$Br^- \times 10^3$	$Br_3^- \times 10^3$	$Br_5^- \times 10^3$	K_3	$\gamma\Sigma c\Lambda$	$\Delta\kappa \times 10^3$
1	0.99961	116.80	113.3	7.940	3.7	7.533	6.596	0.011	889.45	106.15	2.02	15.8	113.43	−0.13
2	0.99961	101.52	...	6.885	3.2	6.505	5.696	.011	905.34	92.75	1.53	15.8	....	....
3	1.00007	63.45	114.8	4.300	2.0	3.994	3.497	.007	940.73	58.746	0.60	15.6	114.89	− .09
4	1.00007	29.97	115.6	2.028	0.9	1.801	1.577	.005	971.81	28.136	.13	16.1	115.72	− .12
5	0.50026	82.71	...	10.83	5.1	10.356	9.651	.017	429.08	69.361	1.84	15.6	....	....
6	.50480	68.19	59.57	8.643	4.0	8.219	7.659	.015	445.50	58.108	1.20	15.9	59.53	+ .04
7	.50477	55.70	59.73	6.92	3.2	6.539	6.094	.013	455.97	48.033	0.78	16.1	59.82	− .09
8	.19825	75.14	23.93	22.03	10.3	21.325	20.704	.041	146.56	49.063	2.67	15.7	23.82	+ .11
9	.20193	46.09	24.90	12.33	5.8	11.823	11.479	.028	168.32	32.701	0.94	16.4	24.82	+ .08
10	.20193	35.15	25.06	9.21	4.3	8.764	8.509	.023	175.88	25.538	.54	16.6	25.04	+ .02
11	.10096	77.51	12.32	37.42	17.5	36.42	36.026	.075	62.996	34.725	3.34	15.1	12.23	+ .09
12	.10096	35.22	12.83	15.30	7.1	14.73	14.570	.042	81.099	19.200	0.70	16.1	12.78	+ .05
13	.10096	14.73	13.14	6.006	2.8	5.648	5.587	.025	91.984	8.884	.12	17.1	13.11	+ .03
14	.10095	12.88	13.14	5.313	2.5	4.974	4.920	.023	93.129	7.753	.09	16.7	13.14	+ .00
15	.10095	12.76	13.14	5.264	2.5	4.927	4.873	.023	93.196	7.690	.09	16.7	13.14	+ .00
16	.050506	12.95	...	7.262	3.4	6.872	6.831	.037	44.545	5.914	.08	19.3	....	....
17	.050480	11.13	6.781	6.53	3.0	6.159	6.122	.034	45.606	4.836	.07	17.2	6.759	+ .022
18	.019999	7.959	2.783	6.35	3.0	5.984	5.966	.050	18.132	1.891	.03	17.4	2.773	+ .010
19	.019999	6.479	2.804	5.153	2.4	4.819	4.805	.045	18.432	1.595	.02	18.0	2.781	+ .023
20	.009995	7.820	1.462	7.01	3.3	6.626	6.619	.073	8.956	1.096	.02	18.5	1.441	+ .019
21	.009995	5.732	1.464	5.149	2.4	4.815	4.810	.061	9.203	0.845	.01	19.0	1.464	.000

higher complex but these assumptions gave a trend much greater than is shown in Table III which is based on the formula Br_5^- for the higher complex. Whether this slight trend is due to experimental errors, or incorrect assumptions as to the auxiliary constants (K_h and K_5) or errors in the assumptions as to the activity coefficients which we have made, cannot be determined with assurance at the present time. We have selected $K_3 = 16.0$ as the most probable value for this constant. We might say, in the current fashion, that these results show that the activity coefficients of the tribromide and pentabromide ions differ from that of the bromide ion or even attempt to compute these activity coefficients from the data. However, in the absence of independent confirmation from data of other kinds this would amount to little more than another form of words for saying that the fundamental equations do not hold exactly.

The specific conductance of these solutions, κ, was also determined both before and after adding the bromine, which permits the mobility of the tribromide and pentabromide ions to be estimated. It is assumed that the conductance coefficient is not changed by the addition of a small amount of bromine.

The fourth column and the last two columns in Table III give the evidence for the values of 43 and 30 for the Λ_3 and Λ_5, respectively. The values of 1000 κ computed from equation (7) using these values of κ are shown in the next to the last column. The last column gives the difference between the experimental values of 1000 κ shown in the fourth column and the computed values. The agreement is sufficiently close to show that Λ_3 and Λ_5 have been determined with adequate precision for our purposes.

Table III is the most important of these tables because it gives the composition of the solution and activity of the free bromine in the actual solutions used for the determination of the standard potential of the bromine electrode recorded in the following paper.

Three independent determinations of the solubility of bromine in pure water at 25° gave the results 0.2141, 0.2142, 0.2140 mole of Br_2 or its equivalent in oxidizing power per liter.

An attempt was made to determine the hydrolysis of these saturated solutions by measurement of the conductivity in the manner already described, but it was found that the conductance increased too rapidly. This effect is clearly due to some slow ion producing reaction.[1] The conductance of the dilute solutions did not change appreciably during the short time necessary for the measurements. After considerable experimentation, we concluded that the hydrolysis of the saturated solutions could be computed from the hydrolysis constant determined with the dilute solutions more accurately than it could be determined directly. The activity coefficient of the hydrogen and bromide ions could not be assumed to be unity, because the hydrogen ion concentration turned out to be about 0.002 N. The figure $f = 0.971$ was used.[13]

Using the average value of $S = 0.2141$, the composition of the saturated solution of bromine in water has been computed to be: $[H^+] = 0.0020$; $[Br^-] = 0.0003$; $[Br_3^-] = 0.0011$; $[Br_5^-] = 0.0006$; and $[Br_2] = 0.2098$. Since the activity coefficient of an uncharged molecule (Br_2) is not appreciably altered by ionic concentrations of only 0.002 N, we may use this figure 0.2098 as the activity of free bromine in all solutions saturated with liquid bromine for the calculations recorded in Table IV and for the computation of the standard potential of the liquid bromine electrode.

The next step was to favor the formation of pentabromide by using solutions of potassium bromide ranging in concentration up to 1 N and then saturating them with bromine by shaking with an excess of bromine in the thermostat for one hour. After standing until the emulsion had separated, a sample was removed and analyzed and the density determined on another sample. The results are recorded in Table IV, which also gives the computed composition of solutions saturated with bromine and the values of K_5 based thereon. The values of K_5 are extremely sensitive to experimental errors and to variations in the auxiliary constants, f_2 and K_3 (but not to K_h), because the amounts of Br_2 and Br_3^- are large even in these saturated solutions and therefore the values for Br_5^- are obtained in the computations as the difference between larger quantities. The value of $K_5 = 40$ was selected as most probable. We have no adequate explanation of the much higher value of 60 obtained with the 1 N KBr. It should be pointed out that the calculations recorded in

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[13] Lewis and Randall, "Thermodynamics," p. 336.

TABLE IV

PENTABROMIDE EQUILIBRIUM CONSTANT FROM DATA ON SOLUBILITY OF BROMINE IN POTASSIUM BROMIDE SOLUTIONS AT 25°

Experimental data				Computed concentrations based on $K_h = 5.8 \times 10^{-9}$, $K_3 = 16.0 f_2$ from Table II $Br_2f_2 = 0.2098$						
KBr		KBr + Br_2								
C	d	S	d	$K^+ \times 10^3$	$Br_2 \times 10^3$	$H^+ \times 10^3$	$Br^- \times 10^3$	$Br_3^- \times 10^3$	$Br_5^- \times 10^3$	K_5
0.99961	1.0809	1.3472	1.2276	936.0	183.7	0.10	132.3	444.2	359.6	62
.99961	1.0809	1.3423	....	936.7	183.7	.10	133.5	448.2	355.2	60
.99941	1.0807	1.3428	1.2275	936.6	183.7	.10	133.4	447.6	355.7	61
.50026	1.0394	0.7531	1.1230	482.5	195.5	.16	76.2	255.6	150.9	45
.50026	1.0394	.7539	1.1229	482.4	195.5	.16	76.0	255.0	151.6	45
.19825	1.0137	.4230	1.0612	194.3	203.7	.25	31.8	106.6	56.3	40
.19825	1.0137	.4241	1.0611	194.2	203.7	.25	31.5	105.8	57.2	41
.10095	1.0056	.3182	1.0411	99.4	207.5	.33	16.6	55.8	27.3	37
.10095	1.0056	.3186	1.0411	99.4	207.5	.33	16.6	55.6	27.6	38
.05048	1.0014	.2640	1.0307	49.83	208.6	.44	8.52	28.59	13.16	35
.05048	1.0014	.2643	1.0310	49.84	208.6	.44	8.47	28.42	13.20	35
.02000	0.9987	.2308	1.0244	19.78	209.2	.64	3.70	12.43	4.28	26
.01996	.9988	.2325	1.0245	19.73	209.2	.67	3.38	11.36	5.65	38
.01996	.9988	.2325	1.0245	19.73	209.2	.67	3.38	11.36	5.65	38
.009986	.9980	.2227	1.0227	9.88	209.6	.92	1.75	5.89	3.15	41
.009986	.9980	.2219	1.0226	9.88	209.6	.88	1.88	6.32	2.56	31

Tables I, II and III are relatively insensitive to the value of K_5 selected, since the degree of saturation was made low in order to minimize the influence of the higher complexes.

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Summary

Equilibria in aqueous solutions of bromine and potassium bromide have been studied at 25° and the following results obtained:

1. The hydrolysis constant of bromine in water has been determined from measurements of the conductance of dilute solutions to be 5.8×10^{-9}.
2. The activity coefficients of bromine in solutions of potassium nitrate 0.1 to 1.0 *N* have been measured.
3. The equilibrium constant of the reaction $Br_2 + Br^- \rightleftharpoons Br_3^-$ has been measured by a new method and found to be 16.0.
4. The total solubility of bromine in water at 25° has been found to be equivalent to 0.2141 mole of Br_2 per liter of which 0.2098 is present as Br_2.
5. The solubility of bromine in potassium bromide solutions 0.01 to 1.0 *N* has been determined and the equilibrium constant of the reaction $2Br_2 + Br^- \rightleftharpoons Br_5^-$ computed to be 40.
6. The equivalent conductance of the tribromide ion has been estimated from conductance measurements to be 43 and of the pentabromide ion to be 30 mhos per cm.

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