

Eliminating this error, we have measured and predicted this potential over a wide range of concentration.

It is shown that the electrometric titration of iodine with chlorine through the iodine point should be accurate within 0.02% if oxygen is excluded and the escape of halogen avoided. This holds only if $[I_2] < 0.1$.

The peculiar experimental curve for the potential of bromine in hydrochloric acid is predicted by taking full account of the reaction between bromine and chloride ion, of bromine chloride formation, and of the various complex ions present.

Electrometric titration through the bromine monochloride point is shown to be unsuitable for analytical purposes, particularly when iodine monochloride is present as well.

CAMBRIDGE, MASSACHUSETTS

RECEIVED SEPTEMBER 24, 1932

PUBLISHED MAY 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Equilibria, Complex Ions and Electrometric Titrations. II. Iodine, Bromine and Hydrobromic Acid. Iodine Tribromide¹

BY GEORGE SHANNON FORBES AND J. HORACE FAULL, JR.

In a previous paper² we showed that solutions of iodine or bromine, or both, in hydrochloric acid, also electrometric titrations in such systems, can be discussed adequately only if complex ion formation between chloride ion and halogens or interhalogen compounds is quantitatively treated. This accomplished, we decided to investigate by similar methods solutions of iodine and bromine in hydrobromic acid. Incidental to this program was a search for interhalogen compounds previously overlooked. In addition we hoped to correlate our equilibrium constants with activity coefficients.

Solubilities in systems containing iodine, bromine and hydrobromic acid have been investigated by Oliveri-Mandalà,³ also by Carter and Hoskins,⁴ who discussed their results in terms of equilibrium constants. Hahn⁵ developed a micro-technique to determine iodide in the presence of bromide and chloride under the conditions of physiological work. He considered the possible importance of the reaction $I_2 + Br_2 + nCl' \rightleftharpoons 2ICl + 2Br' + (n - 2) Cl'$. He extracted iodine with carbon tetrachloride to improve the end-point but did not prove the extraction of bromine and

(1) Complete data and calculations are available in the doctoral thesis of J. Horace Faull, Jr., Widener Library, Cambridge, Massachusetts.

(2) Faull, Jr., and Forbes, *THIS JOURNAL*, **55**, 1809 (1933).

(3) Oliveri-Mandalà, *Gazz. chim. ital.*, **50**, 89 (1920).

(4) Carter and Hoskins, *J. Chem. Soc.*, 580 (1929).

(5) Hahn. *Z. anorg. allgem. Chem.*, **195**, 75 (1931)

iodine bromide to be negligible. He noted with perplexity the pseudo four-electron reaction of the type previously explained by Forbes, Glass and Fuoss.⁶ His observations regarding end-points are discussed below. A systematic treatment of these with due reference to complex formation has not previously been undertaken.

The apparatus, materials, precautions and notation as well as the methods of calculation have been for the most part described.^{2,7} A star denotes total concentration, including the part of the reactant present in the form of complex ions. Bromine and bromide for final measurements were prepared from a sample of potassium bromide which had been elaborately purified in this Laboratory by R. M. Fuoss. Bromine was distilled from bromide, a part of the distillate reduced by recrystallized potassium oxalate, and the rest distilled from this purer bromide. After reduction by oxalate, the solution was boiled with four successive portions of very pure bromine, kindly furnished by Professor G. P. Baxter, to remove iodine. After two crystallizations, the dried solid was fused in a platinum dish with a little permanganate. From this product dry potassium bromide crystals and bromine were obtained. The hydrobromic acid taken as a starting point was said to contain 0.1% of chloride, which could scarcely affect our work. The free bromine present was removed by silver or mercury and the clear liquid carefully fractionated. Potential measurements showed this product to be free from bromine.

The Molal Potential of Bromine in Hydrobromic Acid, 0.974, 4.13 and 4.72 N.—Lewis and Storch⁸ made careful measurements of the molal potential of bromine in solutions not over 0.1 *M* in bromide. In our concentrated solutions, excepting those very dilute in bromine, an important fraction of the bromide ion of the acid entered into complex formation. Also the ratio $[Br_2]/[*Br_2]$ decreases as $[Br_2]$ decreases because $[Br']$ is then increasing.⁹ If b_1 mol of bromine is added to 1 liter of acid having $[Br'] = N_1$, E_1 is measured in a solution where $[*Br_2] = b_1$ but $[Br'] < N_1$. Given the complex constants $[Br'][Br_2]/[Br_3'] = 0.062 = C_4$ and $[Br'][Br_2]^2/[Br_6'] = 0.051$ as measured by Linhart,¹⁰ we calculated in successive approximations the hypothetical concentration $[*Br_2]'$ which would give the same electromotive force E_1 in a solution where $[Br_1']$ excluding complexes actually equals b_1 . It turns out that

$$[Br_2] = [Br_2]' \times \left(1 - \frac{\sum \text{complexes}}{N}\right)^3$$

where N is the (volume) molality of the original acid. It is obvious that when $[*Br_2]$ is to be determined from an actual reading of E , a process of correction substantially the reverse of the above must be undertaken.

(6) Forbes, Glass and Fuoss, *THIS JOURNAL*, **47**, 2902 (1925).

(7) Forbes and Fuoss, *ibid.*, **49**, 143, 146 (1927).

(8) Lewis and Storch, *ibid.*, **39**, 2544 (1917).

(9) See Ref. 1, pp. 85-86.

(10) Linhart, *THIS JOURNAL*, **40**, 158 (1918).

To produce solutions in which $[*Br_2] < 10^{-3}$, the electrolytic method previously described was used.¹¹ For higher concentrations a special bromine pipet¹¹ was used. The absorbent for bromine vapor was soda lime instead of potassium iodide with calcium chloride. Table I shows that the reproducibility of E , also the constancy of E_0 , the molal potential, are good except in the two most dilute solutions where polarization was not negligible. The formation of Br'_5 was proved to be negligible.

TABLE I
MOLAL POTENTIAL OF BROMINE IN HBr 0.974 *N*

E	$\frac{[*Br_2]}{\times 10^4}$	$\frac{[*Br_2]'}{\times 10^4}$	E_0	E	$\frac{[*Br_2]}{\times 10^4}$	$\frac{[*Br_2]'}{\times 10^4}$	E_0
0.9363	1.035		1.0495	0.9351	1.035		1.0483
.9452	2.07		1.0541	.9448	2.07		1.0537
.95052	3.11		1.0548	.95016	3.11		1.0545
.95423	4.15		1.05477	.95401	4.15		1.0545
.95738	5.18		1.05505	.95706	5.18		1.05473
.96014	6.22		1.05521	.95943	6.22		1.05473
.96182	7.25		1.05515	.96150	7.25		1.05483
.98979	62.50	63.9	1.05503	.98981	63.14	64.77	1.05487
.99807	118.0	122.5	1.05490	.99822	119.0	125.2	1.05477
1.00319	172.6	183	1.05481	1.00277	174.7	182.4	1.05446
1.00672	226	240	1.05489	1.00641	229.5	242.2	1.05455
1.01212	336	374	1.05456	1.01262	364	389	1.05454
			Average 1.05492				Average 1.05465

In 4.132 *N* hydrobromic acid, E_0 similarly determined averaged 0.9020 volt, with an extreme deviation of ± 0.0001 in seven measurements. In 4.725 *N* hydrobromic acid, E_0 averaged 0.8706 with an extreme deviation of ± 0.00012 in ten measurements.

The Reaction between Iodine and Bromide Ion, as Influenced by Complex Formation.—The experimental methods and precautions described² in connection with iodine in hydrochloric acid were followed, in spite of the fact that the effects of air were less serious than in that system. Table II indicates the calculation of the true "replacement constant" $[I']^2[Br_2]/[I_2][Br']^2 = K_r$ from $K_r = *K_r([I']^2/[*I']^2)([Br_2]/[*Br_2])([*I_2]/[I_2])([*Br']^2/[Br']^2)$. The necessary methods of approximation have been exemplified¹² in connection with the reaction $Br_2 + 2Cl' \rightleftharpoons 2Br' + Cl_2$. The equation (further discussed below) $[*I_2][*Br_2]/[*IBr]^2 = *K_{IBr}$ yielded the fraction of the original iodine forming iodine monobromide but $*K_{IBr}$ proved to be a function of $[I']$ and of $[Br']$ so that the correct value of $*K_{IBr}$ had to be evaluated for each new solution. The tedious calculations must be omitted here.

The true "replacement constant" K_r was determined also (Table III) in hydrobromic acid 4.130 and 4.725 *N*. Six to eight iodide concentra-

(11) Ref. 7, pp. 143 and 146.

(12) Ref. 7, p. 151.

TABLE II

E	$\frac{1}{2}[I]_t = 0.0020$. K_r in HBr 0.974 N. $[Br_2]/[*Br_2] = 0.0601$										
	$[*Br_2]' \times 10^{16}$	$[*Br_2] \times 10^{16}$	$[KI] \times 10^4$	$K_s \times 10^8$	$[*IBr] \times 10^4$	$[*I^-] \times 10^4$	$[*I_2]$	$[I_2]/[*I_2]$	$[I^-]/[*I^-]$	$*K_r \times 10^{16}$	$K_r \times 10^{16}$
0.6916	603	601	6.97	2.3	2.18	9.15	0.00178	0.073	0.906	2.97	2.01
.6605	54.3	54.0	29.6	2.5	0.64	30.3	.00193	.0664	.915	2.67	2.05
.6245	33.1	32.8	102.2	3.3		102.2	.00200	.0501	.934	1.82	1.91
.6047	7.24	7.20	191.6				.00200	.0382	.950	1.40	2.00
										Average 2.01	
$\frac{1}{2}[I]_t = 0.00571$. K_r in HBr 0.974 N. $[Br_2]/[*Br_2] = 0.0602$											
0.7118	13200	1300	6.08	2.36	5.32	11.40	0.00517	0.0725	0.772	3.54	1.76
.6802	248	244	24.33	2.5	2.31	26.64	.00548	.0681	.782	3.33	1.82
.6355	7.78	7.62	121		0.36	121.4	.00568	.0490	.834	2.08	1.78
										Average 1.79	
$\frac{1}{2}[I]_t = 0.01180$. K_r in HBr 0.974 N. $[Br_2]/[*Br_2] = 0.0607$											
0.7096	2420	2340	5.83	2.2	10.67	16.5	0.0107	0.0726	0.642	6.27	2.17
.6934	692	670	25.53	2.31	5.71	31.24	.01123	.0692	.644	6.12	2.22
.6611	56.8	54.8	95.0	2.8	1.50	96.5	.01165	.0565	.681	4.62	2.29
.6378	9.33	9.02	188.5			188.5	.01180	.0438	.731	2.81	2.16
.5911	0.251	0.243	630			630.0	.01180	.0193	.860	0.87	2.03
										Average 2.17	

tions were used with each of two iodine concentrations in each acid, making twenty-eight complete experiments in all. $K_5 = \frac{[I_2] + [I_2Br']}{[Br_2] + [Br_3]} \div \frac{[IBr] + [IBr_2]}{[I_2]}$.

TABLE III

$$K_r = \frac{[Br_2][I^-]^2}{[I_2][Br^-]^2}$$

[HBr]	$\frac{1}{2}[I]_t$	$K_r \times 10^{18}$	No expts.	Extreme deviation
0.974	0.0118 to 0.0020	2.0	31	0.5×10^{-16}
4.130	.00605 and .0165	0.95	12	$.06 \times 10^{-16}$
4.725	.00247 and .01740	.97	16	$.08 \times 10^{-16}$

Replacement Constants and Activity Coefficients.—Forbes and Fuoss measured $*K_r = \frac{[Br']^2[Cl_2]}{[Br_2][Cl']^2}$ ¹³ in hydrochloric acid, and proved $*K_r$ roughly proportional to $(\gamma_{Br'})^2/(\gamma_{Cl'})^2$ as predicted by theory.

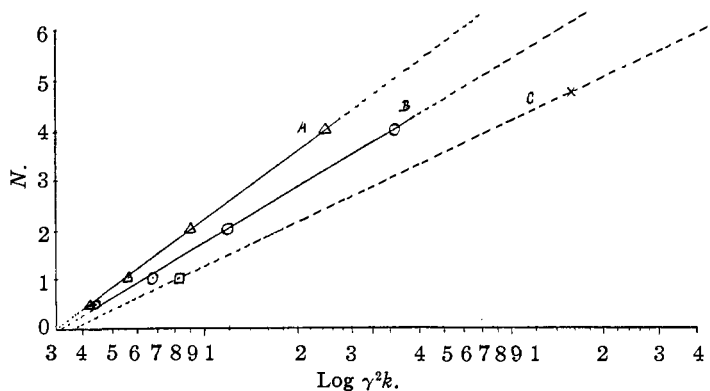


Fig. 1.—Activity coefficients: \square , HI Hantzsch; \circ , HBr Hantzsch; Δ , HCl Hantzsch; \times , I^- in HBr, see text.

The corresponding relation involving K_r instead of $*K_r$ should hold even better because K_r , unlike $*K_r$, is not distorted by complex formation. In Fig. 1 Hantzsch's values¹⁴ for chloride and bromide ion in the corresponding acids are plotted against μ . The slopes agree well with those found from data by Lewis and Randall.¹⁵ Hantzsch gives $\log(k\gamma_{I'})^2$ in normal hydriodic acid only, but from it we predicted $(k\gamma_{I'})^2_{4N} = (K_r)_{4N}(k\gamma_{I'})^2_{1N}(k\gamma_{Br'})^2_{4N}/(K_r)_{1N}(k\gamma_{Br'})^2_{1N}$ assuming, as did Forbes and Fuoss, that γ_{x_2} cancels out in the case of the halogens. A straight line through $\log(k\gamma_{I'})^2_{4N}$ thus calculated and $\log(k\gamma_{I'})^2_{1N}$ according to Hantzsch extrapolates (Fig. 1) to the same value, when $\mu = 0$, as the lines for the chloride and bromide. In addition, its slope agrees with that calculated from the data of Bates and Kirschman¹⁶ on hydriodic acid over the range 6 N to 10 N .

(13) Ref. 7, p. 153, where an obvious misprint occurs.

(14) Hantzsch, *Ber.*, **B58**, 625 (1925).

(15) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 330.

(16) Bates and Kirschman, *This Journal*, **41**, 1991 (1919).

In general it should be possible to interpolate or extrapolate either activity coefficients or replacement constants by the above method.

The Dissociation Constant of Iodine Monobromide in Hydrobromic Acid.—Bodenstein and Schmidt,¹⁷ also Yost,¹⁸ report that $[\text{IBr}]_{\text{gas}}^2/[\text{I}_2]_{\text{gas}}[\text{Br}_2]_{\text{gas}} = K_{\text{gas}}$. We determined $[\text{*IBr}]^2/[\text{*I}_2][\text{*Br}_2]$ starting with iodine in hydrobromic acid and adding bromine in small quantities by electrolysis and in larger quantities from the special pipet. Correction was made for iodide formation with the help of K_r , but the redistribution of iodine in the ratio $[\text{I}_2]/[\text{*I}_2]$ due to complex formation proved to be negligible. Every other one of our series of seventeen experiments appears in Table IV. Each group of experiments in Table IV can be combined with the corresponding group in Table II to give an electrometric titration curve through the iodine point.¹⁹

TABLE IV

* K_{IBr} IN HBr 0.974 N

E	$[\text{*I}_2] = ([\text{I}]_t - [\text{Br}]_t - 2[\text{*I}^-])/2$			$[\text{*IBr}] = [\text{Br}]_t + [\text{*I}^-]$			
	$[\text{*Br}_2]' \times 10^{11}$	$[\text{*Br}_2] \times 10^{11}$	$[\text{I}]_t$	$[\text{Br}]_t$	$*K_r \times 10^{15}$	$[\text{*I}^-]$	$*K_{\text{IBr}} \times 10^8$
0.7281	1.02	1.01	0.00463	0.000692	2.8	0.000219	2.12
.7684	23.0	22.8	.00463	.002947		.000031	2.08
.7198	0.534	0.522	.01105	.000484	3.8	.000584	2.16
.7446	3.65	3.57	.01105	.002436	4.1	.000217	2.08
.7200	0.536	0.512	.02583	.000531	6.4	.00112	1.90
.7360	1.88	1.80	.02583	.002475	6.8	.000643	2.05
.8061	426	386	.02583	.02119			2.05

* K_{IBr} was determined also in hydrobromic acid 4.132 N and 4.725 N with some six different bromine concentrations with each of two iodine concentrations in each acid making 25 experiments in all.

TABLE V

* K_{IBr}

Acid N	$1/2[\text{I}]_t$	* $K_{\text{IBr}} \times 10^8$	No. expts.	M. D.
0.974	0.01291 to 0.002316	2.06	17	0.26 ^a
4.130	.00606 and .0165	3.03	10	.19
4.725	.00486 and .0162	3.00	15	.16

^a Or 0.15 if the worst result is omitted.

We have attempted, unsuccessfully, to account for the fact that * K_{IBr} comes out smaller in normal than in four normal hydrobromic acid.

The Iodine Point in Hydrobromic Acid.—Iodine was added in weighed portions to hydrobromic acid 0.974 N and 4.725 N. E was measured with the usual precautions. The full lines in Fig. 2 show $1/2[\text{I}]_t$ plotted against E and against $[\text{*Br}_2]$. The dotted lines show the same as calcu-

(17) Bodenstein and Schmidt, *Z. physik. Chem.*, **123**, 28 (1926).

(18) Yost, *THIS JOURNAL*, **53**, 2625 (1931).

(19) Compare Ref. 7, pp. 149–150.

lated with the help of C_4 , C_5 , C_6 . The agreement is satisfactory in spite of large variations in $[I']/[*I']$ as figured at the several points.

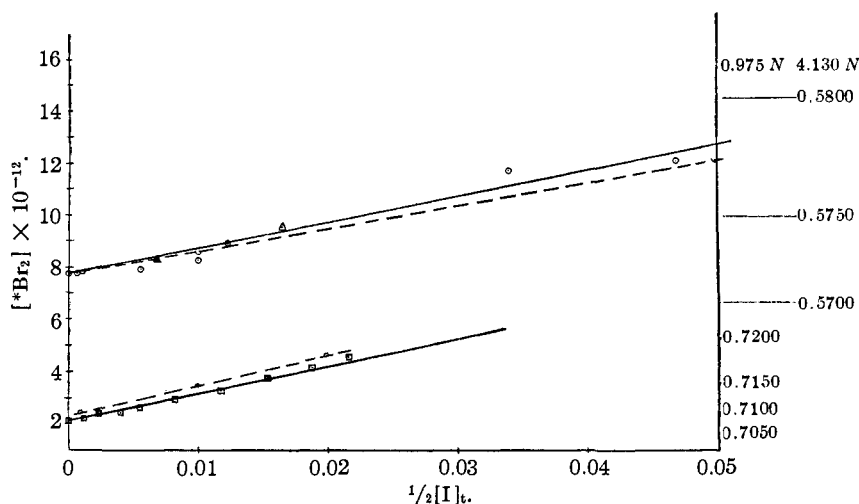


Fig. 2.—Iodine point in HBr: \odot , \triangle 4.1 N experimental; \circ , \triangle 1 N experimental; \square 4.1 N calculated; \circ , \triangle 1 N calculated.

Electrometric Titrations through the Iodine Point in Hydrobromic Acid.—Hendrixson,²⁰ also Kolthoff,²¹ estimate the uncertainty of this

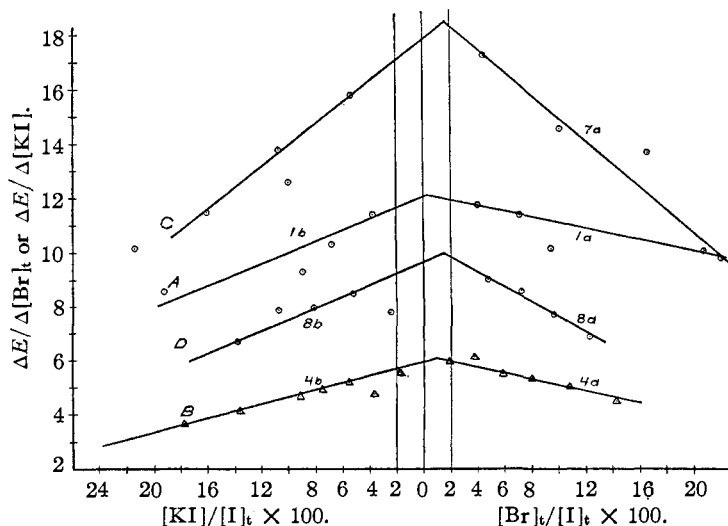


Fig. 3.—Titration from iodine point: A, HBr 4.1 N $\frac{1}{2}$ $[I]_t = 0.0055$; B HBr 4.1 N $\frac{1}{2}$ $[I]_t = 0.016$; C, HBr 1 N $\frac{1}{2}$ $[I]_t = 0.0056$; D, HBr 1 N $\frac{1}{2}$ $[I]_t = 0.013$.

(20) Hendrixson, *THIS JOURNAL*, **47**, 1319 (1925).

(21) Kolthoff, *Rec. trav. chim.*, **40**, 532 (1921).

point as 0.5% whenever bromide exceeds iodide by more than 25%. The difficulty arises from the large amounts of iodide and iodine monobromide inevitably present at the end of the titration. This is a hundred times as much as the iodide and iodine monochloride present in hydrochloric acid under conditions otherwise comparable. Hahn⁵ found the end-point slightly too soon, but did not prove the discrepancy greater than his experimental error.

Figure 3 shows four complete titrations, each a combination of two separate experiments starting with iodine in hydrobromic acid. As might be expected, the end-point was hardest to locate in case B, where $[*Br']$ and $[I]_t$ were the largest. Our error was hardly more than 1% in spite of the presence of a thousand-fold excess of bromide. Two other titrations (not shown) were made in a solution where $[HBr] = 0.8$ and $[HCl] = 3.0$, and the branches of the titration curves met at a much sharper angle.

A refined prediction was made of the slopes when known amounts of bromine are added to a solution where at the start $[I]_t = 0.0998$, $[I']_{\text{excess}} = 0.0004$ and $[Br]_t = 0.1000$. The conditions of an actual titration near the end-point are thus duplicated. Omitting lengthy details, it was proved that the two branches of the titration curve must meet with slopes at a maximum, within 0.01% of stoichiometrical equality. We conclude that the slight excess of oxidant present at our (and Hendrixson's) end-points must be explained upon some other basis.

Electrometric Titrations through the Iodine Monobromide Point in Hydrobromic Acid.—Gorbatscheff and Kassatkina²² state that this

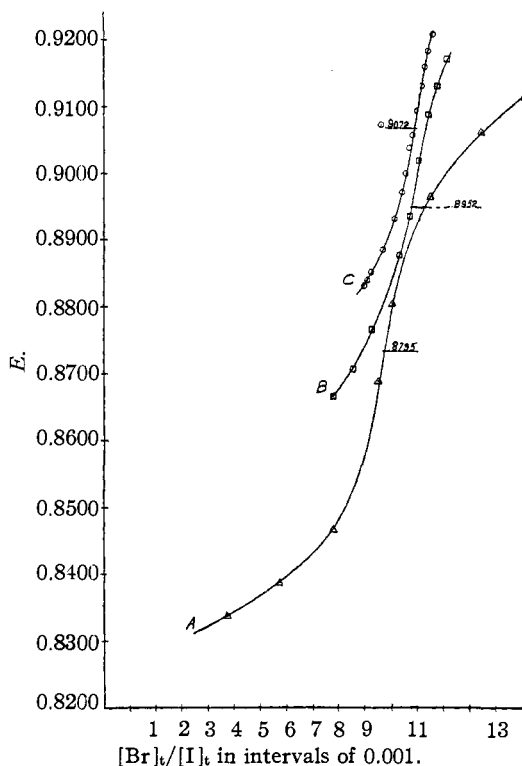


Fig. 4.—Titration through iodine monobromide point in HBr 0.974 N ; A, $[I]_t = 0.00526$; B, $[I]_t = 0.02824$; C $[I]_t = 0.07150$.

(22) Gorbatscheff and Kassatkina, *Z. anorg. allgem. Chem.*, **191**, 105 (1930).

titration is reliable. Hahn⁵ found difficulties with polarization, possibly due to carbon tetrachloride or potassium permanganate or manganese dioxide. His theoretical discussion suffers from inadequate treatment of the equilibrium between iodine, bromine and iodine bromide and he analyzes the titration curves themselves instead of the mathematical relations underlying them.

We made three titrations in 0.974 *N* acid, dissolving a weighed amount of iodine and somewhat less than the equivalent weight of bromine. *E* was read, a measured number of coulombs passed, *E* read again, and so on, until $\Delta E/\Delta[\text{Br}]_t$ had passed well beyond its maximum, which was easily recognizable within 0.01% of total iodine present. The results are graphed in Fig. 4. As the initial $[\text{I}]_t/[\text{Br}]_t$ was not known within 0.01%, proof was still lacking that the maximum slope came when $[\text{I}]_t/[\text{Br}]_t = 1.0000 \pm 0.0001$. We therefore calculated *E* for exact equivalence, assuming

$$[\text{I}]_t = [\text{Br}]_t = \sqrt{^*K_{\text{IBr}}[^*\text{IBr}]^2}$$

whence

$$E_{\text{calcd.}} = E_0 - 0.0295 \log \sqrt{^*K_{\text{IBr}}[^*\text{IBr}]^2}$$

In each case the proper value of $^*K_{\text{IBr}}$ was interpolated from Table IV.²³ Because in each case $E_{\text{calcd.}} = E_{\text{max.}}$ within 0.01% of total iodine, we concluded that $E_{\text{max.}}$ really occurs as close as this to the stoichiometrical end-point. As this outcome was reached without allowance for iodine tribromide, this compound is negligible at the equivalence point. The same conclusion results by solving the equation

$$Z = (\delta \ln [^*\text{Br}_2]/\delta [\text{Br}]_t)[\text{I}]_t = (4[^*\text{I}_2] + [^*\text{IBr}])/2([^*\text{Br}_2][^*\text{IBr}] + [^*\text{I}_2][^*\text{IBr}] + 4[^*\text{Br}_2][^*\text{I}_2])^{24}$$

Substituting arbitrary values for $[\text{Br}]_t$ and $[\text{I}]_t$, *Z* was evaluated in each case.

$[\text{Br}]_t$	0.10000	0.10000	0.1000	0.10000	0.10000
$[\text{I}]_t$.09990	.09999	.10000	.10001	.10010
<i>Z</i>	8730	17,400	17,680	17,400	8700

Clearly *Z*, and therefore $\Delta E/\Delta[\text{Br}]_t$, is at a maximum when $[\text{Br}]_t = [\text{I}]_t$. A further calculation predicted an extremely sharp end-point in such a system if hydrochloric instead of hydrobromic acid was the solvent.

Three similar titrations were made in hydrobromic acid 4.130 *N*, and two in a mixture where $[\text{HBr}] = 1$ and $[\text{HCl}] = 3$. These must be omitted here. The sensitiveness appeared unimpaired in the stronger acids.

The Iodine Tribromide Point. Evidence for Existence of Iodine Tribromide.—To four solutions made up so that $[\text{Br}]_t < 3[\text{I}]_t$, weighed portions of bromine were added from the special pipet. *E* was measured and plotted to give line A, Fig. 5, the slope of which, $m_A = \Delta E/\Delta \log$

(23) Compare Ref. 6, p. 2900, bottom.

(24) Compare Ref. 7, p. 148.

$[I]_t = 0.0276$. For comparison line B is given, $m_B = 0.0295$, corresponding to complete dissociation of iodine tribromide ($\alpha = 1$); also $m_C = 0.0148$ ($\alpha = 0$). The intersection is arbitrary. From $(m_B - m_A)$ we estimated K_{IBr_3} to be 0.2 ± 0.1 .²⁵

More conclusive evidence is obtainable from Table VI. As iodine monobromide is practically undissociated in presence of an extra mole of bromine, we can write $\frac{1}{2}[Br]_t - \frac{1}{2}[I]_t = [*Br_2]$ if no other compounds containing bromine are present. Assume for the sake of argument only that $[*Br_2]$ in any such solution equals $[Br_2]$ in that solution of bromine in hydrobromic acid where E is the same. In all cases $[*Br_2]$ calculated from E was about 10% smaller than $\frac{1}{2}[Br]_t - \frac{1}{2}[I]_t$. Attributing this difference to iodine tribromide, $[IBr_3]$ equals two-thirds the discrepancy. Thereupon $[*IBr] = \frac{1}{2}[I]_t - [*IBr_3]$, and $*K_{IBr_3}$ is readily found (Table VI). Although experimental errors are greatly multiplied in its calculation, the existence of the compound in solution appears to have been substantiated.

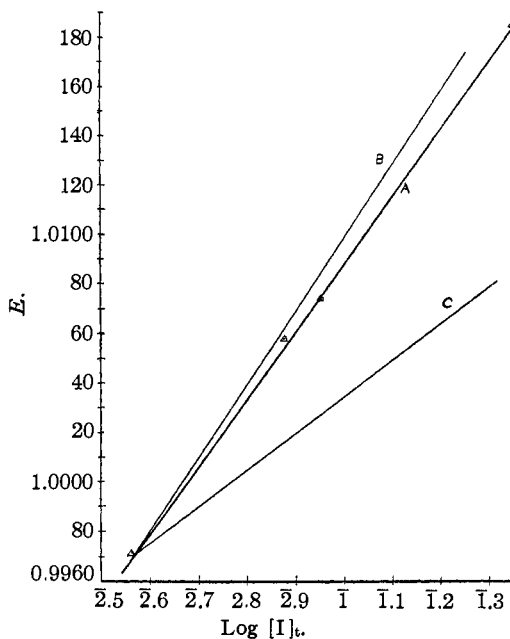


Fig. 5.—The $IBr + Br_2$ point in HBr 0.974 N : A experimental slope, 0.0276; B line with slope, 0.0295; C line with slope, 0.0148.

TABLE VI

E	$[*Br_2]'$	$[*Br_2]$	$\frac{1}{2}[Br]_t$	$[*IBr]$	$[*IBr_3]$	$*K_{IBr_3}$
0.9895	0.00631	0.00492	0.04140	0.0708	0.00073	0.52
.9985	.0127	.00975	.04694	.0701	.00144	.52
1.0176	.0556	.00376	.08109	.0638	.0077	.35
1.0232	.0859	.0542	.1032	.0582	.0133	.29
1.0260	.1067	.0640	.1163	.0549	.0166	.26
1.0292	.1362	.0764	.1353	.0483	.0232	.20

We are indebted to the Milton Fund of Harvard University for financial support in this investigation.

(25) Compare the argument concerning iodine trichloride, Ref. 6, p. 2902.

Summary

Equilibria and electrometric titrations involving iodine and bromine in hydrobromic acid have been experimentally investigated and mathematically analyzed with due reference to complex formation.

It is shown how to correct the molal potential of bromine in concentrated hydrobromic acids for complex formation. The corrected molal potential is constant over a wide range of concentration.

The true "replacement constant" for the reaction between iodine and bromide ion is evaluated, with correction for complex formation. It is 5×10^{-17} in 0.97 normal acid and 8×10^{-18} in 4.7 normal acid. This "constant" is plotted against the activity coefficient of the halide ion so that either can be interpolated or extrapolated.

The dissociation constant of iodine bromide (including complexes) is 2×10^{-8} in 0.97 normal, and 3×10^{-8} in 4.7 normal hydrobromic acid.

Electrometric titrations through the iodine point and iodine monobromide points were subjected to thorough experimental and mathematical treatment. The end-points are shown to coincide with the stoichiometrical end-points within 0.01%.

In solutions where $[Br]_t = 3[I]_t$, striking evidence of the presence of iodine tribromide or its complex ion IBr_3 was obtained. Its dissociation constant appears to be $0.3 \approx 0.2$.

CAMBRIDGE, MASSACHUSETTS

RECEIVED SEPTEMBER 24, 1932
PUBLISHED MAY 6, 1933

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Dipole Rotation and the Transitions in the Crystalline Hydrogen Halides

BY C. P. SMYTH AND C. S. HITCHCOCK

Previous work has shown the occurrence of dipole rotation in solid hydrogen chloride,¹ solid dimethyl sulfate and ice,² and the more obvious factors influencing rotation have been discussed in the paper which includes the latter substances. Measurements of the dielectric constants of crystalline hydrogen chloride, bromide and iodide down to liquid air temperatures and over a wide range of frequency are reported in the present paper in order to give further information on the problem of dipole rotation and to investigate from another point of view the peculiar transitions which have been observed in these hydrogen halides in the solid state.³

(1) Cone, Denison and Kemp, *THIS JOURNAL*, **53**, 1278 (1931).

(2) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932).

(3) Eucken and Karwat, *Z. physik. Chem.*, **112**, 467 (1924); Giaque and Wiebe, *THIS JOURNAL*, **50**, 101 (1928); **50**, 2193 (1928); **51**, 1441 (1929); Simon and Simson, *Z. Physik*, **21**, 168 (1924); Ruhemann and Simon, *Z. physik. Chem.*, **B15**, 389 (1932); Natta, *Mem. acad. Italia Chim.*, **2**, 15 (1931).