cells not containing the basic cadmium sulfate seems to be explainable only on the assumption that independent crystals of the basic mercurous sulfate were formed in the basic cells and the surfaces of the normal crystals were not covered over, while the opposite was the case in the neutral cells.

Summary

Weston standard cells were prepared with buffered electrolytes of varying acidities. The electromotive forces were practically constant over the period of observation, six to sixteen months. Hysteresis was very small in the most acidic and the least acidic groups.

A similar set of cells made with basic mercurous sulfate instead of normal varied in electromotive force with acidity and made it possible to estimate roughly at what acidity basic and normal mercurous sulfates can exist in equilibrium with the same saturated cadmium sulfate solution. It was shown that some of the buffered cells made with normal mercurous sulfate had acidities above this transition point and some below it.

Cells made with a mixture of basic and normal mercurous sulfates at the mercury electrode had high electromotive forces if the acidity was above the transition point and the normal electromotive force if it was below.

When the layer of mercurous sulfate was unusually thin, 1 to 2 mm. in thickness, the cells were quite variable if the acidity was below the transition point, but not if it was above.

An explanation is proposed for the slow decrease in electromotive force often observed in neutral cells.

DURHAM, NORTH CAROLINA

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Equilibria, Complex Ions and Electrometric Titrations. I. Iodine or Bromine in Hydrochloric Acid[1]

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

Two earlier papers[2,3] from this Laboratory have described, and analyzed mathematically the formation, in four and six normal hydrochloric acid, of the iodine chlorides and of bromine monochloride. Unexpectedly, also, it was found that a fifth or more of the bromine added to such acids oxidized chloride ion because the resulting chlorine was firmly bound as bromine monochloride. Such effects cannot be neglected in a precise study of electrometric titrations of mixed halogens or halides. Incidentally, the great stability of the compounds studied suggested the pos-

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

(2) Forbes, Glass and Fuoss, THIS JOURNAL, **47**, 2892 (1925).

(3) Forbes and Fuoss, *ibid.*, **49**, 142 (1927).

sibility of detecting new interhalogen compounds overlooked in previous investigations of these and similar systems.

In the two earlier researches, and in the work discussed below, anomalies were observed which were traced to complex formation involving halide ions and halogens or interhalogen compounds. Corrections for such complications, which now for the most part clarify the equilibria studied, require a new notation. From now on a star will indicate total concentrations including complex ions, and the absence of a star will indicate concentration of a species not present in a complex ion. Thus $[{}^*I_2] = [I_2] + [I_3'] + [I'_5] + [I_2Cl'] + \ldots\ldots$ will replace the symbol $[I_2]$ used with like meaning in the two earlier papers.[4]

The apparatus, experimental methods and precautions, corrections and calculations were as previously described except for certain improvements. The cells measured were of the type $-HgHg_2Cl_2 \mid HCl\ 4\ N \parallel HCl\ 4\ N\ Br_2$ or $I_2 \mid PtIr +$. The liquid connection between the half-cell containing halogen and the bridge beaker now remained attached to the flat end of the stopcock on the half-cell[5] throughout a series of experiments. Calomel electrodes brought to equilibirium in hydrochloric acid 2, 4 or 6 *N* were compared with hydrogen electrodes in the same acids to make our data comparable with those previously published.[2] All concentrations are volume molal, *i. e.*, formula weights per liter of solution.

Hydrochloric acid was purified and standardized as before. Reagent quality iodine and bromine were redistilled from solid iodide and bromide, respectively. Reagent quality potassium iodide was recrystallized and carefully dried. Mr. A. Q. Butler of the Coolidge Memorial Laboratory kindly furnished enough iodine purified for atomic weight determination to check the behavior of our own samples in a number of typical experiments.

Molal Potential of Chlorine in Hydrochloric Acid, E_0.—Calculations were based upon (1) moles of the several reactants taken to form one liter of a given solution, (2) the total concentration of chlorine $[{}^*Cl_2]$ at equilibrium. The fundamental assumption here, as hitherto,[2,3] was that $\log [{}^*Cl_2] = 33.64\ (E - E_0)$ where $(E - E_0)$ is the difference between the "single potential" of the given solution at a platinum–iridium electrode and that of the same electrode against molal chlorine in the same acid. Of course E was likewise a measure of the oxidation potential of any other halogen present. E_0 had previously been found by extrapolating to unit concentration values of $[{}^*Cl_2]$ between 0.006 and 0.16. To shorten the long extrapolation range usually required to find E from E_0, we first redetermined E_0 by liberating very small quantities of chlorine by electrolysis at the platinum iridium anode of the half-cell. The current strength was read on a milliammeter checked against a silver coulometer and also

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(4) Ref. 2, p. 2886; Ref. 3, pp. 146, 149.

(5) Ref. 3, p. 143.

against a standard instrument. $[{}^*Cl_2] = \log^{-1} 33.64\,(E - E_0)$. Details of an experiment in duplicate follow.

TABLE I

CHLORINE IN HYDROCHLORIC ACID, 3.997 N

E	$[{}^*Cl_2] \times 10^4$	E_0	E	$[{}^*Cl_2] \times 10^4$	E_0
1.15163	0.437	1.28123	1.15171	0.437	1.28131
1.16073	.874	1.28133	1.16089	.874	1.28149
1.16602	1.31	1.28142	1.16588	1.31	1.28128
1.16984	1.75	1.28144	1.16970	1.75	1.28130
1.17257	2.18	1.28137		Average	1.28135

Ten measurements in 5.938 N acid gave $E_0 = 1.2185$ with an extreme deviation of 0.0003 from the average. Six in 6.079 N acid gave $E_0 = 1.2140 \pm 0.00015$. These results agree well with those previously determined[6] at chlorine concentrations a thousand times as great.

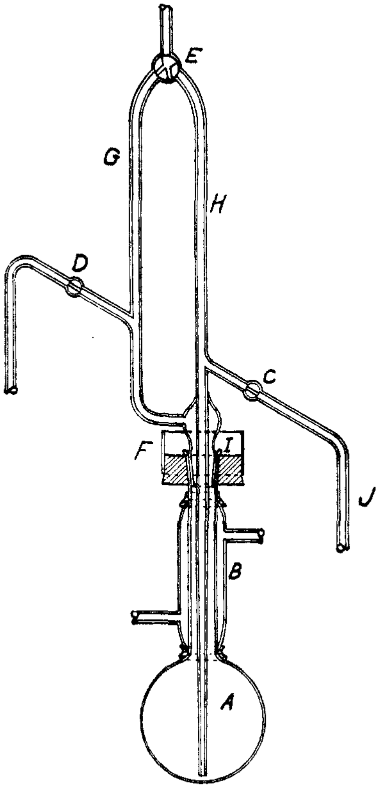

Fig. 1.

The Reaction between Iodine and Chloride Ion, as Influenced by Complex Formation.—In the presence of iodine and especially in light we found that hydrochloric acid is continuously oxidized by air according to the cycle $I_2 + Cl' \rightleftharpoons ICl + I'$ and $4H^+ + 4I' + O_2 \longrightarrow 2I_2 + 2H_2O$. In the absence of such precautions, the electromotive force E was far from reproducible and far too high, a point worthy of note by others who work with similar solutions. To dissolve iodine in the acid and to transfer the mixed solution to its half-cell, without access of air or loss of any constituent, an all-glass apparatus, Fig. 1, was designed. Through E carbon dioxide, previously bubbled through similar acid, could be introduced either below or above the liquid in A. There is a vent, D, and a condenser B to liquefy the vapors produced at temperatures sufficiently high to dissolve the iodine within a reasonable time. The collar F remains full of carbon dioxide while the ground joint I is lifted to admit a weighed quantity of solid iodine. Through J the half-cell was first swept out and finally filled with the cooled

(6) Ref. 2, p. 2896.

solution. All operations involving such solutions were carried out behind curtains of black cloth and with window shades drawn so as to exclude nearly all of the (northerly) light.

The primary equilibrium in such solutions

$$\mathrm{I_2} + 2\mathrm{Cl}' \rightleftharpoons 2\mathrm{I}' + \mathrm{Cl_2} \qquad (1)$$

is complicated by a second, $\mathrm{I_2} + \mathrm{Cl_2} \rightleftharpoons 2\mathrm{ICl}$ and by complex formation[7] of the type $\mathrm{ICl} + \mathrm{Cl}' \rightleftharpoons \mathrm{ICl}_2'$. As stated above

$$[{}^*\mathrm{I_2}] = [\mathrm{I_2}] + [\mathrm{I}_3'] + [\mathrm{I_2Cl}'] \qquad (2)$$

instead of the symbol $[\mathrm{I_2}]$ as used in the first paper, which defined such expressions so as to include complex ions, also

$$[{}^*\mathrm{I}'] = [\mathrm{I}'] + [\mathrm{I}_3'] \qquad (3)$$

and so on. We omit complexes relatively unimportant under given conditions—in this section I_5', for instance. Excluding complexes

$$[\mathrm{I}']^2[\mathrm{Cl_2}]/[\mathrm{I_2}][\mathrm{Cl}']^2 = K_r \qquad (4)$$

which we will term the true "replacement constant" and which should vary little in solution of fixed ionic strength. But if we write

$$[{}^*\mathrm{I}']^2[{}^*\mathrm{Cl_2}]/[{}^*\mathrm{I_2}][{}^*\mathrm{Cl}']^2 = {}^*K_r \qquad (5)$$

then ${}^*K_r$ cannot be constant because $[\mathrm{I}']/[{}^*\mathrm{I}']$, $[\mathrm{I_2}]/[{}^*\mathrm{I_2}]$ .... will vary with the several concentrations. In a particular solution

$$K_r = {}^*K_r([\mathrm{I}']^2/[{}^*\mathrm{I}']^2)([\mathrm{Cl_2}]/[{}^*\mathrm{Cl_2}])([{}^*\mathrm{I_2}]/[\mathrm{I_2}])([{}^*\mathrm{Cl}']^2/[\mathrm{Cl}']^2) \qquad (6)$$

Dissociation constants of several complex ions are known

$$[\mathrm{Cl_2}][\mathrm{Cl}']/[\mathrm{Cl}_3'] = 4.8 = C_1{}^8 \qquad (7)$$
$$[\mathrm{I_2}][\mathrm{Cl}']/[\mathrm{I_2Cl}'] = 0.62 = C_2{}^9 \qquad (8)$$
$$[\mathrm{I_2}][\mathrm{I}']/[\mathrm{I}_3'] = 0.00140 = C_3{}^{10} \qquad (9)$$

Sherrill and Izard[8] showed that C_1 is independent of $[\mathrm{Cl}']$ over a wide range of concentrations, and others have made similar observations in the case of other complexes involving a halide ion.[11]

Our methods are illustrated by a specific example, in which 0.000566 mole of iodine and 0.0526 mole of iodide were present per liter of hydrochloric acid, 3.998 N, at 25.00°. E (corrected) = 0.4597 volt, the potential of the total free chlorine in the solution. Calculated as usual,[12] $[{}^*\mathrm{Cl_2}] = 2.28 \times 10^{-28}$. Assuming the iodide formed at the expense of iodine by the reaction $\mathrm{I_2} + \mathrm{Cl}' \rightleftharpoons \mathrm{I}' + \mathrm{ICl}$ to be negligible, $[{}^*\mathrm{I}'] = 0.0526$, $[{}^*\mathrm{I_2}] = 0.000566$ and $[{}^*\mathrm{Cl}'] = 4$ (arbitrarily), equation (5) gives ${}^*K_r = 7.04 \times 10^{-29}$. To calculate K_r we obtain from (7), (8), (9), the equations

$$[\mathrm{Cl_2}]/[{}^*\mathrm{Cl_2}] = \mathrm{Cl}/([\mathrm{Cl}'] + \mathrm{C_1}) \qquad (10)$$
$$[\mathrm{I_2}]/[{}^*\mathrm{I_2}] = \mathrm{C_2C_3}/(\mathrm{C_3}[\mathrm{Cl}'] + \mathrm{C_2}[\mathrm{I}'] + \mathrm{C_2C_3}) \qquad (11)$$

and

$$[\mathrm{I}']/[{}^*\mathrm{I}'] = \mathrm{C_3}/([\mathrm{I_2}] + \mathrm{C_3}) \qquad (12)$$

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[7] Faull and Baeckström, THIS JOURNAL, **54**, 620 (1932).

[8] Sherrill and Izard, *ibid.*, **53**, 1667 (1931).

[9] Jakowkin, *Z. physik. Chem.*, **20**, 19 (1896).

[10] Jones and Kaplan, THIS JOURNAL, **50**, 1848 (1928).

[11] Carter and Hoskins, *J. Chem. Soc.*, 580 (1929).

[12] Ref. 2 p. 2896.

The final value of $[I_2]$ is found by substituting, in the second approximation of (11), the value of $[I']$ found from (12) in a first approximation. The final value of $[I']$ is found by substituting in (12) a preliminary value for $[I_2]$ found from (11). Continuing this procedure, we obtain $[I']/[{}^*I'] = 1.994$, $[Cl_2]/[{}^*Cl_2] = 0.54$, $[I_2]/[{}^*I_2] = 0.0223$ and $[Cl']/[{}^*Cl'] = 1.00$. Substituting in (6), $K_r = {}^*K_r \times 0.54 \times (0.994)^2/0.0223$. When added iodide was small compared to added iodine, as in the first two cases of Table I, further corrections were made, in the manner of those already described[13] in connection with the reaction between bromine and chloride ion, in order to calculate $[{}^*I_2]$ and $[{}^*I']$.

TABLE II

Initial $[I_2]_i = 0.000566 = [I]_t$ HCl 3.997 N

E	$[{}^*Cl_2] \times 10^{23}$	$[KI] \times 10^4$	${}^*K_r \times 10^{28}$	$K_r \times 10^{27}$
0.6373	21.5	1.296	4.2	1.58
.6196	5.46	2.64	4.2	1.60
.6121	3.06	3.96	5.3	1.99
.5987	1.08	6.00	4.2	1.65
.5908	0.586	8.45	4.6	1.81
.5603	.0552	24.60	3.7	1.65
.5397	.0112	50.0	3.1	1.65
.5100	.00112	127.8	2.0	1.62
.4868	.000186	252.0	1.3	1.65
.4597	.0000228	526.0	0.7	1.72
			Average	1.69

Four other sets of experiments in four normal acid held iodine constant in each set while varying iodide. Four similar sets were carried out in six normal acid. In a subsequent paper we correlate K_r with activity coefficients. Figure 2 shows K_r plotted against $^1/_2[I]_t$, that is, total moles of iodine added per liter. The number of experiments made at each constant iodine concentration is stated. The extreme deviation in any set is measured by a vertical line upon which the average value is dotted. It is seen that K_r increases in each acid, as $[{}^*I_2]$ decreases. To show that the amount of neutral salt added is not disturbing, potassium perchlorate was added to similar solutions in five increments. The final concentration, 0.046, equalled the highest concentration of potassium iodide present in any of the experiments just described. The first and last readings of E were exactly equal, and the extreme deviation is 0.0003 volt.

The Iodine Point in Hydrochloric Acid.—Successive weighed portions of iodide were added to solutions of iodine prepared in the special apparatus (Fig. 1), and E was measured after each addition. Figure 3 presents our data in condensed form. The dotted lines represent $[{}^*Cl_2]$ as calculated with the help of C_1, C_2, C_3 by methods corresponding to those outlined in the preceding section. In spite of all precautions it is doubtful if the ef-

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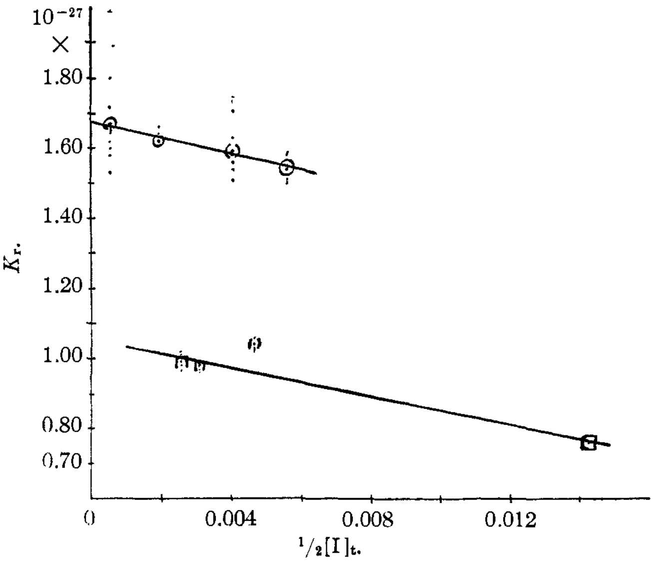
(13) Ref. 3, p. 151.



$$K_r = \frac{[Cl_2]\,[I^-]^2}{[I_2]\,[Cl^-]^2}$$

Fig. 2.—(·), HCl 4 *N*; ⊡, HCl 6 *N*.

fects of atmospheric oxidation were wholly negligible: this system is much more sensitive than it would be if chlorine or iodide had been added

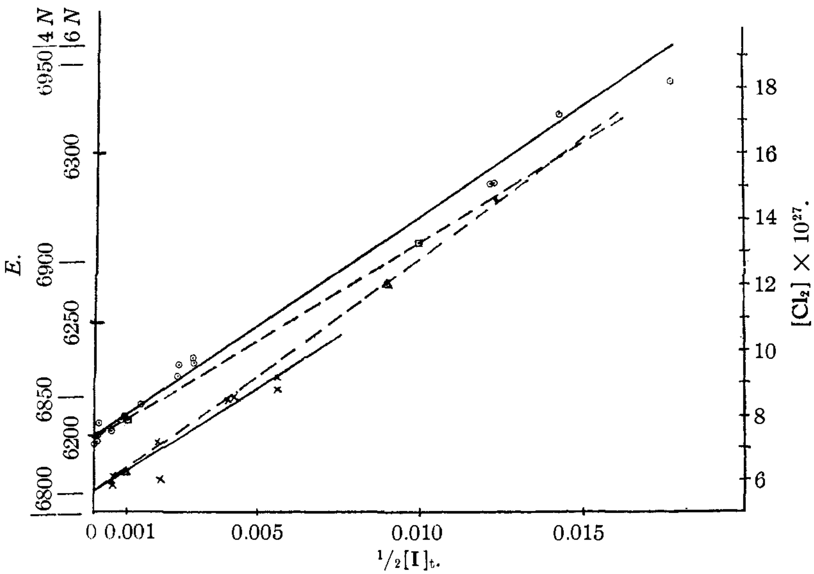


Fig. 3.—Iodine point in HCl: ⊙ 6 *N* experimental; ⊡ 6 *N* calculated; × 4 *N* experimental; △ 4 *N* calculated.

as well as iodine. The fact that the experimental curves do not converge like the calculated ones may be due to such difficulties. Experiment agrees better with prediction in our solutions of bromine in hydrochloric acid and of iodine in hydrobromic acid.

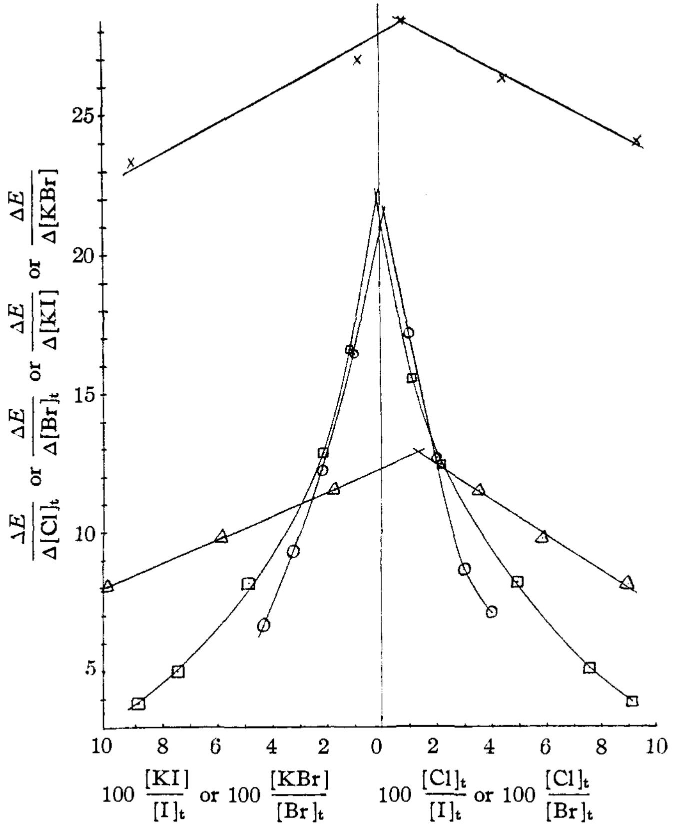


Fig. 4.—Titration from iodine point in HCl or bromine point in HCl: ×, 4 *N* $[\mathrm{Br}]_t = 0.093$; △, 6 *N* $[\mathrm{I}]_t = 0.0349$; □, 4 *N* $[\mathrm{I}]_t = 0.00823$; ⊙, 6 *N* $[\mathrm{I}]_t = 0.00938$.

The Instability of the Compound $ICl \cdot I_2$.—A mathematical study of $^*K_{ICl}$ over ranges where $[^*I_2]$ was large compared with $^1/_2[\mathrm{Cl}]_{\mathrm{total}}$ convinced us that a compound such as $ICl \cdot I_2$ would produce disturbances in K_{ICl} capable of identification if $[ICl][I_2]/[ICl \cdot I_2] < 0.6$. As no such disturbance could be detected it appears that such a compound must be highly unstable if it exists at all.

Electrometric Titrations through the Iodine Point in Hydrochloric Acid.—Three electrometric titrations were carried through the iodine point in 4 *N* acid and three in 6 *N* acid. Each titration involved (1) the addition to iodine of small amounts of chlorine by electrolysis of the hydro-

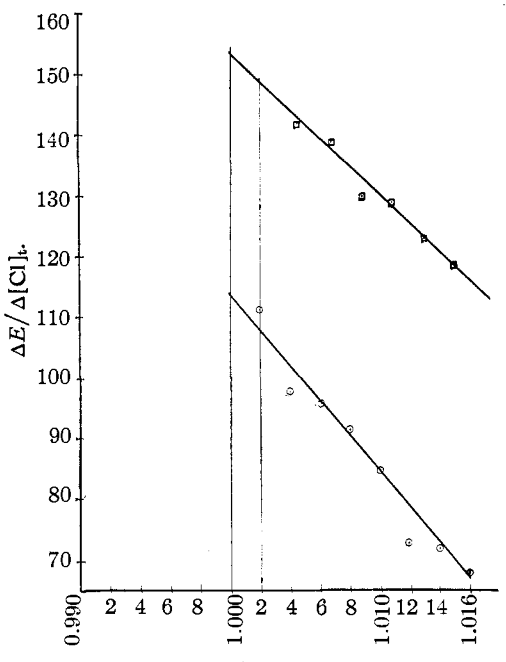


Fig. 5.—Titration from iodine point in HCl: ☐, 2 N $[\mathrm{I}]_t = 0.0124$; ⊙, 6 N $[\mathrm{I}]_t = 0.0207$.

chloric acid and (2) the addition of small weighed quantities of potassium iodide to a similar iodine solution. After each addition E was measured as usual. To exclude oxygen the initial solutions were prepared in the special apparatus (Fig. 1). The slopes $\Delta E/\Delta[\mathrm{Cl}]$ and $\Delta E/\Delta[\mathrm{KI}]$ were plotted together (Fig. 4), the two curves intersecting at or near the iodine point as would be the case if chlorine and iodide or iodine were titrated together. A preliminary study of the pertinent equations predicted no shift from the stoichiometrical end-point. For comparison two titrations made in analogous fashion through the bromine point by Forbes and Fuoss[14] are also graphed. The relative sensitivity of the end-point is greater, the more acute the angle of intersection. Hendrixson's[15] very careful measurements showed that iodide could be titrated (with permanganate) through the iodine point within 0.02%, provided that sulfuric acid, only, was present. The end-point became progressively more obscure as [HCl] was increased from zero upward. This would be predicted from our theory, as the iodine accumulated at the end-point forms iodine chloride and iodide in increasing amounts as [Cl′] increases. At the same time $\Delta[{}^*\mathrm{I}_2]/[{}^*\mathrm{I}']^2$ near the end-point, and therefore ΔE as well, becomes smaller for a given addition of the oxidant. To discover the limitations of the titration when [HCl] = 2 and 6, respectively, we established equal concentrations of iodine in samples of these acids and added chlorine electrolytically, using a more sensitive milliammeter than usual so as to measure $\Delta[\mathrm{Cl}]$ more accurately. Figure 5 plots the results, the abscissa scale being five times as great as in Fig. 4. It appears that the end-point as fixed by extrapolation backward from the chlorine points would coincide with the original iodine point within 4×10^{-6} mole of chlorine, or 0.02% of the iodine present. Larger errors could result from stoichiometrical errors, volatilization of halogen, or oxidation by air. It is

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(14) Ref. 3, p. 149.

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

only fair, however, to point out that our end-points were not subject to complications such as the slow reaction between permanganate and manganous ion or occlusion of halogen by manganese dioxide.

Complex Formation at the Bromine Point in Hydrochloric Acid.—Forbes and Fuoss[16] gave no adequate explanation of the shape of the plot of E against log $^1/_2[\mathrm{Br}]_t$. Figure 6 gives this curve more completely for

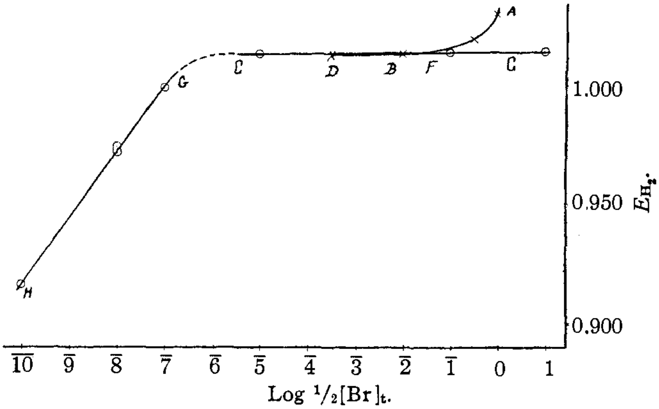

Fig. 6.—Bromine point in HCl 6 N: ⊙ calculated curve × experimental curve.

6 N acid. The data of Forbes and Fuoss cover the interval $1 > {}^1/_2[\mathrm{Br}]_t > 10^{-2}$ (marked AB). Our extension BD reaches $10^{-3.5}$, below which polarization difficulties became unsurmountable. To extend the curve to lower bromine concentrations we solved five simultaneous equations furnished by Forbes and Fuoss

$$\log\ [{}^*\mathrm{Cl_2}] = 33.64\ (E - E_0) \tag{12}$$
$$[{}^*\mathrm{Br_2}][{}^*\mathrm{Cl_2}]/[{}^*\mathrm{BrCl}]^2 = 3.2 \times 10^{-4} = {}^*K_1 \tag{13}$$
$$([{}^*\mathrm{Br'}]^2[{}^*\mathrm{Cl_2}])/([{}^*\mathrm{Cl'}]^2[{}^*\mathrm{Br_2}]) = {}^*K_2 = 2.97 \times 10^{-12} \tag{14}$$
$$[{}^*\mathrm{Br'}] = [{}^*\mathrm{BrCl}] + 2[{}^*\mathrm{Cl_2}] \tag{15}$$
$$^1/_2[{}^*\mathrm{BrCl}] + {}^1/_2[{}^*\mathrm{Br'}] + [{}^*\mathrm{Br_2}] = {}^1/_2[\mathrm{Br}]_{\mathrm{total}} \tag{16}$$

using graphical approximations. The outcome predicted that the slope would become 0.0295 if $^1/_2[\mathrm{Br}]_{\mathrm{total}} < 10^{-7}$, with practically complete conversion of bromine to bromine monochloride and bromide. Polarization ruins any experimental test of this prediction (graphed from G to H in Fig. 6). The mathematical analysis also predicted that the slope would be practically zero if $^1/_2[\mathrm{Br}]_{\mathrm{total}} > 10^{-6}$. The experimental curve CC agrees well with this second prediction from $10^{-3.5}$ to 10^{-2}, but at F it turns sharply upward due to increasing complex formation, and we were able to predict this effect as well. Combining algebraically the three dissociation constants

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(16) Ref. 3, p. 153–154.

$[Br_2][Cl']/[Br_2Cl'] = 0.71 = C_4$,[17] $[Br_2][Br']/[Br_3'] = 0.062 = C_5$, $[Br_2]^2[Br']/[Br_5'] = 0.051 = C_6$[18]

it became possible to predict (details omitted) the magnitude of $^*K_2$ in a given concentrated bromine solution from its fixed value found in any dilute bromine solution—*i. e.*, 3.0×10^{-12} in 6 N, and 5.6×10^{-12} in 4 N acid. Using the proper value of $^*K_2$ in the generally applicable equation

$$[^*Cl_2] = ([^*BrCl]/[^*Br'])\sqrt{^*K_1{}^*K_2[^*Cl_2]}$$[19]

the calculated results agree respectably with experimental values of $[^*Cl_2]$ and of E over the interval FA. The only simplifying assumption made in the process is that $[^*BrCl] = [^*Br']$ and this we proved correct within 0.1% whenever $[Br]_t > 10^{-3}$.

The outcome of these corrections is given more explicitly in Fig. 7, where $[^*Cl_2]$ is plotted against $^1/_2[Br]_t$. The calculated lines intersect at a point close to the intersection of the experimental lines taken from Fig. 4 of the paper of Forbes and Fuoss. The fact that more chlorine is present in the more dilute acid was very puzzling when first noted. It is now proved to be inevitable chiefly because the ratio $[Br']/[^*Br']$ changes faster, with changing $[Br]_t$, in the more dilute acid. This in turn means that $^*K_2$ must vary more rapidly in the more dilute acid.

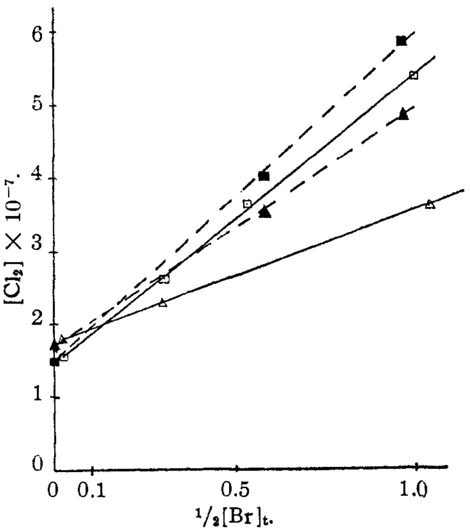

Fig. 7.—Bromine point in HCl: ⊡, 4 N experimental; ■, 4 N calculated; △, 6 N experimental; ▲, 6 N calculated.

The Instability of "Bromine Trichloride" in Hydrochloric Acid.—We applied the general mathematical analysis of Forbes and Fuoss to predict the slope of the electrometric titration curve at the point where $[Cl]_{total} = 3[Br]_{total}$ while assigning various assumed values to $[Br_2][Cl_2]^3/[BrCl_3]^2 = {}^*K_{BrCl_3}$. The condition is imposed that $[Cl]_t = 3[Br]_t$.

TABLE III

SLOPES PREDICTED FROM DISSOCIATION CONSTANTS

K_{BrCl_3}	∞	1.0	0.5	0.1	0.05
$\Delta E/\Delta(Cl)_t$	0.236	0.236	.237	.244	.256

As the predicted slope varied only 0.020 over the range of magnitudes assigned to K_{BrCl_3}, and as our experimental slope falls within the same

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[17] Jakowkin, *Z. physik. Chem.*, **20**, 19 (1896).

[18] Linhart, THIS JOURNAL, **40**, 158 (1918).

[19] Ref. 3, p. 152, last line.

interval, it was concluded that our experimentation would have to be considerably refined to obtain positive evidence of bromine trichloride even if K_{BrCl_3} were no smaller than 0.05. Better evidence of its instability comes from the equation for the "molal potential of bromine trichloride," $0.0295 \log [Br]_t = E - 1.2132$, almost identical with the molal potential of Cl_2, which is $0.0295 \log [{}^*Cl_2] = E - 1.2138$. If bromine monochloride combined appreciably with chlorine its molal potential would be definitely lower than that of chlorine. From the difference it may be shown that $K_{BrCl_3} > 1.4$. There is no evidence that such a compound exists at all.

Electrometric Titration through the Bromine Monochloride Point.—Using the equations of Forbes and Fuoss,[20] we calculated the course of the curve when bromine is titrated with chlorine through the bromine monochloride point. Owing to the limited stability of bromine monochloride we predicted that the maximum slope must occur when added chlorine is only 0.997 of the bromine present. This prediction could not be tested by the experimental data of Forbes and Fuoss. If iodine monochloride, also, were present during the titration, an additional complication would arise. Because iodine trichloride has very nearly the same molal potential as bromine monochloride and K_{ICl_3} is of the same order of magnitude as K_{BrCl}, iodine monochloride and bromine will compete on equal terms for the added chlorine. Therefore the error in titrating bromine with chlorine in the presence of iodine monochloride might amount to $^1/_2[{}^*ICl]$. This electrometric titration offers little in the way of practical value from any standpoint.

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

Summary

Important equilibria, with emphasis upon complex formation and electrometric titrations, all involving iodine or bromine or both, in hydrochloric acid have been investigated. The data, as well as data previously obtained in this Laboratory, have been analyzed mathematically, introducing known values of the dissociation constants of certain complex ions formed by the addition of halide ions to halogens and to interhalogen compounds. Treated thus, many experimental results at first sight anomalous are satisfactorily explained or predicted.

The true "replacement constant," $K_r = [I']^2[Cl_2]/[I_2][Cl']^2$ was found by correcting, for complex formation, corresponding total concentrations. Extrapolated to high dilution, K_r is close to 1.67×10^{-27} in four normal hydrochloric acid and 1.05×10^{-27} in six normal acid.

The potential of iodine in hydrochloric acid appears much too high in the presence of oxygen owing to progressive formation of iodine monochloride.

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[20] Ref. 3, p. 148.

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.

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Equilibria, Complex Ions and Electrometric Titrations. II. Iodine, Bromine and Hydrobromic Acid. Iodine Tribromide[1]

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In a previous paper[2] 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. Hahn[5] 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

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[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)