

4. A reversal of the positions of the iodine and absorbent so that the iodine vapor diffuses against the centrifugal force does not decrease the rate of evaporation but gives the same rate of evaporation that is found when normal diffusion occurs in the centrifuge at rest.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE REACTION BETWEEN BROMINE AND CHLORIDE ION IN HYDROCHLORIC ACID. BROMINE MONOCHLORIDE

BY GEORGE SHANNON FORBES AND RAYMOND MATTHEW FUOSS

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In contrast with systems containing chlorine and iodine, those involving chlorine and bromine have received scant attention. This is due, perhaps, to absence of compounds when chlorine is dissolved in liquid bromine, a topic summarized by Abel.<sup>1</sup> On the other hand, the loss of color by bromine when chlorinated in hydrochloric acid, with the action of the product upon ethylene, has led several investigators<sup>2</sup> to assume bromine chloride present, stabilized by complex formation with the acid. The only attempt at an electrochemical study seems to have been made by Brown,<sup>3</sup> who measured between platinum electrodes the decomposition potential  $E$  of a solution of bromine chloride,  $\text{BrCl} \cdot \text{HCl}$  (strongly hydrolyzed), and found  $EF$  to correspond roughly to the heat of formation of the compound from bromine and chlorine.

The mutual replacement of chlorine and bromine in the presence of their ions, though of obvious importance, has hitherto been completely neglected.

As no quantitative information about this system could be found, we investigated it by methods<sup>4</sup> previously applied in this Laboratory to solutions of iodine and chlorine in hydrochloric acid. We worked in 6  $N$  and 4  $N$  acid partly to avoid hydrolysis, and partly to take advantage of the relation between  $E$  and  $[\text{Cl}_2]$  previously determined in these acids. Further work, in more dilute acids, is projected.

If successive portions of a solid bromine are added to chlorine in hydrochloric acid, the plot of oxidation potential against added bromide has two steeply descending linear portions, recalling the analogous curve for iodine and chlorine. The first of these includes the "bromine monochloride point," as we shall call it, where total bromine equals total chlorine; the other the "bromine point," where added bromide equals initial chlorine, or where pure bromine is dissolved directly in the acid. Using cells of

<sup>1</sup> See Abegg, *Handbuch der anorganischen Chemie*, 4<sup>2</sup>, 294 (1913).

<sup>2</sup> Simpson, *Proc. Roy. Soc.*, 27, 118 (1878). James, *J. Chem. Soc.*, 43, 37 (1883). Delépine and Ville, *Bull. soc. chim.*, 27, 673 (1920).

<sup>3</sup> Brown, *Phil. Mag.*, 31, 449 (1891).

<sup>4</sup> Forbes, Glass and Fuoss, *THIS JOURNAL*, 47, 2893 (1925).

the type— $\text{PtH}_2 \mid \text{HCl} \mid \text{HCl} \mid \text{HCl} + \text{Cl}_2 + \text{BrCl} + \text{Br}_2 + \text{Br}' \mid \text{PtIr} +$  we have carefully studied these two linear portions, as well as solutions of pure bromine in hydrochloric acid. From the data the essential concentration relations were worked out, the slopes predicted and the equilibrium constants evaluated in successive approximations. The normal potential of bromine monochloride was found and the reactions involving bromine and chloride ion were expounded in detail.

### Apparatus

The apparatus of the previous research was modified (Fig. 1) to avoid analyses of vapor phases containing both bromine and chlorine. The cell was provided with a platinum-iridium electrode  $E$ , purchased through a grant from the Cyrus M. Warren Fund, and with a stopcock  $K$ , 8 mm. in bore. Upon shaking, the contents of the cell were effectively stirred by the glass beads  $G$ , of known weight and density. The net volume was 118.5 cc. (later 108.6 cc.) minus the volume of the beads. The rubber connection at  $R$  could not contaminate the solution in the cell. The cell was immersed to  $L$  in the thermostat at  $25.00^\circ$ . The standardization of the thermometer has been previously described.<sup>4</sup> The exit tube of the siphon dipped into the beaker, as did also the hydrogen electrodes (previously described).<sup>4</sup> By suction at  $H$ , with stopcock  $K$  closed, the siphon was filled to  $F$ , the acid concentration being uniform throughout the chain.

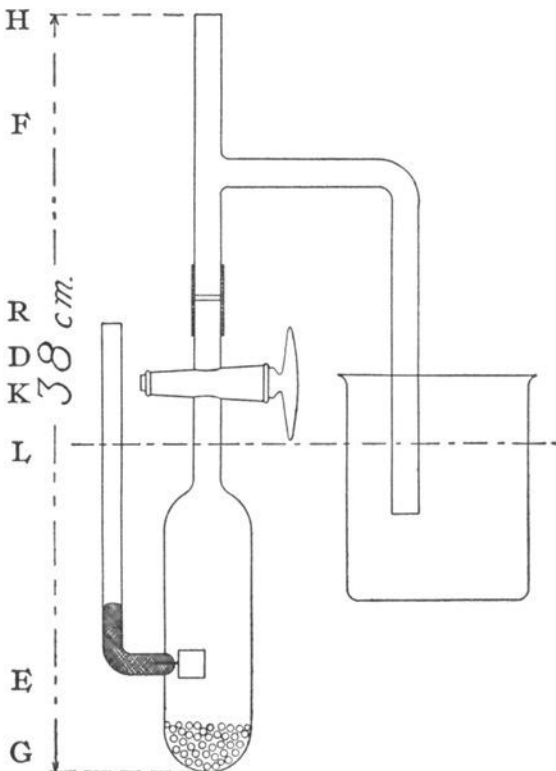


Fig. 1.—Cell for electrometric titration.

Bromine was weighed out from a freezing-point pipet with a very fine delivery tube. The other end was guarded by a small U-tube in which moistened potassium iodide and calcium chloride, both frequently renewed, were confined between asbestos plugs. The weight of the combination seldom varied 1 mg. in an hour. When the cell had been taken out, disconnected at  $R$  and drained to  $D$ ,  $K$  was opened and the tip of the pipet lowered almost to  $D$ . By blowing through a drying tube, the desired amount of bromine was delivered. By suction at the open end of the U-tube, the delivery tube was freed from bromine without loss of bromine vapor, or of moisture from the iodide.

### Materials

The distillation and standardization of hydrochloric acid, 6.079 *N* and 3.997 *N*, have been described.<sup>4</sup> We shall refer to them as 6 *N* and 4 *N*. Chlorine, from manganese dioxide and colorless commercial acid, was bubbled first through a Leidener bottle of acid more dilute than that in the cell, then through one with 6 *N* or 4 *N* acid. Professor G. P. Baxter very kindly supplied 100 g. of bromine, highly purified by the oxalate-permanganate method and distilled from under a potassium bromide solution. The water content of saturated bromine is less than 0.05%.<sup>5</sup> It was shown as follows that the combined correction for water and for vaporization during delivery from the pipet was negligible. Successively heavier portions of bromine were discharged into flasks containing an excess of iodide in dil. hydrochloric acid, under carbon dioxide. These were titrated with thiosulfate standardized against iodine resublimed from iodide and thoroughly dried.

Grams lost by pipet.....	0.0914	0.2191	0.3740	1.3437
Equivalents per g. lost.....	.01249	.01247	.012485	0.01252
Theoretical value.....	.01250			

### Measurement of E.M.F.

The potentiometer and accessories have been previously described. Immersed at 25° after thorough shaking, the cell attained within ten minutes a sharply defined e.m.f. which seldom varied by 0.0001 volt over many hours.

### Corrections

The hydrogen electrodes, frequently replatinized, were corrected to 760 mm. as previously described<sup>4</sup> for barometer and for vapor pressure of their solution. The addition of bromine or of chlorine diluted the acid in the cell. Density measurements showed that free or combined bromine occupied 0.32 cc./g. and combined chlorine 0.5 cc./g. Therefore, new values of *N* were calculated, and *E* was corrected as previously described.<sup>4</sup> No volume correction for *free* chlorine was made, as the equations connecting  $\log [Cl_2]$  with *E* had been formulated without it. Additions of bromine diluted the dissolved bromine and chlorine already present, forcing outside the stopcock an equal volume of solution which had to be rejected, so that further corrections had to be applied. These and the other calculations required weeks of incessant labor.

### Notation

Equilibrium concentrations are given in moles, gram atoms or gram ions per liter, as  $[Cl_2]$ ,  $[Br_2]$ ,  $[BrCl]$ ,  $[Br']$ ,  $[HCl]$ . The symbols  $[Cl]$ ,  $[Br]$ ,  $[KBr]$  indicate only 1000/*V* times the formula weights introduced

<sup>5</sup> Wildermann, *Z. physik. Chem.*, **11**, 407 (1903).

into the cell of volume  $V$ , differing from  $2[\text{Cl}_2]$ ,  $2[\text{Br}_2]$ ,  $[\text{Br}']$  by the amounts reacting chemically. The subscript  $i$  denotes the initial value in a series. Any italicized figure is half a unit greater than that actually determined or calculated.

### The Dissociation Constant of Bromine Monochloride

Indeterminate solutions of chlorine in hydrochloric acid were made up as described under "Materials." The cell was filled, shaken, set up,  $E_i$  measured and corrections were made. Then  $[\text{Cl}_2]_i$  was calculated as described in the previous paper where the stronger acid was 6.078  $N$ .

In 6.078  $N$  acid,  $\log [\text{Cl}_2] = 33.64 (E - 1.2138)$

In 3.997  $N$  acid,  $\log [\text{Cl}_2] = 33.64 (E - 1.2801)$

Successively weighed portions of bromine were then introduced,  $E$  was measured and  $[\text{Cl}_2]$  calculated with all corrections. We wrote provision-

TABLE I  
BROMINE ADDED TO CHLORINE

Acid, $N$	$E$ (corr.)	$[\text{Cl}_2]_i$ $\times 10^3$	$[\text{Cl}_2]$ $\times 10^3$	$[\text{BrCl}]$ $\times 10^3$	$[\text{Br}]$ $\times 10^3$	$[\text{Br}_2]$ $\times 10^3$	$K_1$ $\times 10^4$	$E_{\text{BrCl}}$
6.079	1.1735	88	....	...	...	...	..	....
	1.1065		0.246	87	111	12.1	3.89	
	1.0853		.0476	88	191	52	3.20	
	1.0690		.0134	88	431	171	2.99	1.1296
	1.0590		.00618	88	805	359	2.89	
	1.0472		.00248	88	1850	881	2.84	
						Av. 2.98		
6.079	1.1783	128	....	...	...	...	..	...
	1.1252		.104	126	143	8.4	5.49	
	1.0922		.081	128	269	71	3.50	1.1351
	1.0803		.0322	128	459	166	3.22	
	1.0747		.0208	128	625	249	3.14	
						Av. 3.29		
3.997	1.2343	58	....	...	...	...	..	
	1.1671		.158	56.7	67	5.0	2.46	
	1.1422		.0230	56.9	139	41.0	2.92	1.1906
	1.1268		.0070	56.6	334	139	3.02	
	1.1187		.00371	56.2	640	292	3.46	
						Av. 3.13		
3.997	1.2431	114	....	...	...	...	..	
	1.1813		.476	112	135	11.3	4.25	
	1.1548		.061	113	254	71	3.36	
	1.1462		.0313	113	386	137	3.37	1.1998
	1.1412		.0213	112	510	200	3.38	
	1.1358		.0140	112	720	305	3.36	
	1.1326		.0109	111	920	403	3.44	
						Av. 3.32		

ally  $\text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2\text{BrCl}$  as the sole reaction. Then  $[\text{Cl}_2]_f - [\text{Cl}_2] = \frac{1}{2}[\text{BrCl}]$  and  $\frac{1}{2}[\text{Br}] - \frac{1}{2}[\text{BrCl}] = [\text{Br}_2]$ . Table I gives the data, and the values of  $K_1 = [\text{Br}_2][\text{Cl}_2]/[\text{BrCl}]^2$ . When  $[\text{Cl}]$  exceeds  $[\text{Br}]$ ,  $[\text{Br}_2]$  can only be found as the very small difference between two much larger quantities fixed by experiment, and  $K_1$  cannot be calculated to advantage.

The dissociation constant  $K_1$  of bromine monochloride is then  $3.2 \pm 0.2 \times 10^{-4}$  in either 6 *N* or 4 *N* acid. Its independence of the other concentrations also justifies the inference that  $\text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2\text{BrCl}$  is the main reaction under these conditions. If, as seems probable,  $\text{BrCl}$  is present in a stable complex with chloride ion,  $K_1$  is really a combination of simpler constants.

### The Direct Determination of $E$ and of $\Delta E/\Delta[\text{Cl}]$ at the Bromine Monochloride Point

Starting with indeterminate chlorine in hydrochloric acid,  $[\text{Cl}_2]_f$  was found from  $E_f$ . Bromine in slight excess was at once weighed out. Next, a platinum cathode was placed in the bridge solution, the stopcock loosened slightly, and a current passed through the cell for a suitable interval recorded by a stop watch. The milliammeter needle was kept on the 0.020 mark by uninterrupted regulation of an auxiliary resistance—a tedious process. This mark, checked against a silver coulometer, read 0.0002 ampere too high, and this correction was always applied. After

TABLE II

VARIATION OF  $\Delta E/\Delta[\text{Cl}]$  WITH  $[\text{Cl}]$ 

I	$E = 1.13582$ , $[\text{Cl}_2] = 0.002377$ , $[\text{Br}] = 0.0140$ , $E_f = 1.0453$								
$\Delta[\text{Cl}] \times 10^3$	3.18	2.12	0.74	1.06	0.53	0.53	0.53	0.53	0.53
$\Delta E \times 10^3$	16.49	11.31	4.22	7.55	4.42	5.79	6.71	7.07	
$\Delta E/\Delta[\text{Cl}]$	5.2	5.3	5.7	7.1	8.3	10.9	12.6	13.3	
$\Delta[\text{Cl}] \times 10^3$	0.53	0.53	0.3						
$\Delta E \times 10^3$	6.19	4.94	...						
$\Delta E/\Delta[\text{Cl}]$	11.7	11.1	...						
[Br] = 0.0140, [Cl] = 0.0137, mean value 0.0139, $E = 1.1055$ , all at the bromine monochloride point.									
II	$E = 1.16378$ , $[\text{Cl}_2] = 0.02073$ , $[\text{Br}] = 0.0446$ , $E_f = 1.1035$								
$\Delta[\text{Cl}] \times 10^3$	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.17	1.08
$\Delta E \times 10^3$	2.95	3.38	3.76	4.17	4.32	4.17	3.69	3.25	2.75
$\Delta E/\Delta[\text{Cl}]$	2.73	3.13	3.48	3.89	4.01	3.86	3.42	2.78	2.54
[Br] not accurately known, [Cl] = 0.0463, $E = 1.1201$ , all at the bromine monochloride point.									
III	$E = 1.17962$ , $[\text{Cl}_2] = 0.0707$ , $[\text{Br}] = 0.1466$ , $E_f = 1.1393$								
$\Delta[\text{Cl}] \times 10^3$	0.54	0.54	1.18	0.54	0.64	1.07	2.14		
$\Delta E \times 10^3$	.69	.72	1.65	.63	.72	1.03	1.95		
$\Delta E/\Delta[\text{Cl}]$	1.28	1.34	1.40	1.16	1.12	0.96	0.91		
[Br] = 0.1466, [Cl] = 0.1442, mean value 0.1454, $E = 1.1415$ , all at the bromine monochloride point.									

each electrolysis the cell was shaken to constant  $E$ , and the process was repeated until the maximum value of  $\Delta E/\Delta[\text{Cl}]$  had been passed. A correction was applied to  $E$  for the loss of  $0.080 \times 0.0198 t/F$  equivalents of acid from the anode solution. The cationic transference number 0.80 was extrapolated from the data collected by Foerster.<sup>6</sup> Three experiments, all in 6  $N$  acid, are compactly summarized in Table II. The observed values of  $E$  and of  $[\text{Cl}]$  at any stage of the experiment can be reproduced from Table II by summation, and the derived quantities  $[\text{Cl}_2]$ ,  $[\text{Br}_2]$ ,  $[\text{BrCl}]$  and  $K_1$  calculated.  $E$  denotes the e.m.f. after chlorine, but no bromine had been added, and  $E_i$  the e.m.f. after the first addition of bromine.

As a check, total halogen in the cell at the end of the first run was determined by iodimetry in a tall beaker kept full of carbon dioxide from a cylinder to exclude air while washing out the cell and titrating. Total halogen was 3.41 milliequivalents. The original chlorine was 0.55, the bromine 1.63 and the sum of chlorine added by electrolysis 1.23, or 3.41 milliequivalents in all.

### The Molal Potential of Bromine Monochloride

At the midpoint of the steepest section of each curve we wrote, provisionally,  $[\text{Br}] = [\text{Cl}]$  and  $[\text{Br}_2] = [\text{Cl}_2]$ . The most probable value of total bromine monochloride concentration, inclusive of its dissociation products, is the mean of  $[\text{Br}]$  and  $2[\text{Cl}_2]_i + \Sigma \Delta[\text{Cl}]$ , the  $\Delta[\text{Cl}]$  being summed to the same point. Each of the two in 6  $N$  acid (Table I) where portions of liquid bromine were added, also fixed a bromine monochloride point. Using only experiments where  $[\text{Br}_2]$  was big enough to be calculated respectably,  $K_1$  was averaged. We solved, in each run, the equation  $[\text{Br}_2] = [\text{Cl}_2] = \sqrt{K_1} [\text{BrCl}]$  for  $[\text{Cl}_2]$ , where  $[\text{BrCl}]$  was constant. From  $\log [\text{Cl}_2]$  the corresponding e.m.f. was calculated (last column, Table I) and plotted against  $\log [\text{Br}] = \log [\text{Cl}]_i$ , as were also the three values of e.m.f. (Table II) found directly at the point of maximum slope. Four points (the fifth was several millivolts off) lay close to a straight line of slope 0.0297. Because the two methods agreed within the limit of error, we concluded that the case was not analogous to that of iodine monochloride, and that little bromine trichloride or chlorine tribromide<sup>7</sup> was present when  $[\text{Br}] = [\text{Cl}]$ . We are investigating this point more minutely. We next found the molal potential  $E_0$  when  $\log [\text{Br}] = 0$  from  $E_0 = E - 0.0297 \log [\text{Br}] = 1.1548 \pm 0.0005$ . In 4  $N$  acid there were only two points to fix a line, both of them calculated from  $K_1$ , using the data in Table I. Referred to the hydrogen electrode in 4  $N$  acid,  $E_0 = E - 0.0297 \log [\text{Br}] = 1.221 \pm 0.001$ .

<sup>6</sup> Foerster, "Elektrochemie wässriger Lösungen," Barth, Leipzig, 1922, p. 85.

<sup>7</sup> Ref. 4, p. 2901.

### Mathematical Analysis

The following applies to any of our solutions in which  $[\text{Br}']$  is negligible. For convenience, let  $[\text{Cl}_2] = c$ ,  $[\text{Br}_2] = x$ ,  $[\text{BrCl}] = y$ ,  $[\text{Br}] = a$  and  $[\text{Cl}] = b$ . Then  $a$  and  $b$  are independent variables (that is, they can be chosen at will in each experiment). The equations (1)  $xc = K_1y^2$ , (2)  $2x + y = a$ , and (3)  $2c + y = b$  may be written: (1')  $c = f(x,y)$ , (2')  $a = \varphi(x,y)$ , (3')  $b = \psi(c,y)$ . Since the problem is to find the slope of the titration curve at any point when chlorine is added by electrolysis, the above equations are differentiated with respect to  $b$ ; that is,  $(\partial \ln c / \partial b)_a$  is sought.

Since (1''),  $(\partial f / \partial b)_a = (\partial c / \partial b)_a$ , (2''),  $(\partial \varphi / \partial b)_a = (\partial a / \partial b)_a = 0$  and (3''),  $(\partial \psi / \partial b)_a = (\partial b / \partial b)_a = 1$ , it follows that: (1'''),  $(\partial c / \partial x)_y (\partial x / \partial b)_a + (\partial c / \partial y)_x (\partial y / \partial b)_a = (\partial c / \partial b)_a$ , (2'''),  $(\partial a / \partial x)_y (\partial x / \partial b)_a + (\partial a / \partial y)_x (\partial y / \partial b)_a = 0$  and (3'''),  $(\partial b / \partial c)_y (\partial c / \partial b)_a + (\partial b / \partial y)_c (\partial y / \partial b)_a = 1$ . Eliminating  $(\partial x / \partial b)_a$  and  $(\partial y / \partial b)_a$  from these equations and dividing the result by  $c$

$$\left(\frac{\partial \ln c}{\partial b}\right)_a = 1 / c \cdot \left[ \frac{\left(\frac{\partial a}{\partial x}\right)_y \left(\frac{\partial b}{\partial y}\right)_c}{\left(\frac{\partial a}{\partial x}\right)_y \left(\frac{\partial c}{\partial y}\right)_x - \left(\frac{\partial a}{\partial y}\right)_x \left(\frac{\partial c}{\partial x}\right)_y} + \left(\frac{\partial b}{\partial c}\right)_y \right] \quad (4)$$

This is a perfectly general expression for the slope of the titration curve at any point for any reaction of the type  $n_1 A + n_2 B \rightleftharpoons n_3 A_{n_3} B_{n_2}$ , where products and factors are soluble. Equation 4 can now be applied to the reaction  $\text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2\text{BrCl}$  by evaluating the partials from Equations 1, 2 and 3 and substituting in 4.

$$\left(\frac{\partial \ln c}{\partial b}\right)_a = \frac{4x + y}{2(cy + xy + 4cx)}$$

This result can now be applied to any bromine monochloride point by imposing the condition that  $a = b$ . Since  $a = b$ ,  $x = c = \sqrt{K_1}y$ . Substituting,

$$\frac{d \ln c}{db} = \frac{4\sqrt{K_1} + 1}{2(2\sqrt{K_1} + 4K_1)} \cdot \frac{1}{y}$$

Since  $d \ln c = 77.5 dE$ ,  $\sqrt{K_1} = 1.81 \times 10^{-2}$ ,  $c = [\text{Cl}_2]$ ,  $b = [\text{Cl}]$  and  $y = [\text{BrCl}]$ ,  $dE/d[\text{Cl}] = 0.184/[\text{BrCl}]$ ; and since  $[\text{BrCl}] = [\text{Br}]/(1 + 2\sqrt{K_1})$ ,  $dE/d[\text{Cl}] = 0.191/[\text{Br}]$ .

Our three experimental values,  $0.185/[\text{Br}]$ ,  $0.186/[\text{Br}]$  and  $0.205/[\text{Br}]$ , for this slope average to  $0.192/[\text{Br}]$ . Obviously any electrometric-titration curve could be analyzed in a similar fashion.

### Electrometric Titrations through the Bromine Point

The electrochemical theory of oxidation and reduction, in view of the stability of the compound  $\text{BrCl}$  in solutions containing much chloride ion as proved above, would predict at least three reactions in addition to  $\text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2\text{BrCl}$ . These are  $\text{Br}_2 + 2\text{Cl}' \rightleftharpoons 2\text{Br}' + \text{Cl}_2$ ,  $\text{Br}' + \text{Cl}_2$

$\rightleftharpoons \text{BrCl} + \text{Cl}'$  and  $\text{Br}_2 + 2\text{Cl}' \rightleftharpoons \text{BrCl} + \text{Br}'$ . Given any two of the above four equations, the other two result by combination. We did not attempt to distinguish  $\text{Br}'$  from  $\text{Br}_3'$  and  $\text{Br}_6'^8$  or  $\text{Br}_2$  from  $\text{Br}_2\cdot\text{XCl}'^9$  since the stability of the constants in any one acid indicated that the average velocity constants did not vary with concentrations. Such an assumption might not be permissible when comparing data in different acids.

We could have passed through the bromine point by starting with bromine to which a small measured quantity of chlorine had been added, and then adding small weighed portions of bromide; but the interpolation of the bromine point would have been uncertain, and the accumulating potassium chloride would have called for additional corrections. Instead,

TABLE III  
CHLORINE AND BROMIDE ADDED TO BROMINE

Acid 6 N, $[\text{Br}]_i = 0.348$ and $0.350$ , $E_i = 1.0157$									
$-\Delta[\text{Cl}] \times 10^3$	10.6	7.9	12.7						
$\Delta[\text{KBr}] \times 10^3$				7.4	13.1	15.4	16.3	13.9	20.6
$-\Delta E \times 10^3$	8.5	7.7	14.7	8.5	12.8	12.4	9.0	6.0	7.5
Slope	0.80	0.98	1.16	1.15	0.99	0.81	0.55	0.43	0.36
Acid 4 N, $[\text{Br}]_i = 0.340$ and $0.342$ , $E_i = 1.0821$									
$-\Delta[\text{Cl}] \times 10^3$	10.5	6.4	14.1						
$\Delta[\text{KBr}] \times 10^3$				7.3	13.2	14.7	16.0	13.9	19.9
$-\Delta E \times 10^3$	8.6	6.3	16.3	9.5	13.1	11.1	9.2	6.5	7.5
Slope	0.82	0.99	1.16	1.30	0.99	0.76	0.58	0.46	0.37
Acid 6 N, $[\text{Br}]_i = 0.097$ and $0.088$ , $E_i = 1.0141$									
$-\Delta[\text{Cl}] \times 10^3$	16.5	8.0	3.72	1.60	0.53				
$\Delta[\text{KBr}] \times 10^3$						0.82	7.6	2.82	18.6
$-\Delta E \times 10^3$	15.0	9.7	5.4	2.75	1.24	2.03	17.6	5.1	22.1
Slope	0.91	1.22	1.44	1.73	2.34	2.48	2.33	1.81	1.19
Acid 4 N, $[\text{Br}]_i = 0.093$ , $E_i = 1.0786$ and $1.0787$									
$-\Delta[\text{Cl}] \times 10^3$	9.1	4.52	2.27	1.13	0.56				
$\Delta[\text{KBr}] \times 10^3$						0.89	7.8	2.94	19.4
$-\Delta E \times 10^3$	15.4	10.8	5.9	2.97	1.59	2.40	18.2	5.9	22.6
Slope	1.70	2.39	2.62	2.63	2.84	2.70	2.34	1.97	1.18
Acid 6 N, $[\text{Br}]_i = 0.0409$ and $0.0406$ , $E_i = 1.0136$ and $1.0135$									
$-\Delta[\text{Cl}] \times 10^3$	4.26	4.26	2.13	1.28	0.80				
$\Delta[\text{KBr}] \times 10^3$						5.6	6.7	14.0	
$-\Delta E \times 10^3$	10.5	13.6	8.1	5.2	3.38	18.6	16.9	18.8	
Slope	2.47	3.18	3.80	4.08	4.23	3.34	2.53	1.33	
Acid 4 N, $[\text{Br}]_i = 0.0427$ and $0.0384$ , $E_i = 1.0785$ and $1.0783$									
$-\Delta[\text{Cl}] \times 10^3$	4.70	4.70	2.35	1.41	0.88				
$\Delta[\text{KBr}] \times 10^3$						5.4	6.9	13.5	
$-\Delta E \times 10^3$	11.8	13.5	8.9	5.82	3.73	21.0	15.9	18.7	
Slope	2.51	2.88	3.79	4.12	4.24	3.92	2.30	1.39	

<sup>8</sup> Jones and Hartmann, *Trans. Am. Electrochem. Soc.*, **30**, 295 (1916).

<sup>9</sup> Ráy and Sarkar, *J. Chem. Soc.*, **121**, 1449 (1922).



we started with pure bromine in acid, thus fixing the bromine point directly and added by electrolysis small measured amounts of chlorine. The usual corrections were made and  $[Cl_2]$  was found for each value of  $E$ . Starting a new experiment with the same bromine concentration, thus fixing the same bromine point again, small weighed portions of solid bromide were added,  $E$  was followed, and  $[Cl_2]$  found as usual. Next, both the above experiments were repeated in 4  $N$  acid with the original bromine concentration. Two similar pairs of experiments were completed with a greater but unvaried bromine concentration, and two pairs also with a still greater one. The summary in Table III reverses the actual order and sign of additions of chlorine. Any desired value of  $E$  or of  $[Cl]$  can be found at once by summation, and the derived quantities  $[Cl_2]$ ,  $[BrCl]$ ,  $[Br_2]$  and  $K_1$  calculated.

If any pair of experiments is plotted, the two "halves" of each complete graph meet at the bromine point to form a short straight line passing through it, with curved continuations that are unsymmetrical, largely because  $[Br]$  increases from left to right. Table III would verify this statement even more sharply if the two  $-\Delta E$  values on either side of the bromine point were smaller and if corrections were applied for small differences in  $[Br]_i$ .

### Equilibrium Constants in Two Approximations

Writing  $[Br']^2[Cl_2] = K_2[Cl']^2[Br_2]$ , and using for the moment "formal" instead of thermodynamic concentrations,  $K_2$  can be found from any experiment in which bromide was added to bromine. Taking from Table III the case where  $[Br]_i = 0.088$  in 6  $N$  acid, the calculation is at first made as in Table IV without deduction from  $[KBr]$  for its reaction with the chlorine and with bromine monochloride already present.

TABLE IV

$K_2$  IN THE FIRST APPROXIMATION IN 6  $N$  ACID

$[Br_2] = 1/2[Br]_i$	$[Cl_2] \times 10^7$ from $E$	$[Br'] = \Sigma\Delta[KBr]$	$K_2$
0.0441	1.923	0.0000	
.0441	1.644	.0007	$4.95 \times 10^{-14}$
.0441	0.421	.0084	$1.85 \times 10^{-12}$
.0441	.284	.0113	$2.24 \times 10^{-12}$
.0441	.0515	.0297	$2.80 \times 10^{-12}$

Scrutinizing the variations of  $K_2$  and of  $\Sigma\Delta[KBr]$ , one concludes that most of the bromide should be deducted at the start and progressively less of the later additions. The limiting value of  $K_2$  seems to be near  $3 \times 10^{-12}$ .

From the companion experiment in Table III, in which chlorine was added ( $[Br]_i = 0.097$ ),  $K_1$  is calculated as in Table V, neglecting the action of chlorine on bromide already present, and the increase in bromine mono-

chloride. Here also one concludes that the correction is relatively large at first, but becomes progressively less as chlorine is added. At the end of the experiment,  $K_1$  seems to approach  $3.2 \times 10^{-4}$ , the value found by the first method.

TABLE V  
 $K_1$  IN THE FIRST APPROXIMATION IN 6 N ACID

$[Cl_2] \times 10^7$ from E	$\Sigma \Delta[Cl] = [BrCl]$	$1/2([Br]_i - [BrCl])$	$K_1$
1.918	0.00000		
2.111	.00053	0.0481	$3.60 \times 10^{-2}$
2.610	.00159	.0476	$4.88 \times 10^{-3}$
3.95	.00373	.0465	$1.31 \times 10^{-3}$
8.39	.00797	.0444	$5.84 \times 10^{-4}$
26.74	.01650	.0401	$3.91 \times 10^{-4}$

To calculate these constants in the second approximation, the equations giving  $K_1$  and  $K_2$  are first combined to give  $[Br'] [Cl_2] / [BrCl] [Cl'] = \sqrt{K_1 K_2} = 3 \times 10^{-3}$ . Since  $[Cl'] = 6.08$ ,  $[Br'] / [BrCl] = 1.81 \times 10^{-7} / [Cl_2]$ . From Table IV, Line 1, we write  $[Br'] / [BrCl] = 1.81 \times 10^{-7} / (1.92 \times 10^{-7})$ . But  $[BrCl]$  can be found from Table IV, Line 1, by the  $K_1$  equation, that is,  $0.0441 \times 1.92 \times 10^{-7} = 3 \times 10^{-4} [BrCl]^2$  whence  $[BrCl] = 5.3 \times 10^{-3}$ . The previous equation now gives  $[Br']$ , as  $[Br'] = 1.81 \times 10^{-7} \times 5.3 \times 10^{-3} / (1.92 \times 10^{-7}) = 4.7 \times 10^{-3}$ . From  $[Br]_i$ , that is, 0.0882, we subtract 0.0053 and 0.0047, and half the remainder, 0.0391 is  $[Br_2]$  corrected for monochloride and bromide. Substituting 0.0391 in the  $K_1$  equation,  $[BrCl]$  is now  $5.0 \times 10^{-3}$  instead of  $5.3 \times 10^{-3}$ ,  $[Br']$  becomes  $1.81 \times 10^{-7} \times 5.0 \times 10^{-3} / (1.91 \times 10^{-7})$  or  $4.4 \times 10^{-3}$  and  $[Br_2]$  0.0394. A third approximation gives  $[BrCl] = 5.02 \times 10^{-3}$ ,  $[Br'] = 4.74 \times 10^{-3}$  and  $[Br_2] = 0.0392$ . From the best values of  $[Br']$  and  $[Br_2]$  and the original values of  $[Cl']$  and  $[Cl_2]$ ,  $K_2 = 2.98 \times 10^{-12}$ . So far we have assumed that no bromide was added. If now  $\Delta[KBr]$  is added to the system described on any line,  $n$ , of Table IV, the concentrations on the next line ( $n + 1$ ) are found from the equations  $(x + y) = \Delta[KBr]$  and  $([Br']_n + x) / ([BrCl]_n - y) = 6.08 \sqrt{K_1 K_2} / [Cl_2]_{n+1}$ . Here two approximations suffice. Table VI contains the best approximated values for the several concentrations, also  $K_2$  as calculated from them.

TABLE VI  
 $K_2$ , SECOND APPROXIMATION IN 6 N ACID

$1.8 \times 10^{-7} [Cl_2]$	$[BrCl] \times 10^3$	$[Br'] \times 10^3$	$\frac{[Br_2] = 1/2([Br]_i - [BrCl])}{[BrCl] - [Br']}$	$K_2 \times 10^{12}$
0.94	5.02	4.74	0.0392	2.98
1.10	4.32	4.75	.0399	2.64
4.26	2.50	10.65	.0417	3.13
6.34	2.07	13.15	.0421	3.16
34.9	0.87	30.35	.0433	2.96

Av. 2.97

The method of approximating  $K_1$  is analogous, and equally tedious. Table VII gives the results.

TABLE VII

$K_1$ , SECOND APPROXIMATION IN 6 N ACID				
$1.8 \times 10^{-2}/[\text{Cl}_2]$	$[\text{Br}'] \times 10^3$	$[\text{BrCl}] \times 10^3$	$[\text{Br}_2]$	$K_1 \times 10^4$
0.94	4.96	5.29	0.0433	2.96
.85	4.87	5.75	.0431	2.76
.69	4.29	6.23	.0431	2.90
.45	3.33	7.41	.0430	3.16
.215	2.27	10.59	.0419	3.31
.037	1.27	18.12	.0387	3.15

Av. 3.04

In Fig. 2,  $K_1$  and  $K_2$  are plotted against  $\Sigma\Delta[\text{Cl}]$  and  $\Sigma\Delta[\text{KBr}]$ , respectively, in the first and in the second approximations. We have also completed and plotted two similar sets of approximations for  $K_2$  and

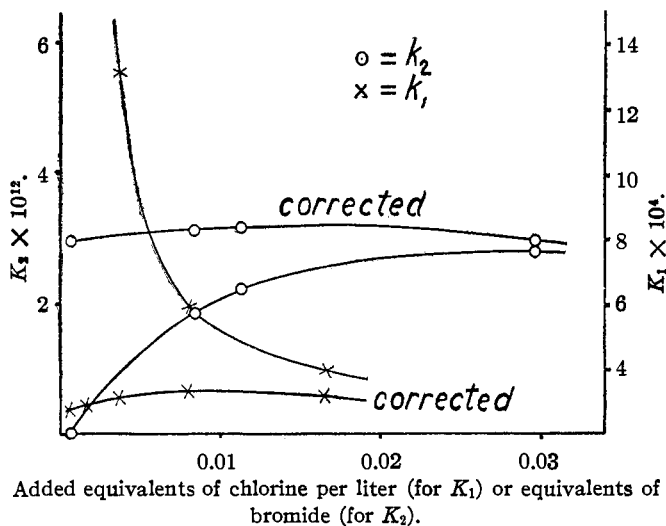


Fig. 2.—First and second approximations of the constants  $K_1$  and  $K_2$  plotted against  $\Sigma\Delta[\text{Cl}]$  and  $\Sigma\Delta[\text{KBr}]$ .

$K_1$  in 4 N acid based upon the companion experiments (Table III) in which  $[\text{Br}]_0 = 0.093$ . As the four curves resulting are very similar in shape to those in Fig. 3, they are not given here.

From the curves giving the second approximations the constant corrected values of the constants are read. In 6 N acid  $K_1 = 3.1 \times 10^{-4}$  and  $K_2 = 3.0 \times 10^{-12}$  while in 4 N acid  $K_1 = 3.2 \times 10^{-4}$  and  $K_2 = 5.6 \times 10^{-12}$ . Also,  $[\text{Br}_2]/[\text{Cl}'] = \sqrt{K_1/K_2} [\text{BrCl}][\text{Br}']$  and  $[\text{Br}'][\text{Cl}_2] = \sqrt{K_1 K_2} [\text{BrCl}][\text{Cl}']$ .

The Role of Activity Coefficients

By two different methods, and in two different acids,  $K_1 = 3.2 \times 10^{-4}$ . As  $K_1$  is expressed in "formal" concentrations, one might infer that the activity coefficients of chlorine, bromine and bromine monochloride vary little with their respective concentrations, and vary uniformly, if at all, in going from 6 N to 4 N acid. Of course these inferences ought to be tested by distribution measurements. Retaining them, however, we can express  $K_2$  in terms of the remaining activity coefficients,  $K_{2,6N}(\gamma_{Br',6N})^2/(\gamma_{HCl,6N})^2 = K_{2,4N}(\gamma_{Br',4N})^2(\gamma_{HCl,4N})^2$ , where total formula weights per liter correspond to the ionic strengths and  $\gamma_{HCl}$  takes the place of  $\gamma_{Cl'}$ . Introducing our experimental values for  $K_2$ , and the ratio of activity coefficients  $\gamma_{HCl,6N}/\gamma_{HCl,4N} = 1.85$  according to Lewis and Randall,<sup>10</sup> we find  $\gamma_{Br',6N}/\gamma_{Br',4N} = 2.5$ . By linear extrapolation of Hantzsch's<sup>11</sup> equivalent activities of pure hydrobromic acid from 4 N to 6 N, we find  $\gamma_{HBr,6N}/\gamma_{HBr,4N} = 2.3$ .

Bromine in Hydrochloric Acid

In studying the relation between  $E$ , or  $[Cl_2]$  and  $[Br_2]$  over a wider concentration range, we used P. W. R. analytical bromine, in some cases distilled from bromide, so as to conserve our best sample. At low concentrations of bromine in a given acid, the two samples gave concordant values of  $E$ . At higher concentrations the corrections for dilution of acid by any sample of bromine are large and uncertain. Fig. 3 shows the plots of  $E$  against  $\log \frac{1}{2}[Br]$  in the two acids, using a double ordinate scale to save space. It will be noted that at the lowest concentrations  $\Delta E/\Delta \log \frac{1}{2}[Br]$  becomes very small, while at the highest concentrations it ap-

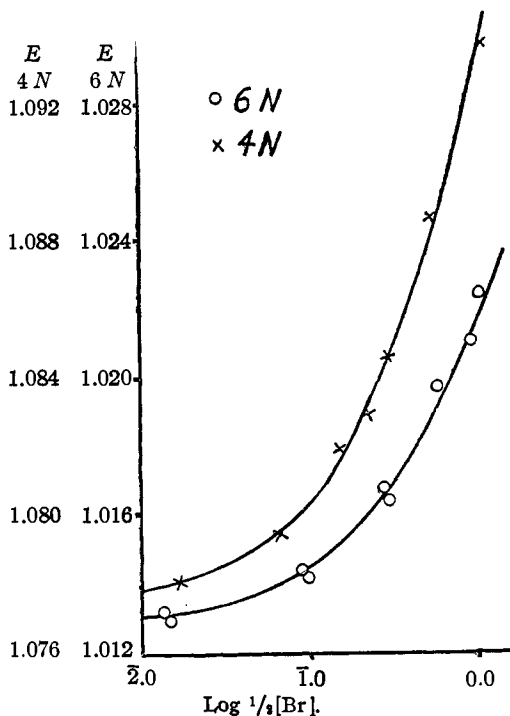


Fig. 3.—Electromotive force plotted against logarithm of total bromine.

<sup>10</sup> Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 336.

<sup>11</sup> Hantzsch, *Ber.*, 58B, 625 (1925).

proaches the conventional value 0.0297. These curves support our fundamental contention that  $E$  is determined primarily by  $[Cl_2]$  and not by  $[Br_2]$ . In Fig. 4, the plots of  $[Cl_2]$  against  $\frac{1}{2}[Br]$  yield two straight lines, intersecting at  $\frac{1}{2}[Br] = 0.15$ . With the help of measurements at lower bromine concentrations we expect to predict this relationship. Above this concentration the 4  $N$  acid actually liberates more chlorine than the 6  $N$  acid.

Without partial differentiation, it is possible to predict roughly at any point the slope of any electrometric-titration curve where bromide ion

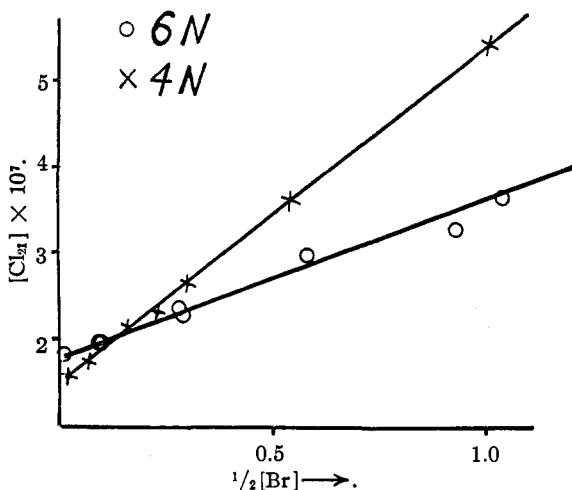


Fig. 4.—Free chlorine plotted against total bromine.

is not negligible. Since  $\ln K_2 = \ln [Cl_2] + 2 \ln [Br'] - \ln [Br_2] - 2 \ln [Cl']$ ,  $d \ln K_2 = 0 = d \ln [Cl_2] + 2 d \ln [Br'] - d \ln [Br_2]$  in any constant acid concentration. As the addition of bromide increases  $[Br_2]$  by a very small fractional amount, we can neglect  $d \ln [Br_2]$ . Then  $-d \ln [Cl_2] = 2 d \ln [Br']$  or  $-d \log [Cl_2] = 2 d \log [Br']$ . Further, as  $d \log [Cl_2] = 33.64 d E$ ,  $-dE = 0.0595 d \log [Br']$ . To verify this prediction we can take the second half of any experiment in Table III, the first for instance, beginning after the first addition of bromide to avoid the largest errors from writing  $[Br'] = \Sigma \Delta [KBr]$ .

TABLE VIII  
SLOPES WHEN  $[Br']$  IS NOT NEGLIGIBLE

$\log [Br'] + 3$	0.869	1.311	1.545	1.716	1.820	1.938
$0.059 \log [Br']$	0.0263	0.0139	0.0102	0.0062	0.0071	
$-dE$ , obs.	.0128	.0124	.0090	.0060	.0075	

#### Extent of Reaction between Bromine and Chloride Ion

Surprising, at first sight, is the percentage of bromine, which is converted into bromide and bromine monochloride, when dissolved in 6  $N$

or in 4 *N* hydrochloric acid. This is plotted against total bromine in Fig. 5. Given molal bromine the percentages are 2.4 and 2.8, respectively, for 0.01 *M* bromine 20 and 18.5, respectively, while at infinite dilution the reaction seems to approach completion. We are investigating bromine solutions less concentrated than 0.01 *M* in 6 *N*, 4 *N*, and more dilute acids to clear up a number of problems raised but not solved by this investigation.

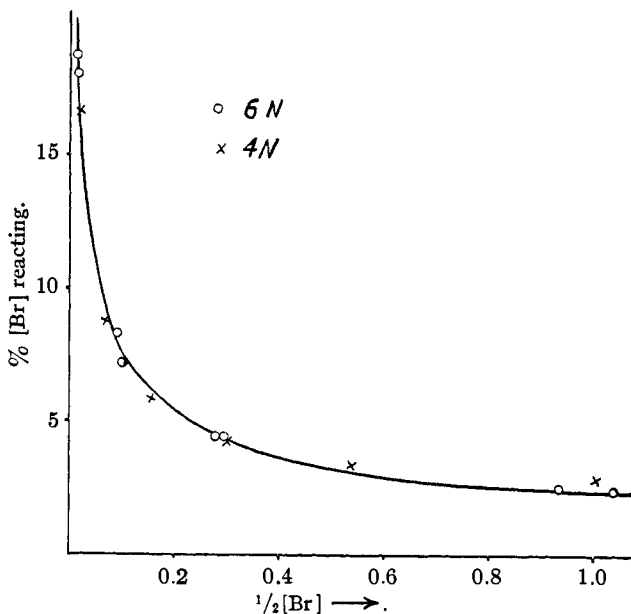


Fig. 5.—Total bromine plotted against percentage which reacts with chloride ion.

### Summary

Known chlorine or bromine solutions in 6 *N* and in 4 *N* hydrochloric acid were prepared. To these known amounts of bromine, chlorine or of a soluble bromide were added. All contained chlorine, bromine monochloride and bromide ion. From measurements of e.m.f. the concentration of free chlorine was found in each case and the other concentrations were calculated, with elaborate corrections.

By adding small amounts of electrolytic chlorine or of a solid bromide, electrometric-titration curves were very accurately constructed through the point where total bromine and total chlorine are present in unit ratio, and also through the point where pure bromine is added to hydrochloric acid. By mathematical analysis two general equations were derived which serve to predict the slope at any point on any of these curves or on similar curves for similar systems.

The "molal potential" of bromine monochloride in 6 *N* acid is 1.1548 ±

0.0005 referred to a hydrogen electrode in the same acid. In 4 *N* acid we find  $1.221 \pm 0.001$ .

In either acid  $[\text{Br}_2][\text{Cl}_2] = 3.2 \times 10^{-4} [\text{BrCl}]^2$ . In 6 *N* acid  $[\text{Br}' ]^2, [\text{Cl}_2] = 3.0 \times 10^{-12} [\text{Br}_2][\text{Cl}' ]^2$ , but in 4 *N* acid this constant is  $5.6 \times 10^{-12}$ . The ratios  $K_{2,6N}/K_{2,4N}$  can be predicted from the activity coefficients of hydrobromic and hydrochloric acids as found by other investigators. The two equilibrium constants were calculated in each acid by successive approximations. Two other constants are derived from them.

If e.m.f. is plotted against the logarithm of bromine concentration, the slope becomes very small at the smallest bromine concentrations, and approaches 0.0297 at the largest.

Given molal bromine, 2.4% reacts in 6 *N* hydrochloric acid to give bromide ion and bromine monochloride. In 4 *N* acid the percentage is actually larger and is 2.8%. With 0.01 *M* bromine the percentages are 20 and 18.5, respectively. At minimal bromine concentrations the reaction apparently would become complete.

Further measurements over other concentration ranges are in progress.

CAMBRIDGE 38, MASSACHUSETTS

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 140]

## THE HEATS OF ADSORPTION OF SEVERAL GASES AND VAPORS ON CHARCOAL

BY FREDERICK G. KEYES AND MELVILLE J. MARSHALL

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### Introduction

Extensive measurements of the heat evolved when gases or vapors are adsorbed on charcoal and other substances have already been made. As early as 1874 Favre,<sup>1</sup> for example, determined the heat evolved for a large number of gases adsorbed on charcoal prepared from a variety of woods. The heat evolved per gram of gas adsorbed was found to be independent of the kind of charcoal, although the total amount adsorbed or the capacity was variable. The results of Favre were confirmed and extended later by Chappuis,<sup>2</sup> Titoff,<sup>3</sup> and Homfray<sup>4</sup> and recently by Lamb and Coolidge.<sup>5</sup> Homfray, however, instead of using a direct method, made an exhaustive study of the pressure-temperature concentration relation for argon, nitrogen, carbon monoxide, methane, carbon dioxide

<sup>1</sup> Favre, *Ann. chim. phys.*, **5**, 1 (1874).

<sup>2</sup> Chappuis, *Wied. Ann.*, **19**, 21 (1883).

<sup>3</sup> Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

<sup>4</sup> Homfray, *ibid.*, **74**, 129 (1910).

<sup>5</sup> Lamb and Coolidge, *THIS JOURNAL*, **42**, 1146 (1920).