

As further illustration is shown diagrammatically, in Fig. 8, the W or Riemann plane graphically representing the quadruple periodicity of the atomic weights from Xe to Nt, or the first quadruple period.

It follows herefrom:

The periodic system of elements, with its single, double and quadruple periodicities, can not be graphically illustrated on a plane, cylinder, etc., but it can be correctly represented on a Riemann surface with singular points

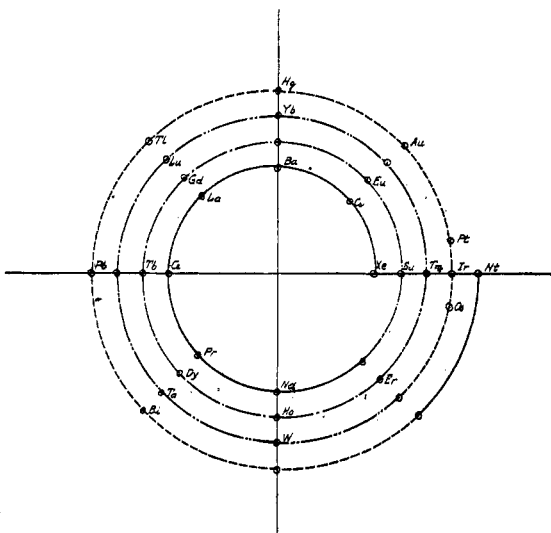


Fig. 8.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 113.]

THE POTENTIALS OF THE BISMUTH-BISMUTHOXYCHLORIDE AND THE COPPER-CUPROUS-CHLORIDE ELECTRODES.

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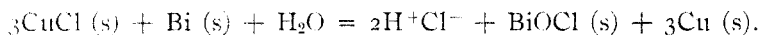
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1. Outline of the Investigation.

The purpose of this investigation was to determine the specific (or normal) potential of the electrode $\text{Bi} + \text{BiOCl}$, $\left\{ \begin{matrix} \text{H}^+ \\ \text{Cl}^- \end{matrix} \right.$ and that of the

electrode $\text{Cu} + \text{CuCl}, \text{Cl}^-$ The problem was attacked in two ways: first, by measuring the electromotive forces at temperatures between 0° and 50° of cells in which these two electrodes were combined with one another and of cells in which each of them separately was combined with a hydrogen electrode; and secondly, by determining the equilibrium conditions at 75° of the reaction¹



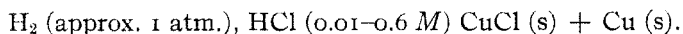
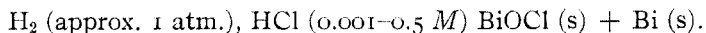
Calorimetric measurements were also made of the heat effect attending this reaction, so as to enable its equilibrium constant to be calculated over to room temperature. These measurements consisted of two series, in which the bismuthoxychloride and the cuprous chloride were caused to react separately with metallic tin. From the equilibrium constant of this reaction the difference between the specific potentials of the two electrodes under investigation was calculated and compared with that derived from the electromotive-force measurements.

Data on cells containing bismuth electrodes have been published by various investigators. Of these the only ones capable of furnishing even an approximate value for the electrode potential of bismuth are those of Neumann² and Rothmund.³ No data on the equilibrium between bismuth compounds and those of another metal are available.

We wish to express to Dr. J. H. Ellis our indebtedness for the great assistance he rendered us in connection with the thermochemical and electromotive-force measurements and in the preparation of the article for publication.

2. Electromotive-Force Measurements.

General Description.—The specific electrode potentials were determined by measuring the electromotive force at 15 , 25 , and 35° of the cells



The apparatus used consisted of a hydrogen half-cell of the type used by Ellis⁴ and of another half-cell containing four platinum spiral electrodes, each with a wire 6 cm. long and 0.06 cm. in diameter. These four electrodes were plated electrolytically either with bismuth or with copper; and the tubes containing them were filled with hydrochloric acid and a large quantity of solid bismuthoxychloride or of solid cuprous chloride mixed with finely divided copper. The hydrogen side of the cell was charged with pure hydrochloric acid of the same concentration containing

¹ The letter (s) appended to a symbol shows that the substance is present in the solid state, (g) that it is in the gaseous state.

² *Z. phys. Chem.*, **14**, 193–230 (1894).

³ *Ibid.*, **15**, 18 (1894).

⁴ *THIS JOURNAL*, **38**, 741 (1916).

no bismuth or copper; hydrogen was furnished to it by an electrolytic hydrogen generator.

Preparation of the Substances.—The best commercial hydrochloric acid was used. The cuprous chloride employed was a sample from Kahlbaum.

Metallic copper was prepared by shaking for several days copper sulfate solution with a quantity of zinc insufficient to precipitate all the copper; it was washed with dilute copper sulfate solution to remove all the zinc, then with water and with dilute hydrochloric acid.

Metallic bismuth was prepared by depositing it on a platinum cathode by electrolyzing with high current density a 2 *M* hydrochloric acid solution in contact with solid bismuthoxychloride, using a copper anode in a separate vessel connected with the cathode compartment by a siphon tube.

Bismuthoxychloride was prepared from Kahlbaum's bismuth nitrate by treating it with strong hydrochloric acid and evaporating off most of the acid. The bismuthoxychloride was then dissolved in strong hydrochloric acid and reprecipitated by pouring into a large volume of water, after which it was washed by decantation, redissolved in hydrochloric acid, and reprecipitated by pouring the hydrochloric acid solution, with vigorous stirring, into a quantity of water insufficient to precipitate all the bismuth.

These substances were all preserved under dilute hydrochloric acid, and were washed just before use with hydrochloric acid of the concentration to be used in the experiment.

Description of the Hydrogen-Bismuth Cells.—To produce the coating of bismuth on the four platinum spirals, the part of the cell containing these spirals was filled with a 5 *M* hydrochloric acid solution nearly saturated with bismuthoxychloride, 3 auxiliary platinum anodes were inserted in such positions as to produce the most uniform deposit of bismuth all over the spirals, and electrolysis was conducted for about 6 hours with a current density varying from about 0.1 ampere per sq. cm. at the beginning to about 0.4 ampere per sq. cm. at the end. The deposit of bismuth obtained in this manner was dark gray and spongy; its inner parts adhered well to the platinum spiral, but the outer layers were less coherent. The exact manner of preparing the bismuth coating was found not to be essential; thus 3 sets of 4 electrodes made up without following closely the above procedure were found to give mutually consistent results.

After the electrolysis was finished, the electrodes were washed 10 or more times with 0.2 *M* hydrochloric acid, allowing them to stand in contact with the acid for half an hour each time. They were then washed 4 or 5 times in the same manner with acid of the concentration to be used in the first set of experiments. A mixture of solid bismuthoxychloride and finely divided metallic bismuth was also washed 5 to 8 times with acid of this concentration, and then a suspension of this mixture in the acid was intro-

duced into the side of the cell containing the bismuth electrodes so as to fill it completely. The hydrogen side of the cell was partially filled with pure acid of the same concentration, but containing no bismuth. Liquid connection between the hydrogen and bismuth half-cells was made by sucking over a small amount of hydrochloric acid from the hydrogen half-cell so as to fill the connecting tube. All the ground joints of the cell were sealed air-tight with beeswax, to prevent evaporation of the solution or entrance of oxygen.

The cell was then set up in the thermostat at 25° and hydrogen was passed through the hydrogen half-cell. After about 3 hours the electromotive force of the hydrogen half-cell against each of the 4 bismuth electrodes was measured by means of a Leeds and Northrup potentiometer reading to 0.01 millivolt. The 4 values thus obtained usually agreed within about 0.0002 volt. The cell was then shaken at intervals of a few hours so as to ensure saturation of the hydrochloric acid with the bismuth-oxychloride at 25°. After a day of this treatment the bismuth electrodes usually agreed within 0.0001 volt. Readings of electromotive force, cell temperature, and the atmospheric pressure were made at intervals until the electromotive force showed constancy within 0.00005 volt over a period of 5 to 10 hours. The cell temperature was then changed to 15° or 35°, and this procedure was repeated. The response to temperature changes was rapid, and no temperature hysteresis was noted.

After measurements of the electromotive force of the cell at each desired temperature had been obtained, the cell was washed and filled with hydrochloric acid of a new concentration and the same procedure was repeated.

The Experimental Data for the Hydrogen-Bismuth Cells.—Table I contains the original data for the bismuth cells at each temperature and concentration studied. The electromotive-force values are those taken after the cell had assumed a constant electromotive force. The first column

TABLE I.—ELECTROMOTIVE FORCES OF THE HYDROGEN-BISMUTH CELLS.

Mols HCl per 1000 g. H ₂ O.	Cell temp.	Hydrogen pressure.	Observed electromotive forces.				Corrected E. M. F.
			Cell I.	Cell II.	Cell III.	Cell IV.	
0.000983	25.00	73.79	0.28208	0.28211	0.28216	0.28209	0.28249
0.001010	25.00	74.05	0.28182	0.28178	0.28181	0.28186	0.28212
0.003175	25.00	74.19	0.26041	0.26045	0.26046	0.26042	0.26071
0.009022	25.00	74.20	0.24256	0.24263	0.24267	0.24262	0.24293
0.02007	25.00	74.17	0.22912	0.22915	0.22917	0.22916	0.22947
0.04586	25.00	74.18	0.21575	0.21580	0.21577	0.21573	0.21606
0.1041	15.00	74.11	0.20407	0.20409	0.20414	0.20417	0.20447
0.1041	25.00	73.61	0.20175	0.20175	0.20179	0.20174	0.20221
0.1041	35.00	71.76	0.19937	0.19938	0.19936	0.19934	0.20011
0.2304	15.00	73.28	0.19115	0.19113	0.19120	0.19114	0.19160
0.2304	25.00	72.46	0.18825	0.18825	0.18830	0.18822	0.18887
0.2304	35.00	69.49	0.18500	0.18497	0.18499	0.18500	0.18617
0.5005	25.00	75.22	0.17547	0.17546	0.17556	0.17552	0.17563

of the table contains the concentration of hydrochloric acid expressed in mols of HCl per 1000 g. water, the second the temperature of the cell, and the third the corrected hydrogen pressure in centimeters of mercury at the hydrogen electrode, obtained by applying to the barometric reading the corrections described by Ellis.¹ The next 4 columns contain the observed electromotive forces of the hydrogen electrode against each of the 4 bismuth electrodes. The last column contains the means of these values corrected to a hydrogen pressure of exactly one atmosphere with the aid of the ordinary logarithmic formula.

Description of the Hydrogen-Copper Cells.—The copper electrodes were prepared by electroplating the spiral platinum wires of the cell with copper from a 0.5 *M* copper sulfate solution, using the same current densities as for the bismuth plating. The coating obtained was a bright red, spongy mass. The electrodes were washed in the same manner as were the bismuth electrodes. Three sets of 4 copper electrodes were made up in this manner, and gave mutually consistent results.

The filling of the cell with hydrochloric acid, cuprous chloride, and finely divided metallic copper was performed in the same manner as the analogous operations for the bismuth cell; but care was taken to make the operation as rapid as possible, so as to avoid any oxidation of the cuprous chloride. The cell was never exposed to strong light, so as to prevent darkening of the cuprous chloride; but no change in electromotive force was noticed in the cases when the cuprous chloride was allowed to darken.

The four cuprous-chloride electrodes showed agreement within 0.0003 volt 3 or 4 hours after setting up the apparatus in the thermostat, but the electromotive force of the whole cell always dropped slowly throughout the course of a day. It then became more constant, and the separate electrodes showed better agreement, usually within 0.0001 volt. Shaking the cell then caused the electromotive force to rise to a value somewhat lower than the original value, but after standing the electromotive force dropped again. Successive shakings caused smaller and smaller rises of electromotive force, until finally no further change was caused either by shaking the cell or by letting it stand. This phenomenon is to be explained by the supposition that the cell as first set up contained a small amount of cupric ion; that this cupric ion was reduced to cuprous ion in the neighborhood of the copper electrode; that by the shaking new amounts of cupric ion were brought up to the copper electrode and slowly reduced, until finally cupric ion was present at the equilibrium concentration and the electromotive force no longer changed on shaking or standing. It was found that the presence of a large amount of finely divided electrolytic copper in the cell greatly reduced the time necessary to secure a constant value of the electromotive force.

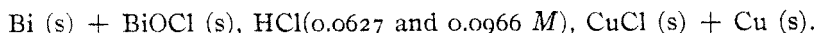
¹ *Loc. cit.*

The Experimental Data for the Hydrogen-Copper Cells.—Table II contains the observed electromotive forces of the hydrogen electrode against each of the 4 copper electrodes at each concentration and temperature. The last column contains the mean value of the electromotive force of the hydrogen-copper cell at each temperature and concentration, after correction has been applied to refer the value to a hydrogen pressure of exactly one atmosphere.

TABLE II.—THE ELECTROMOTIVE FORCES OF THE HYDROGEN-COPPER CELLS.

Mols HCl per 1000 g. H ₂ O.	Cell temp.	Hydrogen pressure.	Observed electromotive forces.				Corrected E. M. F.
			Cell I.	Cell II.	Cell III.	Cell IV.	
0.01447	25.00	74.03	0.34681	0.34694	0.34659	0.34675	0.34718
0.01447	35.00	72.06	0.34677	0.34677	0.34645	0.34655	0.34643
0.04304	25.00	73.29	0.29188	0.29191	0.29172	0.29173	0.29227
0.09596	15.00	75.50	0.25314	0.25330	0.25334	0.25332	0.25340
0.09596	25.00	74.10	0.25131	0.25172	0.25170	0.25175	0.25204
0.09596	35.00	72.42	0.24983	0.24992	0.24994	0.24974	0.25049
0.1876	15.00	75.03	0.22126	0.22115	0.22114	0.22118	0.22134
0.1876	25.00	74.22	0.21895	0.21884	0.21885	0.21886	0.21911
0.1876	35.00	72.74	0.21611	0.21606	0.21601	0.21600	0.21663
0.3253	25.00	73.48	0.19115	0.19116	0.19115	0.19115	0.19158
0.3253	35.00	71.34	0.18743	0.18744	0.18740	0.18740	0.18823
0.6310	25.00	73.33	0.15741	0.15756	0.15750	0.15760	0.15798

The Experimental Data for the Bismuth-Copper Cells.—Owing to the fact that the heat effect calculated from the foregoing electromotive forces at the different temperatures did not agree well with the result obtained from the thermochemical measurements described in Section 8 of this article, an independent series of electromotive-force measurements was undertaken several months after those already described were completed, in order to check the accuracy of the latter. These measurements were made with the cells



The bismuth electrodes and the copper electrodes were prepared as for the previous measurements. Each half-cell contained 2 electrodes of the same kind. By the 4 combinations of these electrodes 4 observed values of the electromotive force were obtained. These are recorded in Table III. The last column contains the mean of the 4 observed values.

TABLE III.—ELECTROMOTIVE FORCES OF THE BISMUTH-COPPER CELLS.

Mols HCl per 1000 g. H ₂ O.	Cell temp.	Observed electromotive forces.				Average E. M. F.
		Cell I.	Cell II.	Cell III.	Cell IV.	
0.06270	15.00°	0.06104	0.06100	0.06103	0.06102	0.06102
0.06270	25.00°	0.06212	0.06214	0.06212	0.06210	0.06212
0.06270	35.00°	0.06327	0.06323	0.06327	0.06324	0.06325
0.09661	0.00°	0.04552	0.04571	0.04570	0.04550	0.04561
0.09661	25.00°	0.04842	0.04838	0.04845	0.04836	0.04840
0.09661	50.00°	0.05008	0.05025	0.05023	0.05009	0.05016

3. The Solubility of Cuprous Chloride in Hydrochloric Acid.

For an exact interpretation of the electromotive-force results it is necessary to know the solubility of cuprous chloride in hydrochloric acid at different concentrations and the nature of the complex ions that result. The investigations of Bodländer and Storbeck¹ have shown that cuprous chloride is present in chloride solutions substantially only in the form of the complex anion CuCl_2^- so long as the chloride solution is of moderate concentration, namely from about 0.05 to 0.30 *N*. In more dilute solutions a considerable proportion of cupric chloride CuCl_2 is present, and in much more concentrated ones a large proportion of the more complex cuprous anion CuCl_3^- exists.

The equilibrium constant K of the reaction $\text{CuCl (s)} + \text{Cl}^- = \text{CuCl}_2^-$, given by the expression $(\text{CuCl}_2^-)/(\text{Cl}^-) = K$, may be found from solubility determinations in moderately concentrated chloride solutions, by taking the ratio of the total dissolved copper (ΣCu) to the difference ($\Sigma\text{Cl} - 2\Sigma\text{Cu}$) between the total chloride and twice the total copper concentration, it being assumed hereby that the complex compound $\text{H}^+\text{CuCl}_2^-$ has the same ionization as hydrochloric acid.

Determinations of the solubility of cuprous chloride in dilute hydrochloric acid solutions at 15° have been made by Abel;² but his results show such irregularities and sudden changes in the values of the calculated constants that they can be regarded as only roughly approximate. The best existing determinations of the equilibrium constant in question seem to be those of Bodländer and Storbeck, who found at 16° for this constant the values 0.04934 and 0.04963 (mean 0.0495) by determining the solubility of cuprous chloride in potassium chloride solutions which were 0.1 and 0.2 *N*, respectively.³

As values were needed at higher temperatures, new determinations of the solubility of cuprous chloride in hydrochloric acid solutions at 25° were carried out in the course of the present work. Precipitated cuprous chloride and precipitated copper were shaken at 25° for 10 days with hydrochloric acid solutions of various concentrations, namely, 1.1650, 0.3165, 0.2156, and 0.0978 *M*. The total chloride concentration of the resulting solutions was found by precipitation as silver chloride and the total dissolved copper by electrolysis, after evaporation with nitric acid. Table IV gives the results obtained. The first column gives the total chloride concentration (ΣCl); the second column gives the total concentration of dissolved copper (ΣCu) and the third column shows the value of the con-

¹ *Z. anorg. Chem.*, **31**, 1, 458 (1902).

² *Ibid.*, **26**, 361 (1901).

³ Abel's constants at 15° for HCl concentrations between 0.093 and 0.53 *M* vary irregularly between 0.052 and 0.068. See Abegg's *Handbuch anorg. Chem.*, **1**, II, 507 (1908).

stant K equal to $\Sigma\text{Cu}/(\Sigma\text{Cl} - 2\Sigma\text{Cu})$. All concentrations are expressed in mols per 1000 g. of water.

TABLE IV.—SOLUBILITY OF CUPROUS CHLORIDE IN HYDROCHLORIC ACID AT 25°.

ΣCl .	ΣCu .	K .
1.2815	0.1165	0.1111
0.3364	0.01988	0.0671
0.2290	0.01340	0.0662
0.1038	0.00596	0.0650

In view of these results we may adopt as the best value of the constant at 25° the mean of the last three values, namely 0.0661.

A value of this constant at 75° can be derived from the equilibrium measurements recorded below in Table IX. Namely, by subtracting from the chlorine concentration (0.4083) twice the copper concentration (2×0.0767) and 5 times the bismuth concentration (5×0.00206), we get the concentration of the uncombined chloride (0.2446) and by dividing the copper concentration by this value we get for the constant K at 75° the value 0.314.

Out of these 2 values of the constant (at 75° and 25°) the value of ΔH_S , the heat absorbed by the solution of 1 mol of CuCl in dilute hydrochloric acid, was calculated by means of the van't Hoff equation.

$$\log_{10} \frac{K_2}{K_1} = \frac{\Delta H_S}{2.303R} \frac{T_2 - T_1}{T_1 T_2}.$$

The value of ΔH_S was thus found to be 6440 cal.

With the aid of this value the solubility constants $(\text{CuCl}_2^-)/(\text{Cl}^-)$ at 0°, 15°, 35°, and 50° were calculated by the same equation. The following values¹ were thereby obtained:

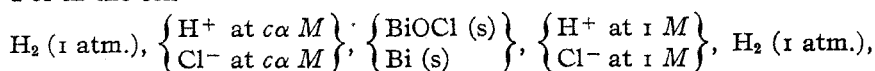
0.0244 at 0°; 0.0453 at 15°; 0.0661 at 25°; 0.0940 at 35°; 0.153 at 50°.

4. Calculation of the Specific Electrode Potentials from the Electromotive Forces.

The Bismuthoxychloride Electrode.—The specific potential of the bismuthoxychloride electrode may be calculated from the corrected electromotive forces E of the hydrogen-bismuth cells given in Table I, by means of the following formula, in which c represents the concentrations and α the activity coefficients of the hydrochloric acid in the cells:

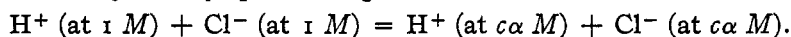
$$\bar{E}_{\text{BiOCl}} = -E - \frac{RT}{3F} \log (c\alpha)^2$$

For in the cell



¹ The value at 16° is calculated to be 0.0473 which is in good agreement with the value (0.0495) found by Bodländer and Storbeck.

whole electromotive force is $E + \bar{E}_{\text{BiOCl}}$; the change in state which takes place when 3 faradays pass through is



The first column of Table V gives the temperature, and the second the values of the hydrochloric acid concentration (c). The third column shows the values of the activity coefficient (α) of hydrochloric acid as determined by Noyes and Ellis.¹ The fourth column gives the values taken from Table I of the corrected electromotive force of the corresponding bismuth cell. And the last column gives the values of the specific potential of the bismuth-oxychloride electrode calculated by the above formula.

TABLE V.—THE SPECIFIC POTENTIAL OF THE BISMUTHOXYCHLORIDE ELECTRODE.

Temperature	Mols HCl per 1000 g. water.	Activity coefficient.	Corrected cell E. M. F.	Specific potential.
25.00°.....	0.5003	0.760	0.17563	—0.1591
	0.2304	0.788	0.18887	—0.1597
	0.1041	0.820	0.20221	—0.1601
	0.04586	0.859	0.21606	—0.1607
	0.02007	0.898	0.22947	—0.1607
	0.00902	0.937	0.24293	—0.1612
	0.00318	0.978	0.26071	—0.1618
	0.00101	0.990	0.28212	—0.1638
	0.000984	0.991	0.28249	—0.1637
				Best value, —0.1599
15.00°.....	0.2304	0.791	0.19160	—0.1633
	0.1041	0.822	0.20447	—0.1638
				Mean, —0.1635
35.00°.....	0.2304	0.784	0.18617	—0.1561
	0.1041	0.816	0.20011	—0.1565
				Mean, —0.1563

The first value of the specific potential at 25° is not accurate because no account has been taken of the appreciable quantity of bismuth which dissolves in hydrochloric acid at this concentration. The last 2 values may also be inexact because of experimental error at the very low concentrations. The intermediate values, though they do not seem to be subject to experimental error, yet show a progressive change, amounting to about 2 millivolts between 0.23 and 0.003 M . As best value we have adopted —0.1599, which is the mean value for the two concentrations 0.2304 and 0.1041 molal, for the reason that it is then directly comparable with the mean values at 15° and 35°.

The Cuprous-Chloride Electrode.—The specific potential \bar{E}_{CuCl} of the copper-cuprous = chloride electrode can be calculated from the corrected electromotive force E of the hydrogen-copper cells given in Table II by

¹ THIS JOURNAL, 39, 2543 (1917).

the following formula, in which (Cl^-) represents the chloride-ion concentration in the copper half-cell, (H^+) the hydrogen-ion concentration in the hydrogen half-cell, c the concentration of the acid, α its activity coefficient, and K the solubility constant of cuprous chloride derived in the preceding section:

$$\bar{E}_{\text{CuCl}} = -E - \frac{RT}{F} \log (\text{H}^+)(\text{Cl}^-) = -E - \frac{RT}{F} \log \frac{(c\alpha)^2}{(1+K)}$$

In the last member of this equation the chloride-ion concentration is replaced by a quantity obtained by correcting the concentration of the hydrochloric acid in the cell for that of the cuprous chloride dissolved in the form of the complex $\text{H}^+\text{CuCl}_2^-$ with the help of the solubility constant K , and multiplying the result by the activity coefficient at that concentration. The concentrations of the dissolved cuprous chloride are given in the third column of the table. The assumption is made in these calculations that the complex acid is ionized to the same degree as hydrochloric acid, and that the mobility of the ion CuCl_2^- is the same as that of the Cl^- ion, so that the liquid potential of the cell is negligibly small.

We have also calculated another specific potential defined so as to represent the potential when the total anion concentration $(\text{Cl}^- + \text{CuCl}_2^-)$ is 1 *M*. The computation was made by the following equation:

$$\bar{E}_{\text{CuCl}} = -E - \frac{RT}{F} \log (c\alpha)^2$$

The specific potentials calculated on these two bases are given in the columns headed I and II, respectively.

TABLE VI.—THE SPECIFIC POTENTIAL OF THE CUPROUS CHLORIDE ELECTRODE.

Temperature.	Mols HCl per 1000 g. water.	Mols CuCl per 1000 g. water.	Activity coefficient.	Corrected E. M. F.	Specific potential.	
					I.	II.
25.00°	0.6310	0.0391	0.758	0.15798	—0.1185	—0.1201
	0.3253	0.0204	0.776	0.19158	—0.1191	—0.1209
	0.1876	0.0116	0.797	0.21911	—0.1199	—0.1215
	0.09596	0.0060	0.825	0.25204	—0.1201	—0.1218
	0.04304	0.0027	0.855	0.29227	—0.1210	—0.1226
	0.01447	0.0009	0.913	0.34718	—0.1233	—0.1249
				Best value,	—0.1200	—0.1216
15.00°	0.1876	0.00820	0.800	0.22134	—0.1261	—0.1271
	0.09596	0.00417	0.827	0.25340	—0.1265	—0.1276
				Best value,	—0.1263	—0.1274
35.00°	0.3253	0.0279	0.772	0.18823	—0.1125	—0.1149
	0.1876	0.0161	0.796	0.21663	—0.1133	—0.1157
	0.09596	0.00824	0.821	0.25049	—0.1132	—0.1156
				Best value,	—0.1132	—0.1156

The "best values" have been derived by taking the means of the values at 0.1876 and 0.09596 *M*; for at the larger and smaller acid concentrations there are present considerable quantities of the bivalent cuprous anion CuCl_3^- and of cupric chloride, respectively.

The Difference between the Two Specific Electrode Potentials.—The difference between the specific potential of the bismuthoxychloride electrode and that of the cuprous chloride electrode (computed for the case the chloride ion is 1 *M*) can be calculated from the average values of the electromotive force *E* of the bismuth-copper cells given in Table III, by the following equation, in which $(\text{Cl}^-)_\text{C}$ and $(\text{Cl}^-)_\text{B}$ represent the chloride-ion concentration in the copper half-cell and in the bismuth half-cell respectively, (H^+) the hydrogen-ion concentration in each half-cell, *c* the concentration of the acid in the cell, α its activity coefficient, and *K* the solubility constant of cuprous chloride defined as in Section 3 above.

$$\bar{E}_{\text{BiOCl}} - \bar{E}_{\text{CuCl}} = E + \frac{RT}{3F} \log \frac{(\text{H}^+)^2 (\text{Cl}^-)^3_\text{C}}{(\text{Cl}^-)_\text{B}} = E + \frac{RT}{3F} \log \frac{(c\alpha)^4}{(1 + K)^3}.$$

The difference between the 2 specific potentials has also been calculated for the case where the cuprous chloride potential is understood to refer to a total anion concentration $(\text{Cl}^- + \text{CuCl}_2^-)$ of 1 *M*. These calculations were made by an equation differing from that given above only by omission of the factor $(1 + K)^3$.

These specific potential differences are given in Table VII; the first type in the column headed I, and the second type in that headed II.

TABLE VII.—DIFFERENCES BETWEEN THE SPECIFIC POTENTIALS OF THE BISMUTHOXYCHLORIDE AND THE CUPROUS CHLORIDE ELECTRODES.

Temperature.	Mols HCl per 1000 g. water.	Activity coefficient.	Average E. M. F.	Specific potential difference.	
				I.	II.
15.00°	0.06270	0.841	0.06102	—0.03745	—0.03636
25.00°	0.06270	0.845	0.06212	—0.04013	—0.03850
35.00°	0.06270	0.847	0.06325	—0.04302	—0.04063
0.00°	0.09661	0.827	0.04561	—0.03426	—0.03369
15.00°	0.09661	0.823	(0.04757)	(—0.03772)	(—0.03650)
25.00°	0.09661	0.821	0.04840	—0.04002	—0.03838
35.00°	0.09661	0.818	(0.04923)	(—0.04330)	(—0.04073)
50.00°	0.09661	0.814	0.05016	—0.04821	—0.04425

The following summary shows how well these directly determined differences agree with those found by subtracting from one another the separate potentials derived from the measurements with the hydrogen cells and given in Tables V and VI. The following values correspond to those for the cuprous chloride half-cell with the chloride-ion concentration 1 *M* (those given under I in the tables). The values given in the last row are the averages derived from the two series of measurements in Table VII, values at 15 and 35° being obtained for the second of these series by interpolation,

TABLE VIII.—SUMMARY OF THE AVERAGE VALUES OF THE SPECIFIC ELECTRODE POTENTIALS.

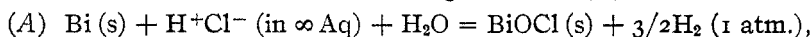
Electrode.	15.00°.	25.00°.	35.00°
Bismuthoxychloride.....	—0.1635	—0.1599	—0.1563
Cuprous chloride.....	—0.1263	—0.1200	—0.1132
Difference (by subtraction).....	—0.0372	—0.0399	—0.0431
Difference (directly deter.).....	—0.0376	—0.0401	—0.0432

5. The Heat Effects Attending the Cell Reactions.

From the specific electrode potentials (\bar{E}_1 and \bar{E}_2) at 15 and 35° given in the preceding paragraph the increase in heat-content ΔH attending the reaction taking place in each of the two cells when N faradays pass through it can be calculated by the Gibbs-Helmholtz equation, best written in the following form:

$$\int_{T_1}^{T_2} \Delta H \frac{dT}{T^2} = N_F \left(\frac{\bar{E}_2}{T_2} - \frac{\bar{E}_1}{T_1} \right)$$

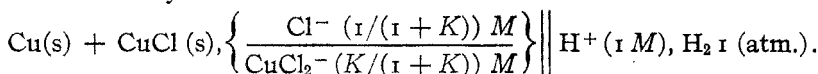
In the case of the bismuth cell ΔH may be considered constant, and the integral is equal to $\Delta H (T_2 - T_1)/T_1 T_2$. To calculate the heat content increase, ΔH_A , which attends the change in state (A):



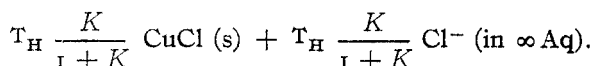
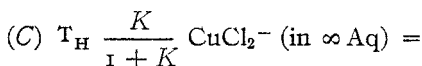
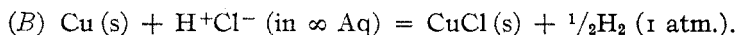
we have therefore the numerical expression

$$\Delta H_A \frac{20.0}{288.1 \times 308.1} = \frac{3 \times 96500}{4.182} \left(\frac{-0.1563}{308.1} - \frac{-0.1635}{288.1} \right).$$

The copper cell corresponding to the specific potentials given under II in Table VI may be formulated as follows:



The heat content increase in this cell is that attending the two changes in state expressed by the following equations, in which K represents the solubility constant ($\text{CuCl}_2^-/(\text{Cl}^-)$) considered in Section 3, and T_H the transference number of the hydrogen ion in dilute hydrochloric acid solution.



The factor T_H arises from the consideration that of the 1 mol of H^+Cl^- destroyed by reaction B only the fraction T_H disappears at the copper electrode, in consequence of the transference in the cell. The heat content increase ΔH is therefore the sum of two heat contents which may be expressed by the following equation, in which ΔH_B and ΔH_C are the heat

content increases attending changes in state (*B*) and (*C*), and ΔH_S is, as in Section 3, that attending the change in state: $\text{CuCl (s)} + \text{Cl}^- (\text{in } \infty \text{ Aq}) = \text{CuCl}_2^- (\text{in } \infty \text{ Aq})$.

$$\Delta H = \Delta H_B + \Delta H_C = \Delta H_B - T_H \frac{K}{1 + K} \Delta H_S.$$

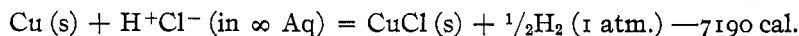
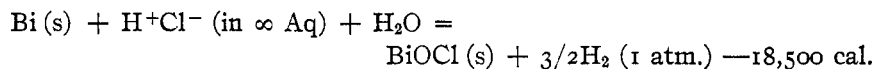
In the integration ΔH_B and ΔH_S may be regarded as constant; but $T_H K/(1 + K)$ changes rapidly with the temperature, and must be expressed as a function of it. The following function reproduces the results sufficiently well.¹

$$T_H \frac{K}{1 + K} = -0.0099 + 9.76 \times 10^{-22} T^8.$$

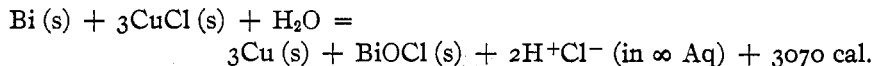
Introducing this function and the value 6440 for ΔH_S derived in Section 3, and for \bar{E}_2 and \bar{E}_1 the values at 35 and 15° given in the last column of Table VI, we get the following numerical expression for ΔH_B , the heat content increase attending change in state (*B*) at 25°:

$$\left(\Delta H_B + (0.0099 \times 6440) \right) \left(\frac{20.0}{308.1 \times 288.1} \right) - \left(6440 \times 9.76 \times 10^{-22} \times \frac{1}{7} (308.1^7 - 288.1^7) \right) = \frac{96500}{4.182} \left(\frac{-0.1156}{308.1} - \frac{-0.1274}{288.1} \right)$$

The increases of the heat content so calculated are +18,500 cal. for the bismuth reaction (*A*), and +7190 cal. for the copper reaction (*B*). We may, therefore, write the following thermochemical equations applicable at 25°:



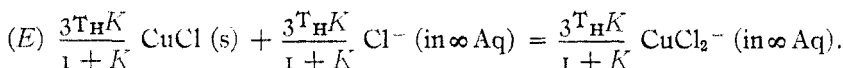
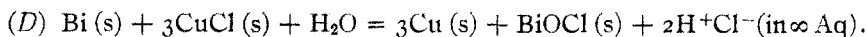
Multiplying the second of these equations by 3 and subtracting it from the first equation, we get the following provisional equation:



¹ The data from which this function is derived and the degree of its correspondence with them are shown in the following table. The values of T_H are computed from the ion conductances given by Johnston (THIS JOURNAL, 31, 1015 (1909)). Those of $K/(1 + K)$ are computed from the values of the solubility constant K given in Section 3. The product of these two quantities is shown in the next to last row of the table; and the value of the same quantity calculated by the above-given empirical temperature function is shown in the last row.

<i>t</i>	0°	15°	25°	35°	50°
T_H	0.854	0.832	0.823	0.813	0.800
$K/(1 + K)$	0.0238	0.0433	0.0620	0.0859	0.1326
$T_H K/(1 + K)$ (obs.).....	0.0203	0.0360	0.0510	0.0698	0.1061
$T_H K/(1 + K)$ (calc.).....	0.0203	0.0364	0.0510	0.0694	0.1061

Independent values for this last heat-quantity can be obtained from the specific potentials derived from the measurements with the bismuth-copper cells and recorded in the last column of Table VII. The heat content increase attending the passage of three faradays through these cells is that corresponding to the changes in state expressed by the two equations

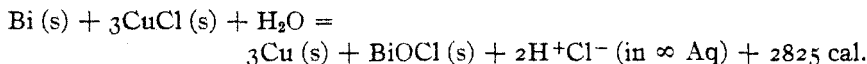


The factor $3T_H$ in the last equation arises from the consideration that 3Cl^- are produced by the electrode process at the copper electrode and that $3(1 - T_H)\text{Cl}^-$ are transferred from that electrode to the bismuth electrode (where 1 Cl^- is destroyed by the electrode process).

For ΔH in the general Gibbs-Helmholtz equation we must therefore substitute $\Delta H_D + \frac{3T_{HK}}{1+K} \Delta H_S$. The numerical equations corresponding to the two sets of measurements recorded in Table VII then become:

$$\begin{aligned} & \left(\Delta H_D - (3 \times 0.0099 \times 6440) \right) \left(\frac{20}{308.1 \times 288.1} \right) + \left(3 \times 6440 \times 9.76 \times \right. \\ & \quad \left. 10^{-22} \times \frac{1}{7} (308.1^7 - 288.1^7) \right) = \frac{3 \times 96500}{4.182} \left(\frac{-0.04063}{308.1} - \frac{-0.03636}{288.1} \right), \\ & \left(\Delta H_D - (3 \times 0.0099 \times 6440) \right) \left(\frac{50}{323.1 \times 273.1} \right) + \left(3 \times 6440 \times 9.76 \times \right. \\ & \quad \left. 10^{-22} \times \frac{1}{7} (323.1^7 - 273.1^7) \right) = \frac{3 \times 96500}{4.182} \left(\frac{-0.04425}{323.1} - \frac{-0.03369}{273.1} \right). \end{aligned}$$

The values of ΔH_D corresponding to these two equations are -2730 and -2678 cal., while that derived above from the measurements with the hydrogen-bismuth and hydrogen-copper electrodes is -3070 cal. The mean of these three values is -2825 cal.; and we may write the following final thermochemical equation:



6. The Equilibrium Measurements.

Preliminary Experiments by F. H. Smyth.—Preliminary experiments on the equilibrium of the above mentioned reaction at 25° were made in this laboratory by Dr. F. H. Smyth, who shook together a mixture of bismuth, copper, bismuth oxychloride, cuprous chloride, and hydrochloric acid solutions of various concentrations, and analyzed the resulting solution after a lapse of time. He found that the reaction proceeded with such slowness in either direction that he was able to fix the equilibrium conditions only

within wide limits; but by approaching the equilibrium from both sides, he determined that the substances are in equilibrium with one another at 25° when the acid concentration is somewhere between 0.50 and 0.20 molal. In his experiments there was this large divergence, even though the time allowed for the attainment of equilibrium was 3 months.

To determine the equilibrium conditions with any degree of accuracy, it is therefore necessary to make experiments at a higher temperature. The rate of the reaction can also be increased by providing a large surface of all the solids and by stirring effectively. All these means were employed simultaneously in the present investigation, in which the experiments were made at 75° .

Apparatus and Materials.—The apparatus used for the equilibrium measurements consisted of a round-bottomed glass tube 26 cm. long and 5 cm. in diameter, closed by a 4-hole rubber stopper, and containing a glass stirrer of propeller form and a conductivity cell. The shaft of the motor-driven stirrer passes through a gas-tight mercury seal. The conductivity cell was of the plunge-type. The conductivity measurement served to show the changes in concentration of the hydrochloric acid, and hence the progress of the reaction towards equilibrium.

The substances employed in the equilibrium measurements were prepared in the same way as for the equilibrium measurements, as described in Section 2 above.

Experimental Method.—The apparatus was set up in a thermostat at 75° ; the reacting substances were introduced into the reaction bottle, which, to avoid oxidation, was filled with carbon dioxide gas; and the stirrer was started. The concentration of the hydrochloric acid in the solution was determined at intervals by means of the conductivity cell and bridge. The conductance in the apparatus at 75° of hydrochloric acid solutions of different concentrations had been previously determined. The cell was immersed in the solution only during the conductivity measurements. It was possible to detect a change in the hydrochloric acid concentration of 0.002 *M*.

When the conductance measurements indicated that the acid concentration was no longer changing, the stirring was stopped, and a 200 cc. portion of the solution was withdrawn through a glass-wool filter tube. This portion was analyzed for its content in chlorine, copper, and bismuth as follows: The chloride was determined in 25 cc. portions by adding nitric acid and silver nitrate, and weighing the silver chloride in perforated crucibles upon asbestos felt. The bismuth was determined in two 100 cc. portions by evaporating them with nitric acid till all chloride was expelled, dissolving the residue in dilute nitric acid, adding ammonium hydroxide and carbonate, filtering out the bismuth oxycarbonate in alundum crucibles, igniting, and weighing the bismuth oxide. The copper was determined

by depositing it electrolytically directly out of the ammoniacal filtrate.

The Experimental Data.—Two preliminary experiments were first made to determine by the conductance measurements the rate of the reaction and roughly the position of the equilibrium at 75°. In these experiments the acid concentrations, which were initially 0.20 and 0.40 *M*, had become, after 72 hours, 0.275 and 0.372 *M*, respectively. A third experiment was then made, starting with 0.273 *M* acid. The concentration became 0.302 after 50 hours and 0.316 *M* after 180 hours. Sample No. 1 was then taken for analysis. In a fourth experiment the acid concentration was 0.386 at the start and 0.325 after 340 hours, when sample No. 2 was taken for analysis. A fifth, more complete experiment was then made. A mixture of 10 g. BiOCl, 5 g. CuCl, 35 g. Bi, 20 g. Cu, and 300 cc. 0.40 molal HCl were put into the reaction bottle. The concentration as indicated by the conductance measurements changed as follows:

Total hours.....	0	3	100	200	400	500	570
HCl concentration	0.386	0.378	0.350	0.335	0.319	0.314	0.312

A 200 cc. sample (No. 3) was then withdrawn and analyzed. To the equilibrium mixture 180 cc. HCl solution were then added, so as to bring its concentration to 0.291 molal. The concentration on continued stirring changed as follows:

Total hours.....	0	6	80	130	190	240
HCl concentration.....	0.291	0.295	0.309	0.312	0.314	0.314

Sample No. 4 was then withdrawn for analysis.

The results of the analyses of these samples are shown in Table IX. The figures for hydrogen are obtained by subtracting from the total chlorine concentration the chlorine combined with the bismuth (as BiCl₃) and with the copper (as CuCl). The concentrations are all expressed in mols per 1000 g. water.

TABLE IX.—ANALYSES OF THE EQUILIBRIUM SOLUTIONS AT 75°.
Concentration in mols per 1000 g. water.

Sample No.	Chlorine.	Copper.	Bismuth.	Hydrogen.
1.....	0.4059	0.0762	0.0033	0.3198
2.....	0.4186	0.0781	0.0044	0.3273
Average....	0.4172	0.0772	0.0039	0.3236
3.....	0.4087	0.0769	0.00225	0.3251
4.....	0.4079	0.0765	0.00196	0.3255
Average....	0.4083	0.0767	0.00206	0.3253

It will be seen from the table that equilibrium was not reached in the preliminary experiments, since Samples 1 and 2 show considerable differences in composition. In the final experiments, however, it was, practically attained, since Samples 3 and 4 gave on analysis closely concordant results. As final values the averages given in the last line of the table will be adopted.

7. Calculation of the Equilibrium Constants at 75°.

The equilibrium constant K of the reaction $\text{Bi} + 3\text{CuCl} + \text{H}_2\text{O} = 2\text{H}^+ + \text{Cl}^- + \text{BiOCl} + 3\text{Cu}$ is evidently expressed by the equation $(\text{H}^+)^2 \times (\text{Cl}^-)^2 = K$, since the chemical activities of all the substances except the hydrogen ion and chloride ion are constant. The hydrogen-ion concentration (H^+) in the solution is the sum of that produced by the ionization of the H^+Cl^- existing as such, by the ionization of the complex acid $\text{H}^+\text{CuCl}_2^-$ formed by the CuCl dissolved in the acid, and by the ionization of the complex acid $\text{H}^+\text{BiCl}_6^-$ formed by the BiOCl dissolved in the acid. The formation of these two complex acids has been shown by Bodländer and Storbeck¹ and by Noyes, Hall, and Beattie,² respectively. Assuming the 3 acids in the solution to have the same ionization-coefficient as pure hydrochloric acid at the same temperature and total concentration, the value of (H^+) is found by multiplying the hydrogen concentration (0.3253) given in the last line of the last column of Table I, by this ionization-coefficient.

The chloride-ion concentration (Cl^-) is found by multiplying by this same coefficient the concentration of the uncombined HCl , which itself is equal to the total chlorine diminished by twice the copper and five times the bismuth concentration. In the equilibrium solution the uncombined HCl has the concentration 0.2446 M (equal to $0.4083 - (2 \times 0.0767) - (5 \times 0.00206)$).

For the ionization-coefficient of the hydrochloric acid we have employed its activity-coefficient as derived by Noyes and Ellis³ from electromotive-force measurements. They computed the activity-coefficient for 0.325 M hydrochloric acid to be 0.779 at 15° and 0.772 at 35°. Provided it continues to decrease at the same rate up to 75°, its value at 75° and 0.325 M would be 0.760.

The equilibrium constant at 75° is then given by the equation

$$K_{75} = (\text{H}^+)^2 \times (\text{Cl}^-)^2 = (0.3253 \times 0.76)^2 \times (0.2446 \times 0.76)^2 = 2.10 \times 10^{-3}.$$

8. Thermochemical Measurements of the Bismuth-Copper Reaction.

Data Available.—The data available for calculating the heat-effect attending the bismuth-copper reaction are the directly measured value of Thomsen⁴ (—98,500 cal.) for the heat of formation of BiOCl (s) + 2HCl (in ∞ Aq) and the indirectly derived values of Thomsen and of Berthelot⁵ (—98,700 and —106,200 cal.) for the heat of formation of 3CuCl (s). The difference between these values (+200 or +7700 cal.) should represent the increase in heat-content attending the reaction under consideration. But since this difference is derived from two much larger quantities,

¹ *Z. anorg. Chem.*, 26, 361 (1901).

² *THIS JOURNAL*, 39, 2532 (1917).

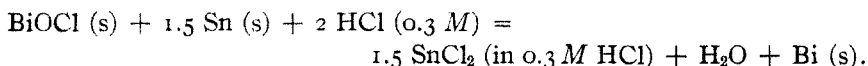
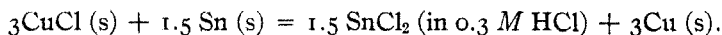
³ *Ibid.*, 2543 (1917).

⁴ Thomsen's *Thermochemische Untersuchungen*, 2, 336 (1882).

⁵ Berthelot's *Thermochimie*, 2, 318 (1897); *Ann. chim. phys.*, [5] 20, 514 (1880).

and since for one of these quantities the two available determinations are discordant, no reliance can be placed on the result. We have therefore undertaken a more direct determination of the heat-effect attending the reaction.

Plan of the New Determinations.—The reaction itself not only proceeds too slowly to permit of its heat effect being measured calorimetrically, but it does not go nearly to completion. In consequence, the plan adopted was to use an auxiliary metal which would displace both bismuth and copper from their chlorides rapidly and completely. Tin was chosen because it fulfils these requirements, and because it is not appreciably acted upon by the dilute hydrochloric acid solution, in presence of which the reactions were carried out. Calorimetric measurements were therefore made of the heat changes at 25° attending the two reactions



By subtraction is found the heat-content change at 25° attending the reaction



The Apparatus and Materials.—The apparatus consisted of a Dewar tube of 6 cm. internal diameter and 22 cm. in length, in which were placed a vertical glass stirrer, a Beckmann thermometer, a second thermometer for measuring the temperature of the gas space above the hydrochloric acid with which the lower half of the Dewar tube was filled, and 2 baskets, one above the other, for holding 2 separate portions of the tin threads.

The bottom of the baskets was made of a hard rubber circular disk with a large hole in the center (through which the Beckmann thermometer passed) and with a large number of small holes to permit circulation of the liquid. The sides of the baskets consisted of a circular row of small vertical glass rods set into holes along the rim of the hard rubber disk. An inner concentric row of vertical glass tubes 25 cm. high was also set into the rubber disk around the central hole, thus making an annular space, in which the tin was placed. Each basket was separately supported by 2 long glass tubes set into the bottom of the basket and extending through the hard rubber cover of the Dewar tube. The 2 baskets could thus be successively pushed down into the solution.

The substances used were the same as before, except for the tin, which was pure block tin turned out into very fine threads in a lathe so as to afford the maximum possible surface.

The Experimental Procedure.—The experimental procedure varied according to whether bismuthoxychloride or cuprous chloride was under investigation. For a determination of the heat of reaction of bismuth-

oxychloride with tin in hydrochloric acid solution, 303 g. of water were put into the Dewar tube from a pipet, the gas space above this water was filled with carbon dioxide, and then 102.91 g. of an approximately 1.5 *M* hydrochloric acid solution (nearly saturated with bismuthoxychloride at 25°) containing exactly 3.741 g. Bi¹ was added from another pipet. This resulted in the formation in the Dewar tube of 4.666 g. of finely divided solid bismuthoxychloride, suspended in about 400 cc. of 0.336 *M* hydrochloric acid solution containing a negligible quantity of dissolved bismuth. This procedure has the advantages that the bismuthoxychloride produced is free from basic compounds, and is in so finely divided a state as to react very rapidly with tin.

The cover of the Dewar tube was then placed in position with the upper and lower baskets filled with known weights of tin threads, and with the 2 thermometers in place, the Beckmann thermometer dipping into the solution, the other thermometer into the gas space. The 2 baskets of tin were suspended above the solution. The room temperature was kept within 1° of 25° during the experiment, so as to make the reaction nearly adiabatic. Carbon dioxide gas was passed into the Dewar tube to displace the air among the tin turnings; and, after waiting for a few minutes to allow the gas space above the solution to come to the same temperature, stirring of the solution was commenced, and the Beckmann thermometer was read every minute for 5 or 10 minutes, or until it showed a constant rate of temperature rise. The Beckmann thermometer used had been compared with a standardized Baudin thermometer. Care was taken to tap it vigorously before each reading.

The lower basket of tin was then introduced into the solution, it being raised and lowered gently during the rest of the experiment to furnish stirring. The Beckmann thermometer showed a rapid rise of temperature, which continued for about 7 minutes. At the end of this time the second basket of tin was lowered into the solution to hasten the reaction. After 3 minutes more the rise of temperature had practically ceased, but readings of the thermometer were taken for about 5 minutes more. This completed the experiment.

The use of 2 baskets of tin turnings introduced successively into the solution rendered the end point of the reaction much sharper, and contributed much to the accuracy of the determination.

To make sure that all the bismuthoxychloride had been reduced to bismuth, titrations with iodine solutions were made in 3 of the experiments to ascertain the amount of stannous chloride produced by the reaction, precautions being taken to prevent any oxidation of the stannous chloride during titration. In no case was the amount of stannous chloride pro-

¹ 52.90 g. of this solution yielded in 2 analyses 2.144 g. and 2.146 g. Bi₂O₃.

duced found to be different by more than 0.4% from the amount of bismuthoxychloride introduced into the calorimeter.

In the experiments with cuprous chloride the above procedure required modification, since the solubility of cuprous chloride in hydrochloric acid is not sufficient to enable the production of the requisite quantity of solid cuprous chloride in the Dewar tube, and since the tendency of moist cuprous chloride to oxidize is very great. The method adopted was as follows:

A weighing tube was filled with a weighed amount of dry cuprous chloride (prepared free from cupric chloride, as proved by testing it with potassium iodide starch solution, by washing precipitated cuprous chloride with glacial acetic acid and drying in the air at 100°); and then, after all was in readiness, this cuprous chloride was poured from the tube into 375 cc. of 0.28 *M* hydrochloric acid contained in the Dewar tube and covered with an atmosphere of carbon dioxide gas. After the calorimeter and contents had come to constant temperature, the experiment was proceeded with exactly as described above for bismuthoxychloride. With cuprous chloride the reaction proceeded much more rapidly than with bismuthoxychloride, and was completed within 7 minutes, even though both baskets of tin were introduced at the same time. The solution was analyzed for stannous chloride as before; and the amount formed was always found equivalent within 0.4% to the amount of cuprous chloride taken.

The observed temperature rises were in each case corrected for heat radiation in the usual manner. The heat effects to which they corresponded were calculated with the aid of data on the heat capacity of the different systems used. These heat data were obtained in independent experiments in which a nearly equal rise of temperature was produced in a system nearly identical with that used above by the introduction of a measured amount of electrical energy. The only differences between the systems used in the measurements of the heat of reaction and in the determinations of the heat capacity were the presence in the latter system of a small heating coil of enamelled resistance wire and the absence of the cuprous chloride. These small differences were corrected for with the aid of data on the specific heat capacities of tin, cuprous chloride, and the resistance wire,—data which need be only approximately accurate.

The quantity of heat introduced electrically in the heat-capacity experiments was determined by measurements of the resistance at 25° of the heating coil, of the potential difference (12 volts) applied by a storage battery to the terminals of this resistance (20.53 ohms) and of the time of application (about 15 minutes). The resistance was measured to 0.1% by means of a Wheatstone's bridge, the voltage to 0.01 volt by means of a calibrated Weston voltmeter, and the time to a fraction of a second by means of a watch.

The Experimental Data.—Typical sets of data for a determination with bismuthoxychloride, for one with cuprous chloride, and for one of the heat capacity of the system used in an experiment with bismuthoxychloride are given in Table X.

TABLE X.—TYPICAL EXPERIMENTAL DATA FOR THE HEAT OF REACTION MEASUREMENTS.

Time in min.	Thermometer readings in experiments on		
	BiOCl.	CuCl.	Heat capacity.
0	0.141	0.754	0.212
1	0.140	0.756	0.219
2	0.140	0.757	0.227
3	0.140	0.759	0.233
4	0.140	0.760	0.239
5	0.140 ¹	0.762	0.245
6	0.270	0.764	0.251
7	0.470	0.766 ¹	0.257
8	0.635	1.140	0.450 ³
9	0.755 ²	1.510	0.665
10	0.840	1.650 ²	0.880
11	0.940	2.010	1.110
12	1.010	2.035	1.335
13	1.040	2.054	1.560
14	1.050	2.077	1.775
15	1.055	2.084	1.990
16	1.057	2.091	2.205
17	1.059	2.098	2.420
18	1.061	2.105	2.640
19	1.063	2.112	2.860
20	1.065	2.118	3.080
21	1.067	3.295
22	3.510
23	3.725
24	3.940
25	4.155 ⁴
26	4.367
27	4.360
28	4.354

These data show the immediate evolution of heat when the first basket of tin was lowered, and the increase in rate of reaction caused by lowering the second basket. They indicate that the reaction was practically complete after 10 minutes in the case of the bismuth experiments, and after 7 minutes in the case of the copper experiments. They show also the rate of temperature change before and after the reaction.

Six experiments similar to the above were made upon bismuthoxychloride.

¹ First basket lowered.

² Second basket lowered.

³ Current turned on.

⁴ Current turned off.

TABLE XI.—EXPERIMENTAL DATA ON THE HEAT OF REACTION OF BISMUTHOXYCHLORIDE AND TIN IN HYDROCHLORIC ACID SOLUTION.

Experiment No.	I.	II.	III.	IV.	V.	VI.
Mols BiOCl used	0.01798	0.01798	0.01798	0.01798	0.01798	0.01798
Mols HCl per { Initial	0.336	0.336	0.336	0.336	0.336	0.336
1000 g. H ₂ O { Final	0.246	0.246	0.246	0.246	0.246	0.246
Grams of tin	35.48	45.09	41.40	30.06	44.80	42.88
Initial thermometer reading	0.133	0.140	0.789	1.810	0.945	1.476
Final thermometer reading	1.038	1.053	1.681	2.716	1.924	2.426
Radiation correction	+0.009	—0.009	—0.002	—0.006	—0.033	—0.040
Corrected temperature rise	0.914	0.904	0.890	0.900	0.946	0.910
Temperature of solution	24.10	23.06	23.29	24.31	23.45	23.98
Temperature of baskets	24.22	23.05	23.02	24.19	24.60	24.20
Heat capacity of baskets	13.5	13.5	13.5	13.5	13.5	13.5
Heat capacity of Tin	2.0	2.5	2.3	1.7	2.5	2.4
Total heat capacity	437.8	438.3	438.1	437.6	438.3	438.2
Calories evolved	400.1	396.3	390.1	393.9	414.7	398.8
Heat introduced by baskets	1.8	0.0	4.3	1.9	1.6	3.5
Calories evolved (corrected)	398.3	396.3	394.4	395.8	396.3	395.3
Calories per mol BiOCl	22150	22047	21930	22010	22090	21990

TABLE XII.—EXPERIMENTAL DATA ON THE HEAT OF REACTION OF CUPROUS CHLORIDE AND TIN IN HYDROCHLORIC ACID SOLUTION.

Experiment No.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Grams CuCl used	5.7674	4.8670	4.6809	4.4557	4.8610	4.5547	4.7343	4.6882
Mols CuCl used	0.05824	0.04915	0.04727	0.04499	0.04909	0.04599	0.04781	0.04734
Mols HCl per 1000 g. H ₂ O	0.278	0.278	0.278	0.278	0.278	0.278	0.278	0.248
Grams of tin	38.38	46.96	47.82	52.08	55.55	58.93	60.63	50.61
Initial thermometer reading	0.411	0.766	0.483	0.230	0.503	0.676	0.510	0.397
Final thermometer reading	1.958	2.077	1.784	1.422	1.800	1.944	1.779	1.669
Radiation correction	-0.026	-0.030	-0.024	-0.011	-0.017	-0.040	-0.021	-0.024
Corrected temperature rise	1.512	1.281	1.277	1.181	1.280	1.228	1.248	1.248
Temperature of solution	24.79	25.15	24.86	24.61	24.88	25.06	24.89	24.78
Temperature of baskets	24.81	25.30	26.00	25.04	24.95	25.88	25.08	25.20
Heat capacity of baskets	13.5	13.5	13.5	13.5	13.5	13.5	13.5	13.5
Heat capacity of tin	2.14	2.61	2.66	2.90	3.09	3.28	3.38	2.87
Heat capacity of CuCl	0.80	0.67	0.65	0.62	0.67	0.62	0.65	0.65
Total heat capacity	41.03	410.37	410.40	410.61	410.85	410.99	411.11	410.61
Calories evolved	623.66	525.68	524.08	484.93	525.89	504.70	513.07	512.44
Heat introduced by baskets	0.03	2.52	19.15	7.31	1.21	13.75	3.34	7.14
Correction for heat of solution of CuCl	-41.6	-41.6	-41.6	-41.6	-41.6	-41.6	-41.6	-41.6
Calories evolved (corrected)	582.0	481.6	463.3	436.0	483.1	449.3	468.1	463.7
Calories per mol CuCl	9990	9800	9780	9690	9860	9770	9790	9800

ride, 8 on cuprous chloride, 3 for determining the heat capacity of the bismuth system, and 5 for the heat capacity of the copper system.

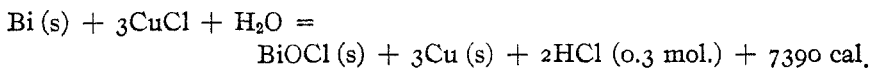
The 3 determinations of the heat capacity of the bismuth system resulted in the figures 436.06, 436.04, and 435.70 calories per degree, for a temperature of 25°. The average of these is 435.93 calories per degree; but from this is to be subtracted the heat capacity of the resistance coil (0.13), leaving 435.80 calories per degree. To this figure is to be added the heat capacity of the quantity of tin used in the baskets in any particular experiment, giving the heat capacity of the bismuth system in that experiment.

The 5 determinations of the heat capacity of the copper system resulted in the figures 407.10, 407.27, 407.28, 407.13, and 407.28 calories per degree, the average being 407.29. Subtracting 0.13 as before, we get 407.16 calories per degree, a figure to which must be added the heat capacities of the tin and of the cuprous chloride used in a given reaction experiment.

The results of the 6 experiments on bismuthoxychloride are given in Table XI; these of the 8 experiments on cuprous chloride in Table XII.

9. The Heat Effect Attending the Bismuth-Copper Reaction.

The mean value given by the above experimental data for the heat evolved at 25° when 1 mol of bismuthoxychloride reacts with tin and hydrochloric acid of concentration about 0.3 *M* is 22040 (a. d. 60) calories, and that for the heat evolved when 1 mol of cuprous chloride reacts with tin and hydrochloric acid of the same concentration is 9810 (a. d. 60) calories. By combining these two results we get for the reaction whose equilibrium we studied the following equation expressing the heat effect at 25°:



This result is different by 4565 cal. from the value (2825 cal.) derived in Section 5 from the electromotive-force measurements. As a careful consideration of the measurements makes it seem improbable that either of these results can be in error by even 500 cal., we are entirely unable to account for the discrepancy.

10. The Equilibrium Constant at 25° and the Corresponding Difference in the Two Specific Electrode Potentials.

The equilibrium constant at 25° (K_{298}) can be computed from that at 75° ($K_{348} = 0.00210$) and the increase in heat content ΔH by the equation

$$2.303 \log_{10} \frac{K_{298}}{K_{348}} = \frac{\Delta H}{1.989} \left(\frac{1}{348.1} - \frac{1}{298.1} \right).$$

According as we adopt the value of ΔH derived from the electromotive forces (—2825 cal.) or that derived from the heat measurements (—7390 cal.), we find at 25° for the equilibrium constant K_{298} , equal to $(\text{H}^+)^2 \times$

$(\text{Cl}^-)^2$, the value 0.00416 or the value 0.0126, corresponding to an equilibrium concentration of ionized hydrochloric acid of 0.254 *M* or of 0.335 *M*.

From these values of *K* we may calculate the difference in the two specific potentials by means of the equation

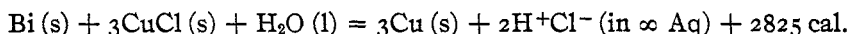
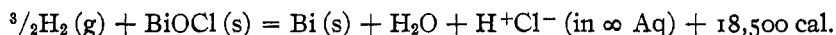
$$\bar{E}_{\text{BiOCl}} - \bar{E}_{\text{CuCl}} = \frac{RT}{3F} \log K = 0.01972 \log_{10} K.$$

The difference in the two potentials is thus found to be -0.0469 volt or -0.0375 volt at 25°. The value derived directly from the electromotive forces, as given in Table VIII was -0.0401 volt, thus intermediate between the 2 values derived from the equilibrium measurements with the aid of the 2 independently determined heat effects. Incidentally it indicates that the true heat effect may be intermediate between the 2 values.

11. Summary.

In this research the specific or normal potentials at 15, 25, and 35° of the electrodes $\left. \begin{matrix} \text{Bi} \\ \text{BiOCl} \end{matrix} \right\}, \text{H}^+ \text{ and } \left. \begin{matrix} \text{Cu} \\ \text{CuCl} \end{matrix} \right\}, \text{Cl}^-$ have been derived from measurements of cells formed by combining these electrodes separately with a hydrogen electrode (H_2, H^+) and with each other. The final results will be found in Table VIII.

From the change of the electrode potentials with the temperature the corresponding heat effects at 25° have been computed, and found to be those expressed by the following equations:



The heat effect attending the last of these reactions was also determined by thermochemical methods, allowing metallic tin to act in one case on cuprous chloride and in another case on bismuthoxychloride, in the presence of dilute hydrochloric acid. The value found (7390 cal.) differs considerably from that (2825 cal.) derived from the electromotive-force measurements—a discrepancy that can not be at present accounted for.

The equilibrium condition of the last of these reactions was determined at 75° by preparing and analyzing an equilibrium mixture. The equilibrium constant, equal to $(\text{H}^+)^3 \times (\text{Cl}^-)^2$, was found to be 0.0021 at 75°. Its value at 25°, calculated with the aid of the heat effect, is shown to accord fairly well with the difference between the 2 specific electrode potentials derived from the electromotive-force measurements.