of K_1, in that they first decrease slowly, pass through a minimum, and then increase rapidly. This result shows that the actual conditions are intermediate between those assumed in computing the constant K_1 and the constant K_2, and makes it probable that the two complex acids $H^+BiCl_4^-$ and $H^+_2BiCl_5^=$ are both present in the solution. The H_2BiCl_5 doubtless predominates in the more dilute solutions where there is a large excess of free hydrochloric acid,[1] and the $HBiCl_4$ in the more concentrated solutions, where ultimately (in the last three solutions) there is not even enough chloride present to convert all the bismuth into the $BiCl_5^=$ ion (since ΣCl is less than $5\Sigma Bi$). Alkali salts of both of these complex acids have previously been separated from their solutions.[2]

6. Summary.

In this article have been presented measurements on the electrical conductance at 25° of solutions of bismuth chloride in aqueous hydrochloric acid. The results show that the conductance of this acid is considerably reduced by dissolving bismuth chloride in it, and indicate the formation of a complex acid of the form $HBiCl_4$ or H_2BiCl_5.

Experiments on the solubility at 25° of bismuth oxychloride in hydrochloric acid through a wide range of concentration have also been presented. The results considered from the mass-action standpoint are shown to be intermediate between those required by the assumption that the complex acid is $HBiCl_4$ and the assumption that it is H_2BiCl_5. The latter doubtless predominates in solutions containing a considerable excess of hydrochloric acid; and the former, in those in which this is not the case.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 111.]

THE FREE ENERGY OF HYDROCHLORIC ACID IN AQUEOUS SOLUTION. II.

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CONTENTS.—1. Introduction. 2. Description of the Apparatus. 3. The Effect of Light on the Silver Chloride Electrodes. 4. The Experimental Results. 5. Decreases in Free Energy and in Heat Content Calculated from the Electromotive Forces. 6. Discussion of the Free-Energy Values. 7. Computation of the Specific Electrode Potentials. 8. Relative Activities of the Ions of the Acid at Various Concentrations. 9. Summary.

1. Introduction.

In a previous article[3] were presented the results of measurements

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[1] It will be noted that, while ΣBi increases from 0.0038 to 0.053, the constant K_2 decreases only 10%, a decrease that might be accounted for by ionization effects.

[2] Abegg, "Handbuch d. anorg. Chem.," 3, III, 653.

[3] Ellis, THIS JOURNAL, 38, 737–762 (1916).

of the electromotive force of the cells H_2 (1 atm.), HCl (4.5 to 0.01 *M*), Hg_2Cl_2 (solid) + Hg; and from these were computed various energy quantities and activity values for the ions of hydrochloric acid. It was found impossible by the use of this cell to secure reliable results at acid concentrations below 0.03 *M*,[1] and it was necessary to employ the data of Jahn[2] to extend the table of activity values to still lower concentrations. The desirability of additional electromotive-force data to confirm and supplement the work of Jahn at low concentrations led to the undertaking of this work, in which the calomel electrode previously used was replaced by a silver-chloride electrode in the hope that it would give more accurate measurements at very low acid concentrations.

The silver chloride electrodes were found in fact to give more reliable results with dilute acid than did the calomel electrodes; but even they failed when the acid concentration reached 0.0003 *M*, and at 0.001 *M* they were, perhaps, unreliable. The difficulties of electromotive-force measurements at low acid concentrations will be appreciated when it is mentioned that an excess or deficiency in chloride ion of only 0.0003 mg., even if uniformly distributed throughout the contents of the 20 cc. electrode vessels used, produces an error of 0.00001 volt at an acid concentration of 0.001 *M*—an effect which might well arise from adsorption phenomena.

The work was carried on with the assistance of a grant made to A. A. Noyes by the Carnegie Institution of Washington. In the preliminary experiments we had the assistance of Mr. Frank Hall, and in the final work that of Mr. M. Chow. For all this aid we wish to express our indebtedness.

2. Description of the Apparatus.

With the exception of the cell and the silver-chloride electrodes the apparatus used was identical with that employed for the measurements with calomel cell. The hydrogen electrodes were made as before, and acted in the same excellent manner. The hydrochloric acid solutions were prepared by dilution in the same way. The type of cell used for the present work is shown in half its natural size in Fig. 1, where the left-hand side of the figure shows only one of two identical vessels used to contain the silver-chloride electrodes.

Each of the four silver-chloride electrodes was prepared as follows: A platinum wire 0.6 mm. in diameter and 5 cm. long was wound into a helix of 0.3 cm. outside diameter, and one end was silver-soldered to a

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[1] The failure of the calomel electrode at low hydrochloric acid concentrations is probably due to the formation of a small amount of mercuric chloride by the oxygen dissolved in the hydrochloric acid solution, and subsequent reduction of this mercuric salt. At low concentrations this may result in a considerable percentage change in the acid concentration.

[2] *Z. physik. Chem.*, 33, 545–576 (1900).

copper wire. The helix was then sealed into a glass tube which could be made fast in the electrode vessel by a ground joint. The helix was cleaned by boiling it with strong nitric acid, and it was plated with silver from a potassium silver cyanide solution, using a current of 0.006 ampere for 4 hours. It was then washed for two days in frequent changes of conductivity water to remove all cyanide, after which it was coated with a paste of precipitated and washed silver oxide suspended in water. This paste was made to fill the interstices of the helix and cover the platinum wire completely. The coated electrode was allowed to dry in a hot closet, and was then heated for six hours at 400° in an electric oven, whereby the brown silver oxide was converted into shining, white, porous metallic silver. A coating of silver chloride was deposited on this silver by electrolyzing it as anode in 0.75 *M* hydrochloric acid for 5 hours with 0.004 ampere. The electrode was then transferred to the cell and washed in place four times or more with acid of the strength to be used in the measurements, allowing it to stand in the acid half an hour each time, and taking care the last time to fill the silver chloride cell completely with the acid. Properly prepared, four electrodes of this kind show agreement within 0.00005 volt, and remain constant in value for at least several days.[1]

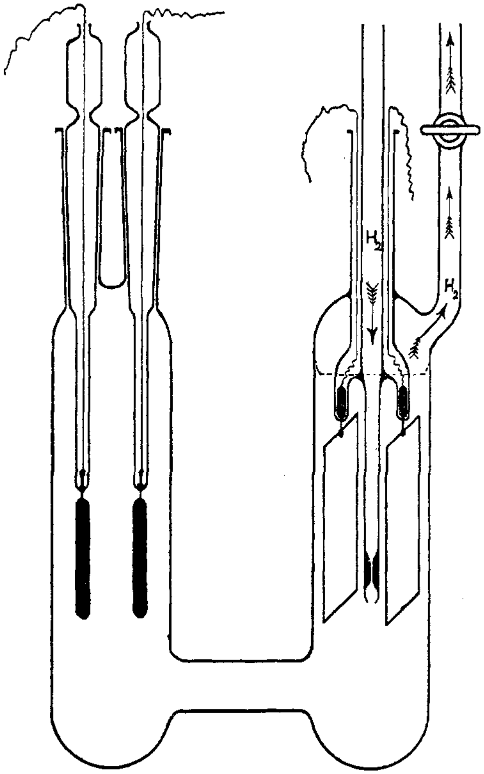

Fig. 1.

In spite of the large temperature coefficient of the solubility of silver chloride, only a slight lag (about 0.00002 volt) of electromotive force is observed when the temperature of the electrode vessel is changed rapidly

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[1] This method of preparing silver electrodes has been described by Lewis (THIS JOURNAL, 28, 166 (1906)). Of a number of methods tried this is the only one which was found reliable for the preparation of these electrodes. Its success probably depends upon the fact that it furnishes a porous, annealed basis of silver. It is probable that no electrolytically deposited silver can give definite results unless the strain in it are removed in some manner.

from 35 to 15°, or *vice versa;* and it is unnecessary and inadvisable to provide means for stirring the solution around the electrodes. The lag disappears of itself in less than an hour.

3. The Effect of Light on the Silver Chloride Electrodes.

Experiments were made on the effect of light upon the electrode potential of silver-chloride electrodes, using acid about 0.3 M and a type of cell in which the solution around the electrodes could be circulated by means of a pumping device. Four silver chloride electrodes were prepared in total darkness, and their mean electromotive force in combination with a hydrogen electrode was found to be constant at 0.29261 volt. They were then illuminated for fifteen minutes with a naked 6-ampere carbon arc, when the value changed to 0.29256 volt. After fifteen minutes' more illumination it had dropped to 0.29255 volt, after which exposure to the light for thirty minutes more caused no further measurable change in the electromotive force. Left in darkness for nine hours, it rose to 0.29259 volt, when ten minutes' illumination caused it to fall again to 0.29252 volt. After five hours of darkness it rose again to 0.29266 volt, but the agreement between separate electrodes was not so good as usual. The pumping device was then operated, when the agreement became normal and the electromotive force changed to 0.29262 volt, practically its original value.

These results may be explained by the supposition that illumination causes some decomposition of silver chloride into silver and chlorine, the chlorine raising the electrode potential. In darkness the products either recombine or else the chlorine diffuses away from the electrode, so that a return to its original potential results. They show that the effect of even strong illumination is small, and that whether in light or in darkness the silver-chloride electrode has a definite potential. The measurements of this article were made with the cells in subdued daylight or artificial light. No differences in the electromotive force in the daytime and night-time were ever observed.

4. The Experimental Results.

The experimental data obtained with the hydrogen silver-chloride cells are presented in Table I. The first column gives the temperature of the cell; the second column the corrected hydrogen pressure in cm. of mercury; the third the time elapsed after the first measurement; the fourth the electromotive force of the Weston standard cell as measured by the potentiometer; and the fifth, sixth, seventh and eighth columns give the observed electromotive forces of the four cells obtained by combining a hydrogen electrode with each of the four silver-chloride electrodes.

From these data, by applying the corrections for the hydrogen pressure, for the observed electromotive force of the standard cell, for small deviations from round temperatures, etc., described in the previous article on

TABLE I.—EXPERIMENTAL DATA ON THE ELECTROMOTIVE FORCE OF THE HYDROGEN-SILVER-CHLORIDE CELL.

Temperature.	Hydrogen pressure.	Elapsed time.	Observed electromotive forces.				
			Std. cell.	Cell I.	Cell II.	Cell III.	Cell IV.
Acid Content: 0.33314 mol HCl per 1000 g. water.							
25.00	73.70	0 : 00	1.01861	0.29317	0.29314	0.29316	0.29318
25.05	73.75	2 : 00	1.01857	0.29316	0.29314	0.29317	0.29319
24.96	74.47	12 : 30	1.01870	0.29332	0.29330	0.29333	0.29335
34.63	72.87	20 : 00	1.01867	0.28924	0.28921	0.28922	0.28926
34.66	73.02	25 : 00	1.01859	0.28924	0.28921	0.28922	0.28925
25.06	74.72	39 : 10	1.01865	0.29327	0.29324	0.29326	0.29328
25.06	74.60	48 : 00	1.01862	0.29326	0.29324	0.29325	0.29327
15.06	75.56	52 : 15	1.01861	0.29684	0.29681	0.29681	0.29684
15.00	75.53	53 : 20	1.01864	0.29679	0.29677	0.29678	0.29680
14.99	75.52	54 : 15	1.01864	0.29679	0.29676	0.29677	0.29680
Acid Content: 0.09534 mol HCl per 1000 g. water.							
25.01	74.27	0 : 00	1.01858	0.35424	0.35427	0.35434	0.35428
25.01	74.22	2 : 00	1.01860	0.35424	0.35426	0.35434	0.35427
25.00	74.14	8 : 00	1.01862	0.35426	0.35428	0.35434	0.35427
25.00	74.04	10 : 40	1.01864	0.35425	0.35426	0.35432	0.35426
34.99	72.15	14 : 00	1.01864	0.35188	0.35190	0.35195	0.35190
34.99	72.16	15 : 15	1.01860	0.35188	0.35190	0.35194	0.35189
15.02	75.17	16 : 45	1.01859	0.35592	0.35595	0.35597	0.35595
15.02	75.16	18 : 15	1.01857	0.35591	0.35593	0.35598	0.35594
8.01	75.62	20 : 15	1.01856	0.35665	0.35668	0.35673	0.35668
Acid Content: 0.03324 mol HCl per 1000 g. water.							
25.00	73.61	0 : 00	1.01857	0.40498	0.40499	0.40506	0.40498
25.00	73.57	2 : 00	1.01838	0.40495	0.40496	0.40499	0.40496
25.00	73.59	2 : 15	1.01841	0.40498	0.40499	0.40504	0.40499
34.99	71.77	4 : 00	1.01840	0.40432	0.40433	0.40438	0.40435
34.97	71.75	5 : 00	1.01847	0.40437	0.40438	0.40445	0.40440
15.01	74.67	8 : 15	1.01847	0.40511	0.40511	0.40516	0.40514
15.02	74.71	9 : 15	1.01847	0.40507	0.40508	0.40515	0.40511
25.00	73.62	10 : 15	1.01845	0.40510	0.40510	0.40515	0.40512
24.98	73.69	11 : 55	1.01836	0.40505	0.40506	0.40513	0.40509
35.00	71.83	13 : 05	1.01844	0.40436	0.40436	0.40446	0.40441
34.99	71.85	13 : 55	1.01845	0.40436	0.40437	0.40445	0.40441
Acid Content: 0.00948 mol HCl per 1000 g. water.							
25.00	74.27	0 : 00	1.01858	0.46643	0.46645	0.46645	0.46644
25.00	74.36	1 : 10	1.01860	0.46644	0.46648	0.46649	0.46646
35.00	72.46	2 : 30	1.01859	0.46764	0.46770	0.46771	0.46768
35.00	72.47	3 : 40	1.01858	0.46765	0.46770	0.46770	0.46767
15.00	75.50	5 : 15	1.01859	0.46451	0.46451	0.46451	0.46454
15.00	75.45	6 : 20	1.01859	0.46453	0.46453	0.46454	0.46454
Acid Content: 0.003378 mol HCl per 1000 g. water.							
25.00	74.18	0 : 00	1.01856	0.51669	0.51672	0.51672	0.51675
25.00	74.18	1 : 00	1.01866	0.51673	0.51675	0.51673	0.51675
35.00	72.29	2 : 30	1.01861	0.51958	0.51962	0.51965	0.51966
35.00	72.28	4 : 00	1.01859	0.51960	0.51964	0.51964	0.51965
15.02	75.19	5 : 50	1.01863	0.51319	0.51318	0.51320	0.51326

TABLE I (*continued*).

Temperature.	Hydrogen pressure.	Elapsed time.	Observed electromotive forces. Std. cell.	Cell I.	Cell II.	Cell III.	Cell IV.
Acid Content: 0.000999 mol HCl per 1000 g. water.							
25.00	74.70	0 : 00	1.01834	0.57870	0.57876	0.57870	0.57871
25.00	74.72	1 : 05	1.01849	0.57874	0.57875	0.57867	0.57870
25.00	74.67	2 : 40	1.01865	0.57883	0.57884	0.57877	0.57879
15.00	75.83	4 : 05	1.01860	0.57313	0.57315	0.57309	0.57312
15.00	75.84	5 : 05	1.01860	0.57317	0.57321	0.57312	0.57316
15.01	75.85	5 : 50	1.01861	0.57317	0.57320	0.57313	0.57312
34.99	72.90	7 : 30	1.01862	0.58372	0.58375	0.58376	0.58374
34.99	72.92	8 : 20	1.01865	0.58377	0.58376	0.58380	0.58379

hydrogen calomel cells, the final values of the electromotive force given in Table II were derived. In computing these values, the electromotive force of the standard cell was taken as 1.01843 volts, the mean of two determinations at different times by the Bureau of Standards. The first column of the table gives the concentration of hydrochloric acid in mols per 1000 g. water, correction having been made for air buoyancy. The next three columns give the electromotive forces of the cells H_2 (1 atm.), HCl (0.333 to 0.001 *M*), AgCl (solid) + Ag (solid), with the hydrogen pressure exactly 1 atmosphere, and with the temperatures and acid concentrations as indicated. In the fifth and sixth columns are tabulated values of $10^6\ \alpha_{25}$ and $10^6\ \beta_{25}$, α_{25} and β_{25} being the temperature coefficients in the following equation expressing the variation of electromotive force with temperature for each concentration:

$$E = E_{25}[1 + \alpha_{25}(t - 25) + \beta_{25}(t - 25)^2]$$

TABLE II.—SUMMARY OF THE ELECTROMOTIVE FORCES OF THE CELLS AND THEIR TEMPERATURE COEFFICIENTS.

Mol HCl in 1000 g. water.	Electromotive force At 15°.	At 25°.	At 35°.	Temperature coefficients. $10^6\ \alpha_{25}$.	$10^6\ \beta_{25}$.
0.33314	0.29678	0.29348	0.28958	—1226.6	—10.22
0.09534	0.35600	0.35453	0.35270	—465.4	—5.08
0.03324	0.40530	0.40545	0.40513	—20.97	—5.80
0.00948	0.46452	0.46666	0.46824	+398.6	—6.00
0.003378	0.51325	0.51696	0.52023	+675.0	—4.26
0.000999	0.57308	0.57893	0.58421	+960.7	—4.81
0.10000	0.35375	0.35221	0.35031	—488.3	—5.11

The last line of the table contains values for a cell with acid exactly 0.10000 molal. These values were obtained by interpolating with the aid of empirical equations connecting electromotive force and concentration which satisfy the values for 0.33314, 0.09534 and 0.03324 *M* acid.

5. Decreases in Free Energy and in Heat Content Calculated from the Electromotive Forces.

From these values of the electromotive force and of the temperature coefficients there have been calculated, in the ways described in the previous article, the figures given in Tables III and IV. The free-energy decreases were obtained by multiplying the electromotive forces given in Table II by 193,000. The heat content values were computed by multiplying the free-energy decreases at 25° by $(1 - 298.1\alpha_{25})$.

The second, third, and fourth columns of Table III give the decrease in free energy in joules which attends the reaction $H_2(1 \text{ atm.}) + 2AgCl = 2HCl + 2Ag$ at the temperatures 15, 25, and 35°, respectively, when the hydrochloric acid is produced at the concentrations given in the first column. The last column gives the decrease in heat content in joules attending this reaction at 25°.

TABLE III.—DECREASE IN FREE ENERGY AND IN HEAT CONTENT ATTENDING THE CELL REACTION INVOLVING 2 HCl.

Mol HCl in 1000 g. water.	Free-energy decrease			Heat-content decrease at 25°.
	At 15°.	At 25°.	At 35°.	
0.33314	57279	56642	55889	77350
0.10000	68275	67977	67610	77870
0.09534	68708	68424	68071	77920
0.03324	78223	78252	78190	78740
0.00948	89652	90065	90370	79360
0.003378	99057	99773	100404	79700
0.000999	110604	111733	112753	79730

The second, third, and fourth columns of Table IV give the decrease in free energy in joules which attend the transfer of 1 HCl from the concentration given in the first column to the concentration 0.1000 *M*, at 15, 25 and 35°.[1] The last column gives the decrease in heat content in joules which attends the transfer at 25° of 1 HCl from the concentration given in the first column to 0.1000 *M*.

TABLE IV.—DECREASE IN FREE ENERGY AND IN HEAT CONTENT ATTENDING THE TRANSFER OF 1 HCl FROM VARIOUS CONCENTRATIONS TO 0.1000 *M*.

Mol HCl in 1000 g. water.	Free-energy decrease			Heat-content decrease at 25°.
	At 15°.	At 25°.	At 35°.	
0.33314	+5498	+5668	+5861	+260
0.10000	0	0	0	...
0.03324	—4974	—5138	—5290	—435
0.00948	—10689	—11044	—11380	—745
0.003378	—15391	—15898	—16397	—915
0.000999	—21165	—21878	—22572	—930

6. Discussion of the Free-Energy Values.

The free energies of transfer at 0.33314 and 0.03324 *M* obtained with this silver-chloride cell may be compared with those at nearly the same concentrations (0.33757 and 0.03332 *M*) obtained with the calomel cell

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[1] For the concentration 0.33314 *M* more accurate values, based also on the measurements with the calomel cell, are derived below in Section 7. These are: 5557 joules at 15°; 5730 joules at 25°; and 5909 joules at 35°.

and recorded in Table VII of the previous article. As the concentrations are somewhat different, it is best to compare the values at 25° of the coefficient k which is defined by the following equation, and which changes comparatively slowly with the concentration:

$$(-\Delta F)_2 - (-\Delta F)_1 = k \log_{10} c_1/c_2$$

Moreover, since this coefficient k, which represents the free-energy decrease for a concentration ratio of tenfold, should theoretically approach the value 2.303 $N R T$, or 11418 joules at 25°, as the hydrochloric acid becomes completely ionized and comes to behave as a perfect solute, it is of interest to calculate the values of k for the successive concentration intervals from the data given in Table IV of this article and from the data given in Table VII of the preceding article. The heat-content decreases, which should approach zero as the concentration approaches zero, have been treated in the same way.

The following table contains the values of k at 25° calculated as just described for the concentration intervals given in the first column:

TABLE V.—CHANGES AT 25° OF THE FREE ENERGY OF TRANSFER AND HEAT OF TRANSFER COMPUTED FOR A CONCENTRATION RATIO OF TENFOLD.

	Free-energy decrease.		High-content decrease.	
Concentration interval.	AgCl cell.	Hg_2Cl_2 cell.	AgCl cell.	Hg_2Cl_2 cell.
0.3350–0.1000	10840	11080	500	350[1]
0.1000–0.0333	10740	10820	910	630
0.0333–0.0095	10840	...	570	...
0.0095–0.0034	10830	...	380	...
0.0034–0.0010	(11300)	...	(30)	...
As c approaches 0	11418	11418	0	0

The free energies of transfer as derived from the two different cells are seen to be fairly concordant, when it is considered that these values are differences obtained by subtracting from each other the much larger values corresponding to the cell reaction. The heats of transfer derived from the two cells for these concentration intervals are also in tolerable agreement, considering the multiplication of errors involved in their computation.

It will be seen from the table that even for the concentration interval 0.0095–0.0034, the rate of change of the free energy still differs from the limiting value by 588 joules. Moreover, for the concentration interval 0.0333–0.0095 there is still the considerable heat effect of 380 joules (when computed over to the .tenfold concentration change). These facts make it clear that hydrochloric acid is still far from being a perfect, completely ionized solute, even at the concentration 0.0034 M.

7. Computation of the Specific Electrode Potentials.

Let us now consider the results from a different viewpoint. By subtracting the electromotive forces or free-energy decreases at the concen-

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[1] In Table VII of the previous article $-\Delta H_{25}$ at 0.33757 molal was incorrectly printed as 684 instead of 184 joules.

trations 0.33314 and 0.1000 *M* given in Table II or III for the silver-chloride cell from those given in Table V or VI of the previous article for the calomel cell (after correcting the latter for the small differences in concentration and extrapolating the 18° values to 15°), we can obtain very accurate values of the difference between the potential of the silver-chloride electrode and that of the mercury-calomel electrode, or of the difference between the free energy of formation from the elements of 2 AgCl and that of 1 Hg_2Cl_2. The results so derived are given in Table VI.

TABLE VI.—DIFFERENCE IN THE POTENTIALS OF THE SILVER CHLORIDE AND CALOMEL ELECTRODES AND IN THE FREE ENERGIES OF SILVER CHLORIDE AND CALOMEL.

Mol. HCl per 1000 g. water.		Electromotive force			Free-energy decrease		
		At 15°.	At 25°.	At 35°.	At 15°.	At 25°.	At 35°.
0.33314	Hg_2Cl_2 Cell	0.33919	0.33900	0.33860	65464	65428	65350
	AgCl Cell	0.29678	0.29348	0.28958	57279	56642	55889
	Difference	0.04241	0.04552	0.04902	8185	8786	9461
0.10000	Hg_2Cl_2 Cell	0.39739	0.39904	0.40033	76697	77015	77264
	AgCl Cell	0.35375	0.35221	0.35031	68275	67977	67610
	Difference	0.04364	0.04683	0.05002	8422	9038	9654
	Mean difference	0.0430	0.0462	0.0495	8304	8912	9558

It will be seen that the two sets of differences agree within 1.0 to 1.3 millivolts or within 200 to 250 joules. The "mean difference" in the electromotive forces represents the difference between the specific electrode potential of Ag + AgCl, Cl^- and that of Hg + Hg_2Cl_2, Cl^-, the former half cell being more reducing by this amount. The "mean difference" in the free-energy decreases represents the difference between the free-energy decrease attending the formation of 2 AgCl and that attending the formation of 1 Hg_2Cl_2 from the elements.

The corresponding mean values of the free-energy decrease attending the transfer of 1 HCl from 0.33314 molal to 0.10000 molal are: 5557 joules at 15°; 5730 joules at 25°; 5909 joules at 35°. As these are averages derived from the measurements with the two different cells, they are to be regarded as more accurate than those given in Table IV.

To get the separate values of the two specific electrode potentials, we may first calculate that ($\bar{\mathbf{E}}_{AgCl}$) of Ag + AgCl, Cl^- from the electromotive force ($\mathbf{E}$) of the silver-chloride cell at 0.003378 molal at the three temperatures (as given in Table II) by the equation $\bar{\mathbf{E}}_{AgCl} = \mathbf{E} - 2(RT/\mathbf{F}) \log c\alpha$, assuming that the activity coefficient α is identical at this concentration with the conductance ratio, whose value is 0.985.[1] It will be seen in the next section that the activity coefficient probably increases by a considerable amount beyond this concentration, and,

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[1] Noyes and Falk, THIS JOURNAL, 34, 475 (1912).

therefore that its true value is probable several per cent. less than 0.985; but, as there are no data which make it possible to extrapolate the activity coefficient to lower concentrations, there is at present nothing better to do than to assume identity of it with the conductance ratio at the smallest concentration at which the electromotive forces are probably exact. Having obtained these specific potentials, those of Hg + Hg_2Cl_2, Cl^- are calculated from it by subtracting the mean differences given in Table VI.

The values of the specific electrode potentials so calculated, referred to the molal hydrogen electrode and to a concentration of 1 mol Cl^- per 1000 g. of water, are

For Ag + AgCl,Cl^-: —0.2299 at 15°; —0.2238 at 25°; —0.2172 at 35°.
For Hg + Hg_2Cl_2,Cl^-: —0.2729 at 15°; —0.2700 at 25°; —0.2667 at 35°.

Finally, we may compute the electrode potential at 25° of the normal[1] calomel electrode against the molal hydrogen electrode, that is, the electromotive force of the cell Hg + Hg_2Cl_2, KCl (1 *N*)//H^+ (1 *M*), H_2 (1 atm.), and thus determine the difference between these two basic standards of reference. For this purpose we need to know the activity of chloride ion in 1 *N* potassium chloride solution. MacInnes and Parker[2] and Bates[3] have determined the activity coefficients of potassium chloride by two entirely independent methods with remarkably concordant results,[4] as shown in Table XIII of the previous article. Unfortunately their determinations extend only up to 0.5 *N*; but a fairly accurate value at 1.0 *N* can doubtless be obtained by plotting their values at 0.05, 0.10, 0.20 and 0.50 against log *c*, and extrapolating on the graph, which is not far from a straight line. In this way the activity coefficient at 1.0 *N* is found to be 0.597 with an error that probably does not exceed 1% of this value. By substituting in the equation $\mathbf{E} = \bar{\mathbf{E}} + (RT/\mathbf{F}) \log c\alpha$, for α this value 0.0597, for c the value 1.0327 (representing the mols of KCl per 1000 g. water in a 1 *N* potassium chloride solution at 25°), and for $\bar{\mathbf{E}}$ the value —0.2700 (the above-given specific electrode potential of Hg + Hg_2Cl_2, Cl^- at 25°), we find for **E**, the electrode potential of the normal calomel electrode at 25°, the value —0.2824 volt, which can hardly be in error by more than 0.0005 volt. This value agrees closely with that

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[1] The term normal (*N*) is here used, as it always should be, in the volumetric sense, to signify one equivalent of solute in 1000 cc. of solution at the temperature under consideration.

[2] THIS JOURNAL, 37, 1445–1461 (1915).

[3] *Ibid.*, 37, 1421–1445 (1915).

[4] We wish to take this occasion to call attention to the incorrectness of the conclusion drawn in the previous article from the concordance of the results obtained by the two methods, that the conductance-viscosity ratio is a substantially correct measure of ion concentration. For, as S. J. Bates has kindly pointed out to us, although he employed this assumption in his computations, it is eliminated in the calculation of the activity values.

(—0.2828 volt) recently given by Lewis, Brighton and Sebastian,[1] but it is to be noted that their "normal electrode" is so defined as to include the liquid potential between 0.1 and 1.0 *N* potassium chloride solutions.

8. Relative Activities of the Ions of the Acid at Various Concentrations.

The values at 15, 25, 35° of the relative activity coefficients (α) of hydrochloric acid at different concentrations were calculated from the free-energy values given in Table IV by the equation $-\Delta F = 2RT \log (c_1\alpha_1/c_2\alpha_2)$, as in the previous article. These values are given in Table VII. The first column of this table gives the concentration of the acid. The next three give the ratios at 15, 25 and 35° of the activity coefficient at this concentration to the activity coefficient at 0.1000 *M*.

Table VII.—Activity-Coefficient Ratios for Hydrochloric Acid.

Mol. HCl in 1000 g. water.	Activity-coefficient ratios At 15°.	At 25°.	At 35°.
0.33314	0.945	0.941	0.942
0.10000	1.000	1.000	1.000
0.03324	1.066	1.067	1.072
0.00948	1.134	1.138	1.145
0.003378	1.193	1.200	1.208
0.000999	(1.209)	(1.214)	(1.221)

Reference may first be made to the degree of agreement of these activity coefficients with those derived in the previous article (Tables VIII and XI) at the lower concentrations from Jahn's measurements, and at the higher concentrations from Ellis' measurements with the calomel cell. The previously found values of the ratio of the activity coefficient to that at 0.1000 *M* (at 18°) are given below in the second line, while the ones (at 15°) here presented are given in the last line.

Mol HCl per 1000 g. water....	0.00338	0.00948	0.03324	0.3331
Previous activity ratio.........	1.163	1.127	1.061	0.961
Present activity ratio..........	1.193	1.134	1.066	0.945

The agreement is seen to be fairly close, except at the lowest concentration.

When these new activity coefficients are plotted against the logarithm of the concentration it is seen clearly that the activity coefficient is still increasing rapidly at 0.0033 *M*, and that its limiting value can hardly be less than 1.25 and may be considerably larger. This result is in general accord with the conclusion of Washburn[2] that strong electrolytes become normal solutes only at concentrations below 0.0001 *M*. The plot also indicates that the value of the electromotive force at 0.000999 *M* is affected by a considerable error. These two facts make it impracticable to extrapolate the activity coefficients to zero concentration; and there seems

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[1] This Journal, 39, 2258 (1917).

[2] *Proc. Nat. Acad. Sciences*, 3, 575 (1917).

nothing better to do at present than to assume that at the lowest concentration (0.003324 *M*) at which the electromotive forces are still fairly exact the activity coefficient has the same value (0.985)[1] as the conductance ratio. On this basis the following complete table of activity coefficients has been calculated from the values given in Table VII of this article and in Table VIII of the previous article. In the last column of the table are given the values of the conductance-viscosity ratios at 18° interpolated from those given in Table XI of the preceding article.

TABLE VIII.—ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID.

Mol. HCl per 1000 g. water.	Activity coefficients				$\Lambda\eta/\Lambda_0\eta_0$ at 18°.
	At 15°.	At 18°.	At 25°.	At 35°.	
4.484	...	2.160	2.082	1.959	...
1.928	...	1.029	1.005	0.977	...
1.038	...	0.836	0.823	0.809	...
0.7714	...	0.796	0.785	0.773	...
0.5095	...	0.769	0.760	0.752	...
0.3350	0.787	0.789	0.782	0.775	0.889
0.1000	0.826	0.824	0.821	0.815	0.925
0.03324	0.880	...	0.876	0.874	0.953
0.00948	0.936	...	0.934	0.934	0.972
0.00338	0.985	...	0.985	0.985	0.985

The activity coefficients given in the previous article do not differ greatly from those here tabulated; and there is nothing to add to the general discussion of them there presented.

9. Summary.

In this article are presented (in Table II) the results of measurements of the electromotive force at 15, 25 and 35° of the cells H_2 (1 atm.), HCl (0.3 to 0.001 *M*), AgCl + Ag. From these data are calculated the free-energy decrease and heat-content decrease attending the change in state which takes place in these cells (see Table III), and also those attending the transfer of 1 HCl from various concentrations to 0.1000 *M* (see Table IV).

The results show that even at 0.0034 *M* hydrochloric acid is still far from being a completely ionized perfect solute (see Table V).

From the results and those obtained in the previous article the difference between the electrode potentials of the half cells Ag + AgCl, Cl^- (1 *M*) and Hg + Hg_2Cl_2, Cl^- (1 *M*) were computed (see Table VI); and the separate values of these specific potentials referred to the molal hydrogen electrode were found to be

For Ag + AgCl,Cl^-: —0.2299 at 15°; —0.2238 at 25°; —0.2172 at 35°.
For Hg + Hg_2Cl_2,Cl^-: —0.2729 at 15°; —0.2700 at 25°; —0.2667 at 35°.

The electrode potential of the normal calomel electrode, Hg + Hg_2Cl_2, KCl (1 *N*), at 25° was found to be —0.2824, in fair agreement with the value —0.2828 recently published by Lewis, Brighton and Sebastian.

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[1] Noyes and Falk, THIS JOURNAL, 34, 475 (1912).

Upon the assumption that at the lowest concentration (0.0034 *M*) at which the measured electromotive forces are exact the ion activity is equal to the ion concentration, a revised series of activity coefficients for hydrochloric acid from 0.0034 to 4.5 *M* was computed (see Table VIII). These again show a divergence of about 10% from the conductance ratio (Λ/Λ_0) at 0.1 *M*. They attain a minimum value at about 0.5 *M* and increase very rapidly at concentrations above 1 *M*.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE POTENTIAL OF THE BROMINE ELECTRODE; THE FREE ENERGY OF DILUTION OF HYDOGEN BROMIDE; THE DISTRIBUTION OF BROMINE BETWEEN SEVERAL PHASES.

BY GILBERT N. LEWIS AND HYMAN STORCH.

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The potential of the bromine electrode has been studied in much detail by Boericke,[1] but unfortunately, as in most of the earlier investigations of electromotive force, the use of concentrated solutions, the lack of information concerning the corrected degree of dissociation, and the introduction of liquid potentials of uncertain magnitude render it difficult to make accurate calculations from the measurements. Thus, Boericke, who used various concentrations of bromine in solutions of potassium bromide between molal and tenth molal, obtained values for the normal electrode potential which varied by 0.008 volt. In this paper we shall attempt to fix the value of the normal electrode potential within a few tenths of a millivolt.

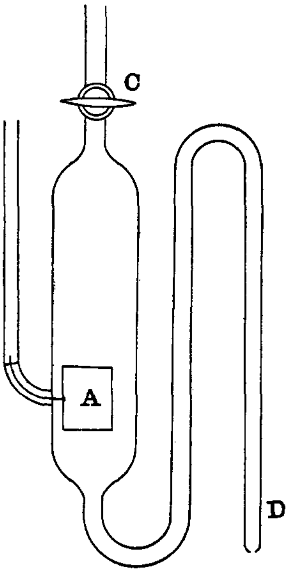

Fig. 1.

Potential Measurements in Potassium Bromide.

The first measurements were made in solutions of potassium bromide which were brought to a definite bromine content by shaking with successive portions of a known solution of bromine in carbon tetrachloride. Electrodes of platinum-iridium, faintly iridized to improve their reversibility, were contained in a vessel of about 20 cc. capacity shown in Fig. 1. In order to avoid change in concentration through evaporation, the solution of bromine in potassium bromide was introduced into the cell at D, not through suction at C, as is the common practice with

[1] Boericke, *Z. Elecktrochem.*, **11**, 57 (1905).