[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

THE CALOMEL AND SILVER CHLORIDE ELECTRODES IN ACID AND NEUTRAL SOLUTIONS. THE ACTIVITY COEFFICIENT OF AQUEOUS HYDROCHLORIC ACID AND THE SINGLE POTENTIAL OF THE DECI-MOLAL CALOMEL ELECTRODE

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RECEIVED OCTOBER 18, 1927 PUBLISHED APRIL 5, 1928

In a careful investigation Gerke[1] found 0.0455 v. for the potential of the cell

$$\text{Ag (elect. crystals)} + \text{HgCl(s)} = \text{AgCl(ppt.)} + \text{Hg(l)} \qquad (1)$$

at 25°, with either molal potassium or hydrogen chlorides as the electrolyte. He also measured the potential of the chlorine electrode against calomel and silver chloride electrodes and found 1.0904 and 1.1362 v., respectively, a difference of 0.0458 v. Gerke used finely divided crystalline silver[2] prepared by rapid electrolysis, and silver and mercurous chlorides "precipitated metathetically in the ordinary granular form from dilute solutions of pure salts."

Brönsted,[3] using a platinum wire plated with silver 0.5 mm. in thickness and with silver chloride after the method of Jahn,[4] obtained 0.0471 and 0.0475 v. at 25° (interpolated) for a cell corresponding to that of Equation 1, with 0.1 *N* and 0.01 *N* potassium chloride in gelatin as an electrolyte.

Numerous measurements of the potential of the hydrogen–calomel and hydrogen–silver chloride cells have been reviewed by Lewis and Randall,[5] who found that most of the measurements would fit the same curve if the electromotive force of the cell of Equation 1 was assumed to be 0.0466 v. Later measurements by Harned and Brumbaugh,[6] Harned and Fleysher,[7] Harned and Swindells[8] and by Scatchard,[9] on the hydrogen–silver chloride cell, and by Harned[10] and Randall and Breckenridge[11] on the hydrogen–calomel cell confirmed the value 0.0466 for the difference between these cells.[12]

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[1] Gerke, THIS JOURNAL, **44**, 1684 (1922).

[2] Lewis, *ibid.*, **28**, 158 (1906).

[3] Brönsted, *Z. physik. Chem.*, **50**, 481 (1904).

[4] Jahn, *ibid.*, **33**, 545 (1900).

[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, pp. 335, 407.

[6] Harned and Brumbaugh, THIS JOURNAL, **44**, 2729 (1922).

[7] Harned and Fleysher, *ibid.*, **47**, 82 (1925).

[8] Harned and Swindells, *ibid.*, **48**, 126 (1926).

[9] (a) Scatchard, *ibid.*, **47**, 641 (1925); see also (b) *ibid.*, **47**, 2098 (1925).

[10] Harned, (a) *ibid.*, **42**, 1808 (1920); (b) *ibid.*, **48**, 326 (1926).

[11] Randall and Breckenridge, *ibid.*, **49**, 1435 (1927).

[12] This discrepancy was attributed to the silver–silver chloride electrode by (a) Lewis and Randall, ref. 5, and to different forms of silver by (b) Scatchard, THIS JOURNAL, **47**, 707 (1925). Gerke's low value (0.0455 v.) was attributed to poisoning of the

Linhart[13] used silver and silver chloride prepared in about the same manner as that used by Gerke.[1] Scatchard[9a] used platinum gauze electrodes plated with silver and then chloridized electrolytically[4,14] in the solution in which they were to be used. Noyes and Ellis[15] used spirals prepared by heating silver oxide[2] supported by a silver plated platinum wire, and then electrolyzed in hydrochloric acid solution. These three forms of silver–silver chloride electrodes appear to agree with other acceptable forms.

The reproducibility of the measurements of the hydrogen–calomel[16] cell is not so great as that of the hydrogen–silver chloride cells. The value 0.3989 v. has been generally accepted as the value of the 0.1 *M* hydrogen calomel cell at 25°. Yet, notwithstanding the weight of evidence in favor of this value, we shall show that this is too high, and that the true value of the 0.1 *M* cell is 0.3976 v.

The Reproducibility of Silver–Silver Chloride Electrodes

In the course of these experiments more than 100 electrodes have been used. We shall give only a brief summary of the intercomparisons.

In the first series silver was deposited electrolytically from potassium cyanide solution on platinum foil electrodes about 1 cm. square. These were then covered with a layer of electrolytic silver chloride.[4,17] Three sets of six electrodes each were prepared, but the potentials differed by 0.1–2 mv. Lewis, Brighton and Sebastian[16g] and Güntelberg[18] also prepared and discarded this type of electrode. Horsch[19] prepared several electrodes in this manner, which showed a maximum difference between themselves of 0.9 mv., and which when measured against the hydrogen electrode in 0.01 *M* acid gave a potential 2.2 mv. higher than our final accepted value. Brönsted's[3] plated electrodes were also high. We may therefore definitely discard the plated platinum foil electrode. It was the experience with these plated electrodes which at the outset led us to ascribe the discrepancies mentioned in the previous section to the silver–silver chloride electrode.

Various forms of silver crystals made by electrolysis have been studied. Large crystals produced by electrolysis with a low current density from silver nitrate solution are far from reproducible. Electrolytic crystals prepared as recommended by Gerke,[1] following the method of Linhart,[13] from a molal solution of silver nitrate, electrolyzed at 90–100° on a point of platinum wire with a current of about 6 amp., were satisfactory.

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silver–silver chloride electrode by calomel by (c) Nonhebel and Hartley, *Phil. Mag.*, [6] **50**, 729 (1925).

[13] Linhart, This Journal, **41**, 1175 (1919).

[14] MacInnes and Parker, *ibid.*, **37**, 1445 (1915).

[15] Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[16] See (a) Loomis and Acree, *Am. Chem. J.*, **46**, 585 (1912); (b) Tolman and Ferguson, This Journal, **34**, 232 (1912), 18° values only; (c) Myers and Acree, *Am. Chem. J.*, **50**, 396 (1913); (d) Harned, This Journal, **37**, 2460 (1915); (e) Ellis, *ibid.*, **38**, 737 (1916); (f) Loomis and Meacham, *ibid.*, **38**, 2310 (1916); (g) Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917); (h) Linhart, *ibid.*, **39**, 2601 (1917).

[17] Halla, *Z. Elektrochem.*, **17**, 179 (1911).

[18] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[19] Horsch, This Journal, **41**, 1787 (1919).

More finely divided crystals were made in the same manner from 0.1 *M* silver nitrate solution. The deposit when first formed was a brownish-black sponge, which when touched with a glass rod turned to a grayish-white and dropped to the bottom of the beaker. This form of silver was readily reproduced and electrodes made from it never varied by more than 0.4 mv. when checked against each other or against the best silver–silver chloride spirals.

The spiral oxide-silver, electrolytic silver chloride electrodes (later referred to as silver spirals) were essentially the same as those recommended by Lewis,[2] except that we used a spiral of silver wire, 99.8% pure, instead of a platinum wire spiral plated with silver. A number of the plated platinum spirals were also used, but the greatest difference between the two forms was 0.1 mv. As it shortened the procedure, silver wire was used in later work.

Silver chloride was prepared in the form of "large" granules by metathesis in cold 0.01 *M* solutions. In the earlier work it was precipitated from silver nitrate solutions with hydrochloric acid after the method of Richards,[20] but it was found more satisfactory and the potentials more reproducible if the precipitation was made from silver perchlorate solutions. In the final experiments the silver chloride was immersed in dilute hydrochloric acid and heated at 90–100° for at least twenty-four hours.

The Potential of Silver–Silver Chloride against Mercury–Calomel

In the preliminary experiments several hundred measurements were made of the various silver–silver chloride electrodes against calomel electrodes prepared as described by Lewis, Brighton and Sebastian.[16g] Mercury and calomel were placed in one side of an H-type cell and silver crystals and precipitated silver chloride in the other. One or two silver spiral electrodes were inserted through well paraffined cork stoppers in each limb of the cell. With 0.01, 0.02, 0.1 and 0.5 *M* potassium chloride the cells came to equilibrium within an hour.

The difference in potential[21] between the spirals, or between the precipitated silver chloride electrodes with finely divided silver crystals electrolyzed from 0.1 or 1 *M* silver nitrate solution, or prepared from pure silver oxide by heating, and the calomel was always between 0.0455 and 0.0458 v. In nearly all cases the difference was 0.0455 v. with no measurable difference between the silver–silver chloride electrodes after one hour, and in practically every other case the value approached 0.0455 v. after from fifteen to sixty days. Under the same conditions large electrolytic crystals, prepared at low current densities, gave values between 0.0435 and 0.0445 v. The results are in accord with those of Gerke.[1]

Similar cells, using 0.01, 0.02 and 0.1 *M* hydrochloric acid instead of potassium chloride, gave erratic results. The potential between the spirals and the calomel gradually increased within a few hours to about 0.0466 v., and after a week to from 0.0469 to 0.0472 v. In acid solution the finely divided silver crystals and precipitated silver chloride usually came to an apparent equilibrium in about twenty-four hours with a potential against the mercury and calomel of 0.0466 v. On standing for several weeks the potential of many of the electrodes decreased, and often reached a value of approximately 0.0455 v. For a time we believed that the difficulty was with the silver–silver chloride electrodes. A glass tube reaching just to the surface of the silver–silver chloride mixture was inserted, and on renewing the electrolyte from a reservoir in the thermostat the value in a few cases decreased several tenths of a millivolt. The same treatment at the calomel electrode caused a similar decrease.

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[20] Richards, This Journal, 32, 28 (1910).

[21] The electrical system was the same as that used by Randall and Langford, This Journal, 49, 1445 (1927).

The sign of the effect on the renewal of the solution about the calomel electrode indicated that some chloride ions had been removed from the solution in contact with the mercury and calomel.[22] On the other hand, the sign of the effect about the silver–silver chloride electrode indicated that chloride ions were added to the solution, which did not appear to be a plausible explanation. This led us to examine the rate of a possible reaction between hydrochloric acid and mercury.

The Reaction between Dilute Hydrochloric Acid and Mercury.—From the potential of the hydrogen–calomel cell we may predict that hydrochloric acid and mercury will not react to form calomel and hydrogen at atmospheric pressure unless the molality of the hydrochloric acid is above 11.62 *M*. However, if oxygen is present mercury will react with dilute hydrochloric acid.

Samples of distilled mercury and 0.01 and 0.1 *M* hydrochloric acid were sealed in Pyrex flasks and rotated in a thermostat at 25°. After twenty-four hours a slight cloudiness was noted on the surface of the mercury. The reaction then proceeded more rapidly until at the end of four days a voluminous precipitate of calomel was observed. The experiments were repeated, but this time the air was removed from the acid solution by boiling under an atmosphere of hydrogen, in one case, and of nitrogen, in another. The air in the flask was displaced by hydrogen, or nitrogen, before the introduction of the acid. The flasks were then sealed and rotated for seven days without the appearance of any change, and after standing for several months the mercury surfaces were still bright.

Silver–Silver Chloride, Mercury–Calomel and Hydrogen Electrodes

A hydrogen electrode of the form used by Lewis, Brighton and Sebastian[16g] was sealed to the cross piece of the H-cell. No precaution was taken to eliminate air, and the mercury and calomel were shaken or ground in a mortar with the acid in the ordinary manner. The potential of the cell corresponded to a difference of approximately 0.0466 v. between the two chloride electrodes and the potential against the hydrogen electrode was the same as that previously found for each electrode. On standing the difference between the chloride electrodes rose, at times to as high as 0.0480 v. However, on replacing the acid immediately over the mercury by some of the original acid the difference dropped to 0.0455 v. and the potential of the silver–silver chloride hydrogen cell remained constant to 0.0001 v.

Several cells were then set up with calomel which had been rotated, in the absence of air, with mercury and acid which had been boiled in a vacuum. These cells gave the potentials shown in the first four rows of Table I. The first column gives the molality

TABLE I

POTENTIAL OF SILVER–SILVER CHLORIDE, MERCURY–CALOMEL AND HYDROGEN ELECTRODES IN HYDROCHLORIC ACID AT 25°

M	Ag (cryst.) vs. H_2	Spirals vs. H_2	Calomel vs. H_2	Spirals vs. calomel
0.1015	0.3514	0.3514	0.3976	0.0462
.0972	.3536	.3536	.3994	.0458
.0974	.3537	.3539	.3995	.0456
.1233	...	.3422	.3877	.0455
4.095	...	.1194	.1649	.0455
14.84	...	−0.0953	−0.0494	.0459

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[22] (a) Clark, Myers and Acree [*J. Phys. Chem.*, **20**, 264 (1916)] suggest the possibility of oxidation of mercurous to mercuric chloride. (b) See also Gerke, *Chem. Rev.*, **1**, 377 (1925).

of the acid, the second the potential of the finely divided silver crystals and precipitated silver chloride against hydrogen, the third the potential of the spirals against hydrogen, the fourth the potential of mercury–calomel against hydrogen and the last the difference between the spirals and the calomel electrodes.

The Effect of Air in the Acid Calomel Electrode

From the tabulation in a later section it will be found that the results of Table I correspond to a potential of the mercury–calomel hydrogen cell of 0.3977 v. instead of 0.3989 in 0.1 *M* hydrochloric acid as previously accepted. The following experiments were designed to show that the irregular and high results of previous investigators were due to the presence of air.

An H-cell was set up, mercury–calomel electrodes in each side, and silver–silver chloride spirals in the stoppers over each calomel electrode. To make sure that the materials were properly prepared, the potential in 0.1 *M* potassium chloride was measured and found to be 0.0455 v. The potassium chloride was now replaced by approximately 0.1 *M* hydrochloric acid from which the air had been carefully removed. Care was taken to allow no air to enter the cell during the transfer. Temperature equilibrium was established in about fifteen minutes, when the potential was found to be 0.0455 v. between the various spirals and the calomel electrodes. The potential remained constant for five days, when a few bubbles of air were allowed to enter through a glass tube dipping into the calomel. The potential of this electrode rose to 0.0472 against the spirals, but as there was no means of preventing diffusion to the other electrode its potential also rose to about 0.0469 v.

The experiment of the fourth row of Table I was especially designed to test the effect of air. A stopcock was placed in the cross arm of the H-cell. The acid was prepared from constant boiling hydrochloric acid and conductivity water which had been collected in a quartz flask.[23] The air was carefully removed by boiling the solution in a quartz flask with a slow stream of pure nitrogen. Mercury and calomel electrodes were used in place of the silver crystals in the second limb of the H-cell. Both spirals and both calomel electrodes gave the potentials shown in Table I. The stopcock in the cross arm was now closed and a little air introduced at the surface of the mercury. The air was without measurable effect upon the silver–silver chloride spiral, but the potential of the hydrogen–calomel cell with air rose slowly to 0.3882 v. in twenty-four hours and to 0.3894 v. in seven days. The potential of the other calomel electrode remained constant. On replacing the electrolyte over the chloride electrodes with potassium chloride the difference was again 0.0455 v.

It is a remarkable coincidence that so many investigators were able to obtain the same value, 0.3989 v., at 0.1 *M* in the presence of air. Harned[10b] obtained 0.3989 v. at 0.1 *M* but his vacuum technique applied only to the hydrogen electrodes.[24]

Numerous experiments were made with 0.01 *M* acid which had been freed from air by boiling in Pyrex flasks. The difference between the spirals and mercury–calomel was in every case near 0.0455 v., but owing to the interaction of the glass and dilute acid[23] the values against hydrogen were erratic and were therefore discarded. The difference between the spirals and calomel in 0.01 acid was greater than 0.0466 in the presence of air. Other experiments in more concentrated solutions will be described in a later section.

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[23] See (a) Kraus and Parker, This Journal, **44**, 2429 (1922); (b) Randall and Scott, *ibid.*, **49**, 636 (1927).

[24] Private communication.

After the completion of the foregoing experiments, Güntelberg[18] published his excellent results with the silver–silver chloride electrodes and stressed the necessity of the removal of oxygen. He also suggested that a similar procedure would improve the results with mercury–calomel. Gerke[1] also noted the gradual appearance of alkalinity around calomel electrodes in potassium chloride, which he ascribed to oxygen in the solution.

The effect of mercuric chloride upon the potential of the mercury calomel electrode was studied by Carter, Lea and Robinson,[25] who compared the potential of an electrode of mercury and a solution containing 0.05 N mercuric chloride and 3 N hydrochloric acid with that of an electrode of mercury, calomel and a solution of 3 N acid at 18°. The usual grey film of mercurous chloride appeared on the mercury in the first electrode. The measurements were made against calomel electrodes with potassium chloride solution through a number of liquid junctions the potential of which was probably constant in both cells. The potential of the cell with mercuric chloride showed wide fluctuations (as might be expected) for several days, but tended toward the same potential as that of the calomel electrode. Neither electrode was free from oxygen.

In discussing the relation of our results to those of other investigators, we shall review the thermodynamic properties of hydrochloric acid. Lewis and Randall[5] reviewed the older data and chose 0.2234 v. as the standard potential of the hydrogen–silver–silver chloride cell. Scatchard[9a] recently lowered this value to 0.2226 v. and later,[9b] giving much weight to the theoretical equation of the interionic attraction theory, favored a still lower value, 0.2223 v. We shall find the value 0.2221 v. more consistent with the theory and the experimental results. All available data have been included.

Activity Coefficient from the Freezing Point Measurements

We show in Fig. 1 the values of the freezing point lowering function,[26] $j/m^{1/2}$, for all investigators,[27] plotted against the square root of the molality.

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[25] Carter, Lea and Robinson, *J. Chem. Soc.*, **131**, 1906 (1927).

[26] Randall. This Journal, **48**, 2512 (1926). $j = 1 - \theta/(\nu\lambda m)$, where θ is the freezing point lowering, ν the number of ions formed per molecule of acid, λ is a constant = 1.858, and m is the molality.

[27] (a) Barnes, *Trans. Nova Scotian Inst. Sci.*, **10**, 129 (1900); (b) *Trans. Roy. Soc. Canada*, [2] **6**, 37 (1900); (c) Chambers and Frazer, *Am. Chem. J.*, **23**, 512 (1900); (d) Cornec, *Compt. rend.*, **149**, 676 (1909); (e) Dernby, *Medd. Vetenskapsakad. Nobelinst.*, **3**, No. 18 (1916); (f) Hausrath, *Ann. Physik*, [4] **9**, 522 (1902); (g) Jones, *Z. physik. Chem.*, **12**, 623 (1893); (h) Jones and Bassett, *Am. Chem. J.*, **34**, 290 (1905); (i) Jones and Getman, *Am. Chem. J.*, **27**, 433 (1902); *Z. physik. Chem.*, **46**, 244 (1903); (j) Jones and Pearce, *Am. Chem. J.*, **38**, 623 (1907); (k) Klein and Svanberg, *Medd. Vetenskapsakad. Nobelinst.*, **4**, No. 1 (1918); (l) LeBlanc and Noyes, *Z. physik. Chem.*, **6**, 385 (1890); (m) Loomis, *Ann. phys. chim.*, [3] **57**, 493 (1896); *Phys. Rev.*, [1] **3**,

All the values have been converted as far as possible to present atomic weights, and moles per 1000 g. of water in vacuum.[28] For the most part the values of $j/m^{1/2}$ of Hausrath[27f] below 0.002 M are above 0.4. The values of the several series of Randall and Vanselow[27o] are differentiated in the plot. The values of the other investigators cannot be given too much weight. It is noted that the value of $j/m^{1/2}$ tends to decrease rapidly as the molality is decreased below 0.01 M. It was shown by Kraus and Parker[23a] and by Randall and Scott[23b] that the conductance of acid solutions more dilute than 0.01 M decreased with time when measured in glass cells. The effect is larger the more dilute the solution. As the solution remained in the freezing point apparatus longer than the standardizing solution remained in the cell, the tendency would be for the measured conductance to represent a lower molality than that actually present, and consequently[28b] a smaller j. We have, therefore, drawn the curve to pass to the theoretical limit[26,28] for completely dissociated electrolytes, namely, 0.375. The values of $j/m^{1/2}$ in the more concentrated solutions are shown in Fig. 2. The average values of the freezing point calculated from the values of $j/m^{1/2}$, read from the plots of Figs. 1 and 2, are given in Col. 2 of Table II. Col. 3 gives the logarithm of the activity coefficient at the freezing point, log γ', Col. 4 the logarithm of the activity coefficient at 25°, calculated from the values of log γ'

TABLE II

LOGARITHM OF ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID TO 1 M

m	θ (calcd.)	$-\log \gamma'$	$-\log \gamma_{298}$(F. P.)	$\log \gamma_{298}$	a_1 (298)
0.001	0.003675	0.0150	0.0153	−0.0153	0.999965
.002	.007318	.0207	.0211	− .0211	.999928
.005	.018152	.0315	.0322	− .0322	.999825
.01	.036028	.0427	.0438	− .0438	.999650
.02	.07143	.0569	.0585	− .0585	.999310
.05	.17666	.0788	.0812	− .0812	.998295
.1	.35209	.0957	.0993	− .0993	.99660
.2	.7064	.1104	.1155	− .1156	.99321
.3	1.0689	.1144	.1210	− .1213	.98975
.4	1.4403	.1145	.1222	− .1227	.98623
.5	1.8225	.1115	.1203	− .1210	.98262
.6	2.2166	.1065	.1162	− .1171	.97891
.7	2.5801	.1002	.1108	− .1118	.97509
.8	2.9050	.0926	.1046	− .1058	.97124
.9	3.2175	.0842	.0972	− .0987	.96726
1.0	3.5172	.0755	.0897	− .0915	.96324

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270 (1896); (n) Nernst, see Roloff, *Z. physik. Chem.*, **18**, 572 (1895); (o) Randall and Vanselow, THIS JOURNAL, **46**, 2418 (1924); (p) Roloff, *Z. physik. Chem.*, **18**, 572 (1895); (q) Roth, "Physikalisch-chemische Übungen," 3d ed., L. Voss, Leipzig, **1921**, p. 58; (r) Zecchini, *Z. physik. Chem.*, **19**, 431 (1896).

[28] See similar discussions, (a) Randall and White, THIS JOURNAL, **48**, 2514 (1926), and (b) Randall and Scott, *ibid.*, **49**, 647 (1927).

and the preliminary values of the partial molal heat content and of the partial molal heat capacity.[29] Col. 5 gives the final values of log γ taken after a careful study of the electromotive force data. The last column gives the values of the activity of the water at 25°, calculated by means of Equation 8 to be derived later.

Since the foregoing was written and the curves of Figs. 1 and 2 were drawn, we have received the results of a series of freezing point measurements by Chadwell.[30] We have plotted the values of $j/m^{1/2}$ calculated from his freezing points, and find that they are in excellent agreement with the curves as drawn. This confirmation of our interpolation gives us confidence in our method.

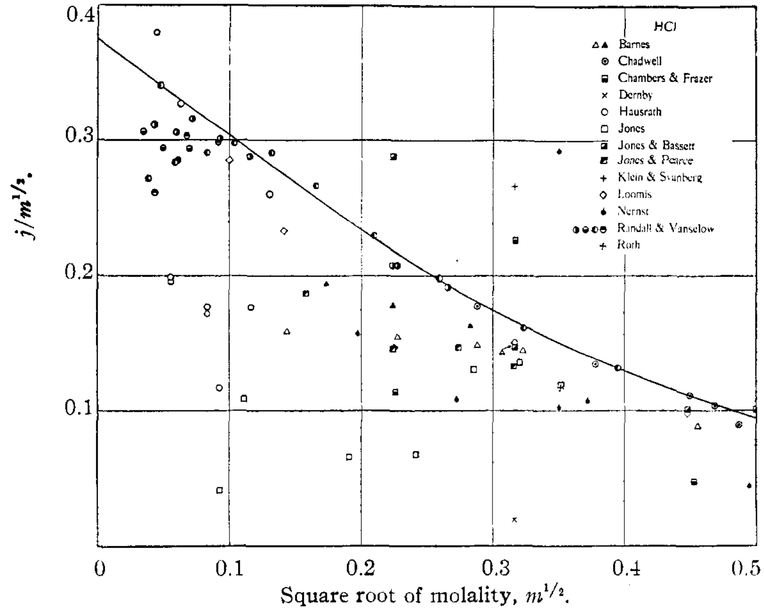

Fig. 1.—Freezing point function for hydrochloric acid.

Calculation of the Activity Coefficient at 25° from the Activity Coefficient at the Freezing Point.—The calculation of the activity coefficient to 25° may be made by three different methods, all of which, theoretically, will give identical results. It may also be made by a fourth method which will give a result differing by a very small amount at 1 *M*. The first of these methods is that given by Lewis and Randall.[31] The values of their function x plotted against $1/m$ are shown in Curve A of Fig. 3.

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[29] (a) Randall and Rossini (private communication); (b) Randall and Ramage, THIS JOURNAL, **49**, 93 (1927).

[30] Chadwell, private communication; see also THIS JOURNAL, **49**, 2895 (1927).

[31] Ref. 5, p. 348.

There is some uncertainty in estimating the area under the curve to the limit of very dilute solutions.

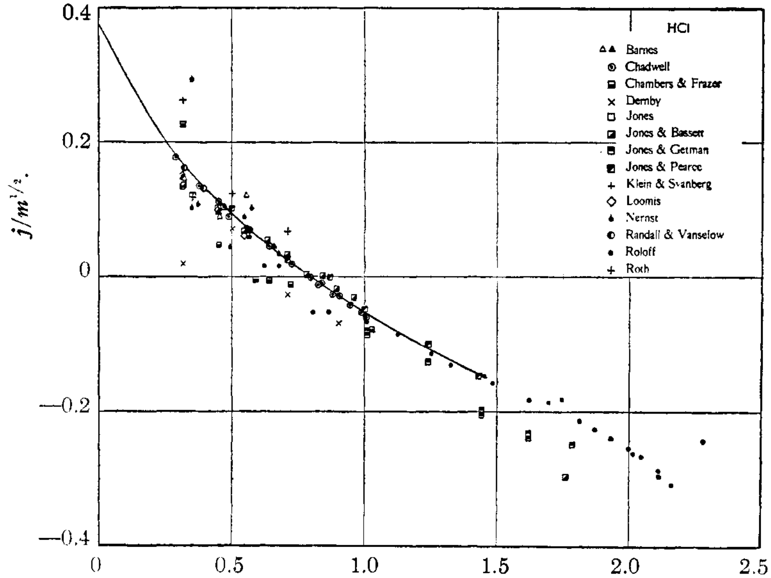

Fig. 2.—Freezing point function for hydrochloric acid.

The same result can be attained if we first calculate in the same manner the activity coefficient at 0° by means of the following equation

$$x' = -\bar{L}_{1_{298}}(y - 0.00006707) + \Delta C_{p_1}(z - 0.00086) \qquad (2)$$

in which $\bar{L}_1$ is the partial molal heat content of the water at 25°, ΔC_{p_1} the increase in partial molal heat capacity at 25° and y and z have the same significance as before, and then change to 25° by means of Equation 5, Appendix III,[5] using the values of $\bar{L}_2$ and ΔC_{p_2}. The values of x' are shown plotted against $1/m$ in Curve B of Fig. 3, from which it will be noted that the uncertainty in estimating the area to the limit of zero concentration is much smaller than in the case of Curve I. The magnitude of the area is also much smaller and the estimation of the area can be made more quickly. (A larger scale plot was used for the estimation.)

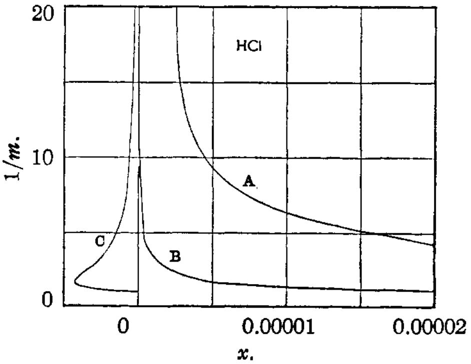

Fig. 3.—x-Function for hydrochloric acid.

The third method was the alternative method of Lewis and Randall in which, for example, the activity coefficient at −3.87°, the freezing point of 1 *M* acid, was first determined, and the value then calculated to 25°, using the heat content and heat capacity of the solute. The values of x'' are shown in Curve C of Fig. 3. The area is very small [$\log (\gamma'/\gamma_{269.23} = 0.0005$]. In employing this method it would be necessary to make a curve for each freezing point, a laborious process. The last calculation, however, illustrates the real significance of $\log \gamma'$, which is nearly but not exactly the activity coefficient at the freezing point, differing for a substance like hydrochloric acid which has a relatively high heat content by only 0.1% at 1 *M*. The difference at 0.2 *M* is quite negligible.

We may thus suggest the fourth method which we have used as an approximate method, which assumes that $\log \gamma'$ is actually the activity coefficient at the freezing point and uses the equation

$$\log (\gamma_{298}/\gamma') = -\bar{L}_2\, y + \Delta C_{p_2} z \tag{3}$$

For accurate work in concentrated solutions the second method used is by far the most accurate and convenient.[32]

Activity Coefficient at 25° from Electromotive Force Measurements in Hydrochloric Acid

The reliability of the extrapolation to infinite dilution of the freezing point measurements can be estimated by comparing the activity coefficients found with the results of the electromotive force measurements. For this purpose the quantity, $\log \gamma$ + const., was calculated from the measurements of the various authors[33] by means of the following equation[34]

$$\log \gamma + \text{const.} = -\mathbf{E}/(0.00019844 \times 2T) - \log m_{\pm} \tag{4}$$

in which **E** is the measured electromotive force and m the molality of the acid. The various values of ($\log \gamma$ + const.) were plotted on transparent paper against the square root of the molality and compared with the curve of $\log \gamma$, calculated from the freezing points and the temperature coefficient. In this way the best value of the constant was determined to be −1.9964 at 15°,[15] −1.9030 at 18°,[6] −1.9374 at 20°,[18] −1.8778 at 25°,[6,8,9a,13,15,35] −1.8178 at 30°,[6] and −1.7626 at 35°,[15] and −1.8770 for the silver–silver chloride electrode of Harned and Fleysher[7] at 25°. Subtracting these constants at the various temperatures from the calculated values of ($\log \gamma$ + const.) we obtain the values of $\log \gamma$. The difference, to 0.2 *M*, between the values of $\log \gamma$ from the freezing points and that thus calculated from the measurements of the various authors, is shown in Fig. 4.

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[32] The treatment of results of boiling point measurements is entirely similar.

[33] See Refs. 6–16, 18.

[34] Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

The uncertainty in the values of the constants is about 0.0005, corresponding to about 0.1% in the activity coefficient. Comparison shows that the silver–silver chlorides used by the various authors gave like potentials, as was indicated by our experiments in the earlier part of this paper. There the electrolytic silver–precipitated silver chloride electrodes as used by Linhart[13] were found to be slow in coming to equilibrium. His dilute acids were in contact with glass for about a month and it has been shown by Kraus and Parker[23a] that the conductivity of dilute acid solutions decreased rapidly with time. This effect is explained by assuming a disappearance of hydrogen ion, which would give the high values of the e.m.f. observed by Linhart.[13] We thus find $E°_{298} = 0.2221$ v. for the standard potential of the hydrogen silver–silver chloride cell. Scatchard[9] placed great reliance upon the dilute acid measurements of Linhart[13] and used $E°_{298} = 0.2226$ v. This value, however, cannot be consistent with Scatchard's results, the later results of Güntelberg[18] and the freezing point measurements, shown in Fig. 1.

The recent careful measurements of Nonhebel[35] with the hydrogen–silver–silver chloride spirals in acid between 0.0001 and 0.05 M are in complete agreement with the measurements of Linhart[13] and confirm the conclusion regarding the identity of electrolytic crystal silver with platinum gauze plated with silver, and of precipitated silver chloride with electrolytic silver chloride. In his experiments he used Jena glass vessels and thus his experiments are open to the same objection as those of Linhart,[13] owing to the reaction of the hydrogen-ion constituent with the glass. Until measurements in the dilute solutions are made using quartz apparatus the question of the correct value of the standard potential and, therefore, of the activity coefficient, will be in doubt. Nonhebel used $E°_{298} = 0.2228$ v., but owing to the known effect of the glass and the agreement of the value $E°_{298} = 0.2221$ with the freezing point measurements of hydrochloric acid and the relation of these measurements to those of other salts, we will choose as the final value, $E°_{298} = 0.2221$ v.

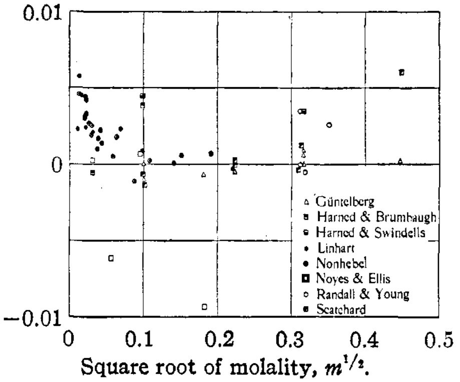

Fig. 4.—Difference between log γ calculated from freezing point and electromotive force data.

The values of $(\log \gamma)/m^{1/2}$, calculated from the above constants, are plotted[11] in Fig. 5 against the square root of the molality for solutions above 0.2 M. The activity coefficients from Güntelberg's measurements

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[35] Nonhebel, *Phil. Mag.*, [7] **2**, 1085 (1926).

are calculated to 25° by the same values used in transforming the freezing point data. The values of (log $\gamma_{298})/m^{1/2}$ taken from the freezing point measurements (see Table II) would fall upon the curve within the limits of plotting. A curve corresponding to the curve of Fig. 5 would have fitted the freezing point measurements just as well.

Figure 5 also shows points taken from the various hydrogen–calomel cell measurements. In calculating these points we used the values of the constant, -2.2731 (Ellis[16e]), -2.2757 (Linhart,[16h]) and -2.2722 (Harned,[10b]) (Randall and Breckenridge[11]). The constant for the hydrogen–calomel cell in vacuum would be -2.2624.

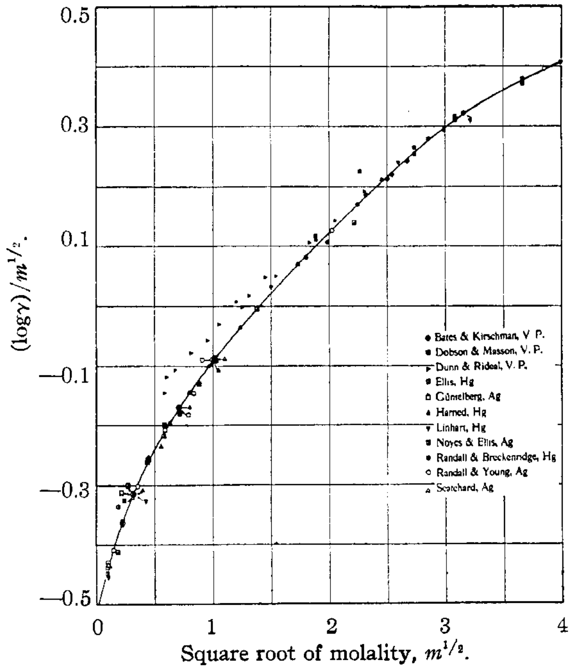

Fig. 5.—Function $(\log\gamma)/m^{1/2}$ for hydrochloric acid.

New Measurements in Concentrated Solutions.—We have obtained two measurements in concentrated solutions (see Table I). Owing to the solubility of the silver chloride in strong acid, the spirals were dipped into the acid for a few minutes during readings after the hydrogen electrode had come to equilibrium. These confirm the difference between the silver–silver chloride and mercury–calomel electrodes in vacuum. When air was admitted to the calomel cells the difference rose to higher non-concordant values. The results of these measurements are also shown in Fig. 5.

Activity Coefficient from Vapor Pressure Measurements

Since the review of the data by Lewis and Randall[5] and Scatchard,[9] several new measurements of the vapor pressure of concentrated solutions have appeared. The values of (log γ + const.) = log ($p^{1/2}/m$) were plotted[34] against the square root of the molality. By superimposition of the plot upon Fig. 5 we found the constant to be -3.152 at 25°. Fig. 5 shows the values of (log γ)/$m^{1/2}$ obtained in this way.

$$\text{HCl (aq.)} = \text{HCl (g)};\ \Delta F^\circ_{298} = 1364.9 \times 2 \times 3.152 = 8604 \text{ cal.} \qquad (5)$$

The measurements of Bates and Kirschman[36] at 25° and 30° are the most reliable. The pressures given by Dunn and Rideal[37] at their five lowest molalities when multiplied by a factor of 10 agree with their other measurements. Those of Dobson and Masson[38] are less reliable than those of the former authors. Those of Allan[39] at 18.4° and of Wrewsky, Sawaritsky and Scharloff[40] at 19.95°, 55.2° and 75.9° are in fair agreement with our final curve, while those of Gahl[41] at 25°, of Mitsukuri,[42] and of Yannakis[43] at 50° are erratic. The old measurements of Dolezalek[44] at 30° are in good agreement with the final curve. There appears to be a systematic error in all the measurements, especially below 2 *M*, where the difficulties of attaining equilibrium are great. (The error is probably caused by entrainment of particles of liquid in the gas stream.)

From the measurements of Dobson and Masson,[38] Dunn and Rideal,[37] Wrewsky, Sawaritsky and Scharloff[40], and Yannakis[43] of the pressure of water over some concentrated solutions, the values of the activity coefficient obtained by the usual methods,[34] are in fair agreement. The interpolated values of the activity of the water of the first two investigations agree with the calculated values in Table III.

Knight and Hinshelwood[45] measured the distribution of hydrochloric acid between benzene and water. Their values of (log γ + const.) = log ($c^{1/2}$(benzene)/m) were plotted[34] against $m^{1/2}$, but the curve so obtained is much less steep than the curve of log γ against $m^{1/2}$, showing that either the activity of the acid in the benzene phase is not proportional to its concentration or that the experiments are in error.

The final value of the logarithm of the activity coefficient at 25° at

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[36] Bates and Kirschman, THIS JOURNAL, **41**, 1991 (1919).

[37] Dunn and Rideal, *J. Chem. Soc.*, **125**, 676 (1924).

[38] Dobson and Masson, *ibid.*, **125**, 668 (1924).

[39] Allan, *J. Phys. Chem.*, **2**, 120 (1898).

[40] Wrewsky, Sawaritsky and Scharloff, *Z. physik. Chem.*, **112**, 97 (1924); **113**, 490 (1924).

[41] Gahl, *ibid.*, **33**, 178 (1900).

[42] Mitsukuri, *Sci. Rep. Tohuku Imp. Univ.*, **14**, 251 (1925).

[43] Yannakis, *Compt. rend.*, **177**, 174 (1923).

[44] Dolezalek, *Z. physik. Chem.*, **26**, 321 (1898).

[45] Knight and Hinshelwood, *J. Chem. Soc.*, **131**, 466 (1927).

round molalities, the pressure of the hydrochloric acid and the activity of the water as calculated in the next section are given in Table III.

TABLE III

LOGARITHM OF ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID AT 25° IN CONCENTRATED SOLUTION

m	log γ (298)	p(HCl) atmos.	a_1 (298)	m	log γ (298)	p(HCl) atmos.	a_1 (298)
1.2	−0.0743	5.08×10^{-7}	0.95482	5	0.3757	7.01×10^{-5}	0.73890
1.4	− .0556	7.61×10^{-7}	.94605	6	.5078	1.853×10^{-4}	.67106
1.6	− .0359	1.077×10^{-6}	.93696	7	.6403	4.64×10^{-4}	.6027
1.8	− .0153	1.499×10^{-6}	.92753	8	.7705	1.104×10^{-3}	.5361
2.0	.0080	2.06×10^{-6}	.91750	9	.9000	2.54×10^{-3}	.4720
2.5	.0610	4.11×10^{-6}	.89224	10	1.0189	5.42×10^{-3}	.4146
3.0	.1205	7.78×10^{-6}	.86452	12	1.2367	2.13×10^{-2}	.3162
3.5	.1818	1.405×10^{-5}	.83515	14	1.4368	7.27×10^{-2}	.2371
4	.2460	2.46×10^{-5}	.80401	16	1.6276	0.230	.1740

Activity of the Water[46]

For calculation of the activity of the water we may use the thermodynamic equation,[47]

$$d \log a_1 = -(\mathrm{N}_2/\mathrm{N}_1) d \log a_2 \qquad (6)$$

Substituting for $\mathrm{N}_2/\mathrm{N}_1$, $m/55.51$, and for a_2, $a_{\pm}^{\nu}$, where $\nu = 2$, the number of ions formed

$$d \log a_1 = -(\nu m\, d \log a_{\pm})/55.51 \qquad (7)$$

Adding $(\nu m\, d \log m)/55.51$ to both sides of Equation 7, and writing γ for $a_{\pm}/m$ we have,

$$d \log a_1 + \frac{\nu\, m}{55.51} d \log m = -\frac{\nu\, m}{55.51} d \log \gamma \qquad (8)$$

Since, when $m = 0$, $\log a_1 = 0$, the integration constant is 0, and we can write Equation 8 in the form

$$\log a_1 = -\frac{2m}{55.51 \times 2.303} - \frac{2}{55.51} \int_0^m m\, d \log \gamma \qquad (9)$$

The integral may be evaluated graphically by plotting m as ordinate against log γ as abscissa as in Fig. 6, and finding the area under the curve between a given value of log γ and log $\gamma = 0$. The values of a_1, which we have already given in the fourth column of Table III, were calculated in this manner.

Standard Reference Potentials

Ag(s), AgCl(s), Cl⁻.—Adopting the usual convention that the standard potential of the Pt, H_2(g), H^+ electrode is zero and using our new value of $\mathbf{E}°_{298}$ for the hydrogen silver–silver chloride cell, we write

Ag(s), AgCl(s), Cl^-; $E°_{298} = -0.2221$ v.;

$$\mathrm{Ag(s)} + \mathrm{Cl}^- = \mathrm{AgCl(s)} + \mathrm{E}^-; \quad \Delta F°_{298} = 5125 \text{ cal.} \qquad (10)$$

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[46] The derivation was made by Randall and Breckenridge but was not published. We have recalculated their work with the later values of the activity coefficient of the acid.

[47] Ref. 5, p. 285.

Hg(l), HgCl(s), Cl$^-$.—From the value of the hydrogen mercury-calomel cell

Hg(l), HgCl(s), Cl$^-$; $\mathbf{E}^\circ_{298} = -0.2676$ v.;

$$\text{Hg(l)} + \text{Cl}^- = \text{HgCl(s)} + \text{E}^-;\ \Delta F^\circ_{298} = 6175 \text{ cal.} \quad (11)$$

Deci-molal Calomel Electrode.—With mercury and calomel in 0.1 *M* potassium chloride solution, we may follow Lewis and Randall,[5] and if we assume the activity of the chloride ion to be 0.0772 ± 0.0002 (Randall and White[27a,28a]) we find

$$\text{Hg(l), HgCl(s), KCl(0.1 } M\text{); (D. E.); } \mathbf{E}_{298} = -0.3341 \text{ v.} \quad (12)$$

This will be approximately the single potential if we use neutral 0.1 *M* chloride ion or 0.1 *M* chloride ion in acid in vacuum, but if the measurement is made in acid solution in air, as has been the usual procedure, then the single potential in these cases will be about −0.3354 v.

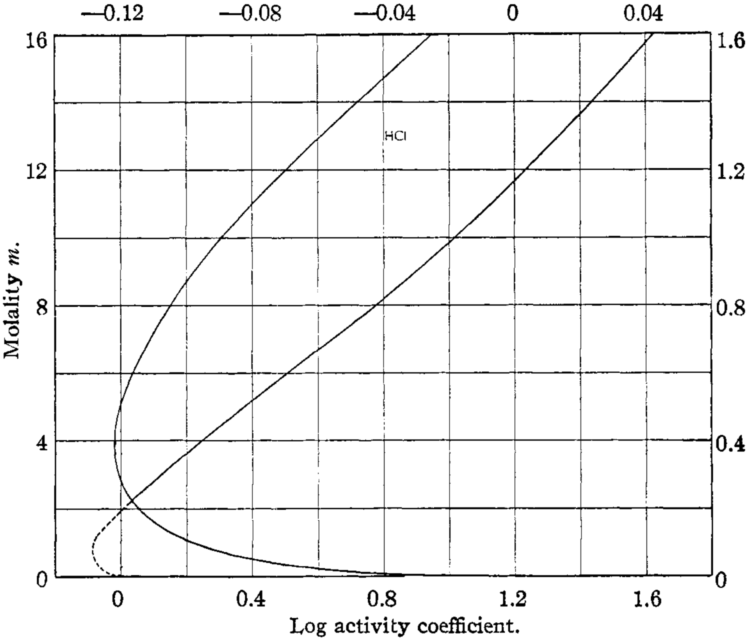

Fig. 6.—Log for hydrochloric acid at 25°. Upper curve shows the dotted portion on a larger scale. Use scale at left and at the top.

Normal Calomel Electrode.—The difference between the decimolal and normal calomel electrodes[5] is 0.0529 v. Hence

$$\text{Hg(l), HgCl(s), KCl(1 mole per liter), KCl(0.1 } M\text{); (N. E.); } \mathbf{E}_{298} = -0.2812 \text{ v.} \quad (13)$$

These new values will alter most of the values for the single potentials of other electrodes by 0.0010 to 0.0024 v. A general revision of the table of single electrode potentials is in progress.

$Cl_2(g)$, Cl^-, Pt.—Combining Equation 10 with the free energy of formation of silver chloride (−26220 cal., Gerke[1]) we find

$Cl_2(g), Cl^-, Pt; E°_{298} = 1.3583$ v.; $^1/_2Cl_2(g) + E^- = Cl^-$; $\Delta F°_{298} = -31345$ cal. (14)

Combining with the free energy of formation of mercurous chloride (−25163 cal., Gerke[1]) we have 1.3581 v. and −31338 cal. The direct measurements of Lewis and Rupert[48] of the cell Hg(l), HgCl(s), HCl (aq.), $Cl_2(g)$ give **E**° = 1.0894 v. with the acid calomel in air. If we assume the value of the acid calomel electrode in air between 0.2686 and 0.2690 v., we have for the potential of the chloride electrode between 1.3582 and 1.3586 v. in entire agreement with the result from Gerke's measurements.

We also have from Equations 14 and 5

$$^1/_2H_2(g) + {}^1/_2Cl_2(g) = HCl(aq.);\ \Delta F°_{298} = -31345 \text{ cal.} \quad (15)$$
$$^1/_2H_2(g) + {}^1/_2Cl_2(g) = HCl(g);\ \Delta F°_{298} = -22741 \text{ cal.} \quad (16)$$

Summary

1. Air causes an error of 0.0010 to 0.0030 v. in the potential of the hydrogen mercury–calomel cell.

2. Dilute hydrochloric acid containing dissolved air reacts with metallic mercury to form calomel.

3. New measurements of the potential of the hydrogen silver–silver chloride cell and of the hydrogen mercury–calomel cell have been made.

4. Air does not seriously affect the potential of the mercury–calomel electrode in neutral chloride solutions.

5. The conditions for the preparation of reproducible silver–silver chloride electrodes have been carefully studied.

6. New values for some important reference electrodes have been calculated.

7. Average values for the freezing point and activity coefficient of the acid, activity of the water and pressure of the acid above solutions of round molalities are given up to 16 *M*.

8. The free energy of formation of chloride ion and gaseous and aqueous chloride ion has been recalculated.

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[48] Lewis and Rupert, THIS JOURNAL, **33**, 299 (1911); see ref. 5, p. 426.