

the experimental values formerly found in the range 250° to 435° . The difference between the temperature scales employed in 1910 and in the present work is within the experimental error.

Measurements by this method may be extended to lower temperatures; and the precision here attained may be improved with respect to pressure as well as to temperature. But such further measurements by this method are perhaps unnecessary in view of the greater simplicity of another method, applicable to this and to many other cases, giving results which it is hoped will be published later.

Summary.

(1) A method adapted to the measurement of rather low vapor pressures has been described, involving the use of two McLeod gauges, hot and cold, respectively.

(2) This method has been applied to the case of mercury, and it has been shown that the equation connecting pressure and temperature published in 1910 to cover the range 250° to 453° may be applied, without modification of its constants, over the range 120° to 250° .

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

POTENTIALS OF THE ZINC AND CADMIUM ELECTRODES.

BY W. GRENVILLE HORSCH.

Received August 20, 1919.

Normal electrode potential has been defined¹ as the electromotive force of a reversible electrode of the pure element against a solution in which the ion of the element is (hypothetical) molal. This paper presents determinations of the normal electrode potentials of zinc and cadmium referred to the potential of the normal hydrogen electrode as zero.

In a previous, unpublished research² a value for the electrode potential of zinc was obtained, based upon measurements of cells containing sulfate solutions as electrolytes. The electromotive force of cells of the type $\underline{\text{Zn}}: \text{ZnSO}_4: \text{Hg}_2\text{SO}_4: \text{Hg}$ was measured³ where the zinc sulfate solutions ranged in concentration from 0.005 *M* up to 0.1 *M*. Using the method of calculation employed by Lewis and Lacey⁴ to obtain the potential of the copper electrode, and their value of the electromotive force corresponding to the free energy of formation of mercurous sulfate, the value 0.76 volt was obtained as the potential of the zinc electrode. It was

¹ Lewis, *THIS JOURNAL*, 35, 22 (1913); 36, 1972 (footnote) (1914).

² W. G. Horsch, *Thesis* for the degree of S.M., Univ. of Calif., 1916.

³ Molal concn. of ZnSO_4 soln., 0.005 0.010 0.020 0.030 0.070 0.100

Electromotive force, 1.5195 1.5144 1.5054 1.4988 1.4880 1.4830

⁴ *THIS JOURNAL*, 26, 804 (1914).

estimated that the value of the potential thus obtained might contain an error as great as 0.01 volt.¹

Because of the unsatisfactory nature of mercurous sulfate, some other insoluble sulfate was sought, the properties of which made it more suitable for use in a reference electrode. The only substance appeared to be lead sulfate, which possesses the advantage of having $1/10$ the solubility of mercurous sulfate. Accordingly, experiments were tried, using electrodes consisting of solid lead sulfate in contact with a liquid containing 1% lead. Cells of the type $\text{Hg} : \text{Hg}_2\text{OS}_4 : \text{ZnSO}_4(0.04M) ; \text{PbSO}_4\text{Pb}(\text{amalg.})$, were measured, in which two mercurous sulfate-mercury electrodes and two lead sulfate-lead electrodes dipped into the same intermediate vessel. The former two differed from each other by less than 0.0001 volt; the latter two differed by 0.0004 to 0.0010 volt. Moreover, the measurements were unsatisfactory for the further reason that the electromotive force of the cell fell off rapidly with the time; thus the electromotive force of the cell changed from 0.954 to 0.946 volt in 18 hours. Lead sulfate-lead against zinc in zinc sulfate solutions gave a continually rising electromotive force, while mercurous sulfate-mercury against zinc sulfate solutions remained constant over long periods. Even greater inconstancy was found by Lewis and Brighton² who used cells which consisted of hydrogen, sulfuric acid, lead sulfate in sulfuric acid, lead. The attempted use of an especially designed electrode in which the contact surface between the amalgam and the solution could be renewed continuously or at will proved unsuccessful. It was therefore evident that sulfates could

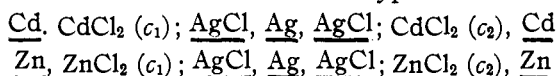
¹ The uncertainty of this value is attributed to the mercurous sulfate. Thus, measurements of the electromotive force of the cell $\text{Zn}, \text{ZnSO}_4, \text{Hg}_2\text{SO}_4, \text{Hg}$ at two different concentrations of zinc sulfate solution should enable us to calculate the free energy of dilution of zinc sulfate solution. The free energy of dilution may be calculated also from freezing-point data. The values obtained by the two methods (using freezing-point data of H. Hausrath (*Ann. Physik*, [4] 9, 550 (1902)), do not agree, but differ by an amount corresponding to 0.005 to 0.008 volt. This discrepancy is greater than can be attributed to the error in either the freezing-point data or the electromotive-force measurements, and is due partly to the solubility of mercurous sulfate. The solubility in pure water is 0.0013 M at 25°, so that the amount of sulfate ion contributed by the mercurous sulfate becomes an important factor in the dil. zinc sulfate solutions. Mercurous sulfate turns yellow and then light brown, as the zinc sulfate solution with which it is in contact becomes more and more dilute. The action is hastened by light, but is prevented by a small concentration of acid. According to Wright and Thompson (*Phil. Mag.*, [5] 19, 29 (1885)), zinc sulfate solution renders the mercurous sulfate more soluble; for example, in a saturated solution of zinc sulfate, the mercurous sulfate had 3 times its solubility in pure water. These considerations indicate that in dil. sulfate solutions the activity of the zinc ions is affected by the presence of the mercurous sulfate. In obtaining the normal potential against hydrogen the calculation was based on the assumption that the mercurous sulfate had the same thermodynamic properties in acid as in dil. zinc sulfate solution.

² THIS JOURNAL, 39, 1908 (1917).

not be employed in the cells if accurate values of the electrode potentials of zinc and cadmium were desired.

Experiments were tried next with chlorides. Measurements of cells of the type $\underline{M} : MCl_2 : \underline{AgCl} : \underline{Ag}$, (A) and $H_2 : HCl(0.01M) : \underline{AgCl} : \underline{Ag}$, (B) where \underline{M} represents zinc or cadmium, were found to give entirely satisfactory results in respect to constancy and reproducibility. It is these measurements which form the basis of the electrode potentials which are presented in this paper. The electromotive force of (B) enables us to calculate the electromotive force corresponding to the free energy of formation of AgCl in (hypothetical) molal H^+ and Cl^- . This value, together with the electromotive force of (A) in a solution so dilute that we may get the activity of M^{++} , enables us to calculate the potential of \underline{M} against (hypothetical) molal M^{++} .

Work of Other Investigators.—H. Jahn¹ determined the electromotive force of the cell Zn (amalgamated rod) $ZnCl_2 (c)$; $\underline{AgCl} : \underline{Ag}$, in concentrations of $ZnCl_2$ from 0.556–2.22 *M*; these will be tabulated along with the author's own values for zinc. H. M. Goodwin² measured the electromotive force of concentration cells of the type



in a few concentrations ranging from 0.001–0.2 *M*. The electromotive forces of a few cells in which Cd was placed against $\underline{AgCl}, \underline{Ag}$ in $CdCl_2$ were measured by Wright and Thompson³ and by E. Biron and B. Afanassjew.⁴ Those of the former were all carried out in solutions of concentration greater than about 0.05 *M*. Details of the work of the latter two investigators could not be obtained.

Apparatus.

Potentiometer.—Measurements of electromotive force were made with a potentiometer of the decade-box type, which has been in use in this laboratory for several years. A complete description is given in a recent paper by Lewis, Brighton and Sebastian.⁵ The potentiometer and all conductors connected therewith were thoroughly protected from stray electric effects by a conducting shield, according to the method recommended by White.⁶ By the use of paraffined glass tubes for supports, all parts of the potentiometer system, including wires leading to the cells and to the galvanometer, possessed a high degree of insulation.

Oil Bath.—All the cells when being measured were immersed in an

¹ *Wied. Ann.*, **28**, 21–43, 491–7 (1886).

² *Z. physik. Chem.*, **13**, 577–656 (1894).

³ *Phil. Mag.*, [5] **19**, 106 (1885).

⁴ *J. Russ. Phys. Chem. Soc.*, **41**, 1175–82 (1909).

⁵ THIS JOURNAL, **39**, 2246 (1917).

⁶ *Ibid.*, **36**, 2011 (1914).

oil bath which was maintained at a temperature of $25^{\circ} \pm .01$ by means of an electric heater and an electrically operated thermostat.

Cells.—Two types of cell were used. For the measurements with the more concentrated electrolytes was employed the ordinary "half" cell, so common in electromotive force work. It consisted of a glass tube about 2 cm. in diameter and 15 cm. in height, closed at the bottom, and with a side arm opening from it near the middle. The metal of which the e. m. f. was desired was placed in the bottom of the tube and contact

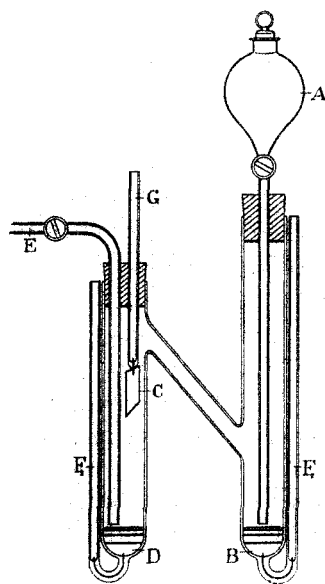


Fig. 1.

made by means of a sealed-in platinum wire. The slight solubility of silver chloride, and the form of the silver-silver chloride electrode (to be described presently) made it possible to insert the latter in the upper part of the same chamber with the zinc or cadmium. The "half" therefore became a complete cell in itself. For the purpose of intercomparison several of these units could be connected, by means of the side arm, with a common intermediate vessel. Where this was unnecessary, the side arm was closed to prevent evaporation and was used merely as a means of support.

For work with dilute solutions, a special cell (Fig. 1) was designed which permitted the circulation of fresh electrolyte through it while it was in the oil bath. Each complete cell of this type carried two metal electrodes, B and D, and one silver-silver chloride reference electrode, C. A small supply of electrolyte, carried in the dropping funnel A, could be allowed to flow down when desired, washing, in turn, the electrode surfaces at B, C, and D, finally passing out through the waste-tube, E. Contact with the potentiometer leads was made by means of mercury placed in the tubes F₁, F₂, and G, in the lower ends of which platinum wires were sealed.

Preparation of Materials.

Standard Metal Electrodes.—Finely divided metals, cadmium and zinc, produced by rapid electrolysis of the chloride solution, were used. A rod of the pure metal served as anode, and a platinum spiral as cathode in this electrolysis. Varying the current density at which the metal was deposited had no effect on the electromotive force exhibited by the metal, except that with very high current density the deposited metal became so spongy as to pack together and thereby prevent efficient washing. With a platinum spiral containing about 20 cm. of No. 18 B. & S. gage

wire the current employed was 0.25 to 0.50 ampere. The tree-like deposit was shaken from this cathode from time to time, and when sufficient amount had been obtained in the bottom of the beaker in which the electrolysis was conducted, it was removed and washed.

Liquid Amalgams of both zinc and cadmium were prepared. These contained 3.6% zinc and 4.6% cadmium, respectively. Weighed amounts of zinc (or cadmium) and mercury were enclosed in an evacuated tube and heated in a steam bath until the solid had dissolved. The mixture was shaken occasionally to hasten the process and after the solid had disappeared a thorough shaking was given to insure homogeneity. Cadmium amalgam gave excellent results in all concentrations of cadmium chloride solution from saturation down to 0.0001 *M*. The zinc amalgam prepared did not give a steady electromotive force in zinc chloride solution of any concentration. It was found, however, that finely divided zinc worked satisfactorily in solutions as dilute as 0.0003 *M*. Therefore, while there is no serious doubt as to the ability of zinc amalgam to give reproducible results, a study of its apparently anomalous behavior was given up, and the pure (spongy) zinc used directly.

Cadmium Chloride solutions were prepared by weighing out the proper amounts of water and of a stock solution of cadmium chloride of known concentration. This stock solution was prepared by dissolving very pure, crystalline cadmium chloride in "conductivity" water. The concentration was determined by 5 analyses, using the silver chloride precipitation method.

Zinc Chloride solutions were prepared likewise by diluting a stock solution of zinc chloride. In this case, however, pure zinc chloride was not available, so that a zinc chloride solution was prepared as follows: Pure hydrogen chloride was obtained by dropping pure, conc. sulfuric acid slowly into pure, conc. hydrochloric acid. The gas was absorbed in conductivity water until the concentration was about 0.5 molal. An excess of spongy zinc, carefully washed, was then added to this acid solution and the mixture warmed gently until no further zinc would dissolve. This solution reddened litmus slowly. The solution was then filtered to remove the excess zinc and the filtrate diluted to about 0.15 *M*, analyzed (as in the case of cadmium chloride), and employed as a stock solution.

Silver-Silver Chloride Electrodes were prepared according to the method already employed successfully by Brighton¹ working in this laboratory. Flat platinum gauze, about 2×1 cm., was fastened to the end of a platinum wire, which in turn was sealed into the lower end of a glass tube of about 4 mm. inside diameter. The gauze was plated with silver from a silver cyanide bath, and then the silver chloride formed

¹ Lewis and Brighton, *Loc. cit.*

as a dark deposit by using the silver as anode in a dil. sodium chloride solution to which a small amount of hydrochloric acid had been added.

Experimental Results.

Amalgam vs. Pure Cadmium.—Three samples of cadmium amalgam were taken, representing approximately the first, middle and last portions drawn from the storage tube. The electromotive force of these against pure cadmium was obtained by measurements of a cell containing the amalgam in one arm and pure cadmium in the other, the electrolyte throughout being 0.5 *M* cadmium chloride solution.¹ The finely divided cadmium did not give concordant or constant results in dil. cadmium chloride solutions, but in 0.5 *M* concentration the agreement was excellent. The cells were kept in the bath from 2 to 5 days, and in each case the electromotive force varied by less than 0.0001 volt during the whole period. The results are as follows:

Portion.	<i>E</i> in volts.
First.....	0.0536
Middle.....	0.0534
Last.....	0.0533

Taking the average of these values we obtain

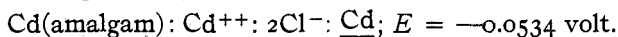


TABLE I.

E. M. F. of the Cell $\text{H}_2(p): \text{HCl}(0.01 \text{ } M): \text{AgCl, Ag.}$

Electrode.	E^2 (observed). Volt.	Barom. Press. (Mm. Hg at 0°.)	E^3 (corrected to 1 atm.). Volt.
1.....	0.4660	751.4	0.4666
2.....	0.4659	751.4	0.4665
4.....	0.4655	751.4	0.4661
4.....	0.4666	751.7	0.4670
5.....	0.4660	745.7	0.4665
5.....	0.4660	756.5	0.4665
6.....	0.4658	753.7	0.4663
6.....	0.4660	759.7	0.4664
6.....	0.4661	757.1	0.4666
6.....	0.4659	755.6	0.4664
7.....	0.4662	759.7	0.4666

Mean value, 0.4665

¹ The electromotive force should be independent of the concentration of Cd^{++} .

² The electrodes were checked up several times at intervals of a few days. *E* represents the mean of the values thus obtained.

³ The calculation of *E* (corrected to a hydrogen pressure of 1 atmosphere) given in Table I, was made as in the following example for Electrode No. 1:

E (observed).....0.4660 volt.

Water vapor pressure at 25° = 24 mm.

Actual hydrogen pressure = 751 — 24 = 727 mm.

Correction = $E = RT/2F \ln 760/p = 0.0296 \log 760/727 = 0.0006$ volt.

$E (p = 1 \text{ atm.}) = 0.4660 + 0.0006 = 0.4666$ volt.

Silver-Silver Chloride vs. Hydrogen.—All the silver-silver chloride electrodes had the same electromotive force within two- or three-tenths of one millivolt, when measured against hydrogen in 0.01 *M* hydrochloric acid. The results are presented in Table I, where *E* represents the e. m. f. of the cell $H_2(p); HCl(0.01M)^1; AgCl; Ag$.

Cadmium Amalgam vs. Silver-Silver Chloride.—Owing to the good agreement of the silver-silver chloride electrodes among themselves, it was unnecessary to correct the individual observations of e. m. f. of cadmium against silver-silver chloride for the deviation of the latter from the mean.

In Table II are presented the original observed e. m. fs. of the cell $Cd(4.6\% \text{ amalgam}), CdCl_2(c), AgCl, Ag; (E_1)$, and of the (calculated) e. m. fs. of the cell $Cd, CdCl_2(c), AgCl, Ag; (E_2 = E_1 - 0.0534)$, the correction term being equal to the e. m. f. of pure cadmium against the cadmium amalgam.

Two or more electrodes always were measured in each concentration of cadmium chloride solution, and it is the mean value of these measurements which is given in the second column of Table II. The cadmium amalgams gave very concordant results in concentrations down to about 0.0005 *M*. The equilibrium value of the electromotive force was taken on very promptly (within 5 or 10 minutes after the cell was prepared and placed in the bath) and did not differ by more than 0.0005 volt from the initial value. This indicated that no appreciable amount of reaction took place between the electrode and the solution. Several cells were left in the bath over a period of 3 or 4 days, during which time they did not vary by more than 0.0002 to 0.0003 volt. In all cases the cells were emptied and refilled with electrolyte several times during the period of the experiment. Where the concentration was about 0.001 *M* or greater, the electromotive force was always reproduced after the refilling. In

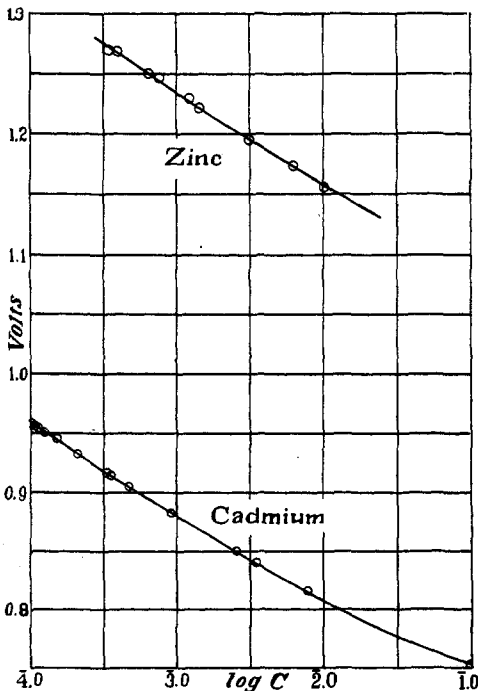


Fig. 2.

¹ The concentration of the hydrochloric acid used was actually 0.00999 *M*.

the very dilute solutions, say below 0.0005 *M*, the several cells did not agree more closely than 0.0005 to 0.0010 volt, and in successive fillings with fresh electrolyte the electromotive force was not reproduced any better than this.

The original observations, as given in Table II, when plotted against the logarithm of the concentration (see Fig. 2) lie on a smooth curve to which the points hold very closely down to a concentration of about 0.00025 *M*. Even below this concentration the maximum deviation of any of the points from the curve is less than 0.0012 volt, so that the least accurate portion of the curve, since it represents an average of the measurements, should give the electromotive force to nearer than 0.001 volt.

TABLE II.

E. M. F. of the Cell : Cd(4.6 amalg.) : CdCl ₂ (c) : <u>AgCl</u> : <u>Ag</u> .		
<i>C</i> (CdCl ₂) mols per 1000 g. of H ₂ O.	<i>E</i> ₁ (observed).	<i>E</i> ₂ (= <i>E</i> ₁ + 0.0534).
6.62	0.62203	0.67540
0.0995	0.6996	0.7530
0.0074	0.76305	0.81645
0.003519	0.7864	0.8398
0.002581	0.7958	0.8491
0.000924	0.8296	0.8830
0.000479	0.852	0.905
0.0003659	0.8614	0.9148
0.0003363	0.8644	0.9178
0.0002144	0.8803	0.9337
0.0001527	0.8926	0.9460
0.0001269	0.8978	0.9512
0.0001137	0.9011	0.9545
0.0001087	0.9023	0.9557
0.0001029	0.9060	0.9594

Zinc vs. Silver-Silver Chloride.—In the work with zinc the pure metal in the finely divided form was used directly. As a "standard" value for the e. m. f. of silver-silver chloride against hydrogen in 0.01 *M* hydrochloric acid, 0.4665 volt was taken. Whenever any of the silver-silver chloride electrodes used in these measurements differed from 0.4665, the corresponding reading was corrected by the proper amount. It has already been pointed out that the finely divided zinc was used instead of zinc amalgam because the amalgam gave unsteady values of electromotive force. Between two samples of the same amalgam the electromotive force varied in an erratic manner, rising and falling rapidly. The finely divided zinc gave a steady value, but left something to be desired in the way of reproducibility in the dilute solutions. For this reason the measurements were not carried out in solutions of zinc chloride more dilute than 0.0003 *M*, and in concentrations below 0.001 *M* the deviation of the individual observations from the mean is 0.002 volt. As in the case of the cadmium measurements, the cells were emptied

and refilled several times with fresh zinc chloride solution, and each value given in Table III represents the mean of the value by at least two separate cells. Whether the silver-silver chloride was in the same tube with the metal (zinc or cadmium), or separated by an intermediate vessel or tube, made only two- or three-tenths of a millivolt difference in the case of the dilute solutions and an undetectable difference in the case of the more concentrated solutions. In Table III are presented the observed e. m. fs. of the cell $\underline{\text{Zn}}; \text{ZnCl}_2(c) : \underline{\text{AgCl}} : \underline{\text{Ag}}$. These values of E are plotted against $\log C$ in Fig. 2.

TABLE III.

E. M. F. of Cell $\underline{\text{Zn}} : \text{ZnCl}_2(c) : \underline{\text{AgCl}} : \underline{\text{Ag}}$.		E (observed).
C (ZnCl_2)	mols per 1000 g. H_2O .	(Volts.)
0.01021		1.1558
0.006022		1.1742
0.003112		1.1953
0.001453		1.2219
0.001253		1.2289
0.000772		1.2475
0.000649		1.2497
0.0003995		1.2699
0.0003478		1.2701

In Table IV are presented three values by H. Jahn¹ to supplement those given in Table III. Jahn used an amalgamated zinc rod instead of pure zinc. Since, as pointed out by Richards and Lewis,² the difference in potential between pure zinc and its saturated amalgam is slight (only a few millivolts) the comparison is a fair one to make.

TABLE IV.

Data of H. Jahn.		E. M. F. of Cell $\underline{\text{Zn}} : \text{ZnCl}_2(c) : \underline{\text{AgCl}} : \underline{\text{Ag}}$.	E (observed).
C (ZnCl_2)	mols per 1000 g. H_2O .		(Volts.)
0.566			1.0306
1.112			1.0171
2.22			0.9740

Activities of the Ions.

In solutions of bi-univalent salts the determination of the thermodynamic degree of dissociation is rendered difficult (1) because of factors which are identical with those appearing in the case of uni-univalent salts, although probably exaggerated in this case; (2) because of uncertainty regarding intermediate ions; and (3) because in the case of zinc and cadmium chloride there is also the possibility of another type of complex anion. Nevertheless, as infinite dilution is approached all of these factors of uncertainty disappear, and if accurate electromotive-force measurements could be made in very high dilution the value of

¹ *Loc. cit.*

² *Proc. Am. Acad.*, 34, 87 (1898).

the normal electrode potential could be calculated at once. At high dilutions, however, not only does the solubility of the material used in the electrode (such as mercuric sulfate or silver chloride) produce some uncertainty, but other errors of unknown origin become highly exaggerated.

In every experimental study of electrode potentials the attempt is made to obtain a curve adequate for the extrapolation of E° values before the anomalies at high dilution appear. One way would be to assume at every concentration complete ionization and obtain the E° value in that way, or, as a first approximation, the degree of dissociation may be assumed to be that given by conductivity. The latter method is employed in this paper. It should be noted that no assumption is made that conductivity values give the thermodynamic degree of dissociation, but that they are used solely as a convenient means of plotting values which by extrapolation give the true E° .

Dissociation of Cadmium Chloride.—The values of the degree of dissociation given by Noyes and Falk¹ were plotted against the logarithm of the concentration, the curve being drawn asymptotic to the line $\alpha = 1$. ($\alpha =$ the degree of dissociation.) The data used for this plot, which is not published herewith, are given in Table V.

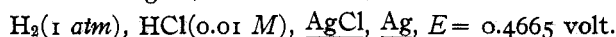
Dissociation of Zinc Chloride.—The degree of dissociation of zinc chloride was obtained from the equivalent conductance Λ , given in the Landolt and Börnstein Tables, and the equivalent conductance at infinite dilution, ($\Lambda_\infty = 112.5$) given by Noyes and Falk (*Loc. cit.*). The degree of dissociation, α , is obtained by taking the ratio Λ/Λ_∞ . Values of α for various concentrations are also given in Table V.

TABLE V.
Dissociation of Cadmium Chloride and Zinc Chloride.

$C(\text{CdCl}_2)$ mols per 1000 g. of H_2O .	α .	$C(\text{ZnCl}_2)$ mols per 1000 g. of water.	Λ 1/ohms.	α .
0.0005	0.931	0.00005	110	0.978
0.0010	0.891	0.00010	109	0.970
0.0025	0.803	0.00025	108	0.961
0.0050	0.735	0.0010	107	0.952
....	...	0.0025	105	0.934
....	101	0.898

Calculation of Normal Electrode Potentials.

The data in Table I give, as a mean value for the cell



We may now calculate E° , which is the electromotive force of this cell when $\text{H}^+(= \text{Cl}^-)$ is (hypothetical) molal, using the equation

$$E = E^\circ - (RT/F)\ln(\text{Cl}^-)(\text{H}^+).$$

¹ THIS JOURNAL, 34, 475 (1912).

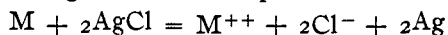
In 0.01 *M* hydrochloric acid solution, the activity of H⁺ (and Cl⁻) has been found to be 0.0093.¹ Using this value we obtain,

$$0.4665 = E^\circ - 0.05915 \log(0.0093)^2,$$

from which we get

$$H_2, H^+(M), Cl^-(M), \underline{AgCl}, \underline{Ag}, E^\circ = 0.2283 \text{ volt.}^2$$

When two Faradays of electricity are passed through the cell $\underline{M}; MCl_2; \underline{AgCl}; \underline{Ag}$, the following reaction takes place:



The e. m. f. of the cell is given by the following equation:

$$\begin{aligned} E &= E^\circ - (RT/2F) \ln(4C^3\alpha^3), \\ &= E^\circ - 0.08873 \log(1.588 C\alpha), \end{aligned}$$

in which E° is the potential when M^{++} and Cl^- are each (hypothetical) molal (*i. e.*, E° is the normal potential of the metal M); R is the gas constant; T is the absolute temperature; F is the faraday (= 96500 coulombs); C is the concentration of the chloride solution in mols per 1000 g. of water; and α is the fraction ionized. In using this equation it is assumed that $C\alpha$ is practically equal to the activity of the metal ion. Using this equation by substituting it in observed values of α belonging to the concentrations C , a series of E° values was obtained. The values thus calculated are given in Tables VI and VII for cadmium and zinc, respectively.

TABLE VI.
Normal Potential of Cadmium.

Log <i>C</i> —10.	α .	<i>E</i> volt.	E° volt.
6.0000	0.975	0.9597	0.6218
6.1000	0.970	0.9523	0.6231
6.2000	0.966	0.9445	0.6240
6.3000	0.961	0.9365	0.6245
6.4000	0.955	0.9282	0.6250
6.5000	0.948	0.9199	0.6253
6.6000	0.940	0.9117	0.6258
6.7000	0.931	0.9035	0.6259
6.8000	0.919	0.8954	0.6262
6.9000	0.904	0.8876	0.6266
7.0000	0.888	0.8801	0.6272
7.6000	0.758	0.8362	0.6306

The curve of observed electromotive force ought to become steeper as the cadmium chloride becomes more dilute, until complete dissociation has taken place, when the slope of the curve should be 0.0887 volt per unit change in log C . Owing to the large effect of impurities, etc., when the solutions are very dilute, the curve not only becomes straight before

¹ Lewis, Brighton and Sebastian, *Loc. cit.*

² From this value of E° might be calculated the free energy of formation of the particular silver chloride used.

the theoretical slope is reached, but actually bends over. Now the true E° curve would continue to fall out to infinite dilution, but the experimental errors at small concentrations cause a rapid fall of the curve, producing a point of inflection. This rapid fall probably has begun to manifest itself even before the point of inflection is reached. It is E° at this point of inflection which is taken as the most probable value of the true E° .

The values of E° in Table VI were plotted against $\log C$ (Fig. 3) and from this plot was obtained the final value, $E^\circ = 0.6255$ volt.

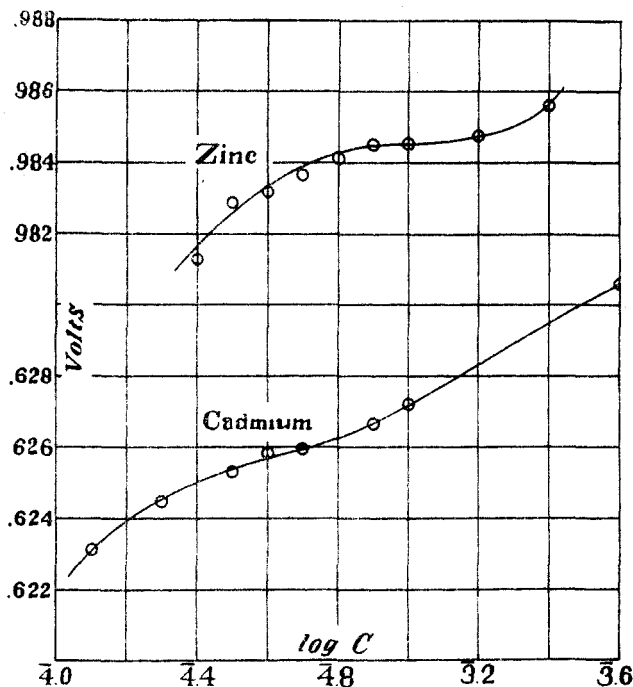
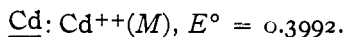


Fig. 3.

We may write for the cell $\text{Cd}, \text{Cd}^{++}(M). \text{Cl}^{-}(M); \underline{\text{AgCl}}; \underline{\text{Ag}}, E^\circ = 0.6255$. As we have already calculated, $\text{H}_2; \text{H}^{+}(M). \text{Cl}^{-}(M); \underline{\text{AgCl}}; \underline{\text{Ag}}, E^\circ = 0.2263$. Combining these two, we obtain, $\underline{\text{Cd}}; \text{Cd}^{++}(M); \text{H}^{+}(M); \text{H}_2; E^\circ = 0.3992$. Since the normal potential of the hydrogen electrode is taken as zero, the e. m. f. of the above cell gives us directly the normal potential of the cadmium electrode



This value probably is good to 0.0010 volt.

TABLE VII.
Normal Potential of Zinc.

Log C -10.	α .	E volts.	E° volt.
6.4000	0.962	1.2844	0.9813
6.5000	0.958	1.2772	0.9829
6.6000	0.954	1.2688	0.9832
6.7000	0.949	1.2606	0.9836
6.8000	0.944	1.2524	0.9841
6.9000	0.937	1.2442	0.9845
7.0000	0.930	1.2356	0.9845
7.2000	0.910	1.2189	0.9847
7.4000	0.886	1.2032	0.9856

The values of E° for zinc (Table VII) were plotted against $\log C$ as in the case of cadmium (see Fig. 3). From this curve we obtain

$$\underline{\text{Zn}}; \text{Zn}^{++}(M) \text{Cl}^-(M); \underline{\text{AgCl}}; \underline{\text{Ag}}, E^\circ = 0.9845.$$

As already given, $\text{H}_2; \text{H}^+(M) \text{Cl}^-(M); \underline{\text{AgCl}}; \underline{\text{Ag}}, E^\circ = 0.2263$.

Combining these two we find $\underline{\text{Zn}}; \text{Zn}^{++}(M); \text{H}^+(M); \text{H}_2, E^\circ = 0.7582$.

The e. m. f. of this cell is the normal potential of the zinc electrode

$$\underline{\text{Zn}}; \text{Zn}^{++}(M), E^\circ = 0.758.$$

On account of the uncertainty in the electromotive-force measurements in the case of zinc, the above value may have an error as large as 0.002 volt.

Free Energy of Dilution.

If we have two cells of the type $\underline{\text{M}}, \text{MCl}_2, \underline{\text{AgCl}}, \underline{\text{Ag}}$, where the concentration of the MCl_2 solutions are C_1 and C_2 , respectively, the difference between the e. m. f. of the two cells multiplied by twice the faraday equivalent and divided by the mechanical equivalent of heat (4.182) gives the free energy of dilution, in calories, of the MCl_2 solution from the concentration C_1 to the concentration C_2 . That is,

$$\Delta F = \frac{\Delta E \times 96500}{4.182}.$$

A series of values thus calculated are given in Table VIII.

TABLE VIII.
Free Energy of Dilution of Cells.

C_1 M.	C_2 M.	$\frac{\Delta F}{(\text{CdCl}_2)}$ Calc.	$\frac{\Delta F}{(\text{ZnCl}_2)}$ Calc.
0.1	0.01	1306
0.05	0.005	1426
0.01	0.001	1615	1719
0.005	0.0005	1705	1858
0.002	0.0002	1818
0.003	0.0003	1888

If the salt were completely dissociated the slope of the electromotive-force curve (Fig. 3) ought to be 0.0887 volt. That is, for a tenfold change

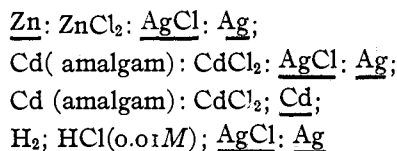
in concentration the free energy of dilution ought to approach the value $0.0887 \times 96500/4.182 = 2046$ calories, in the more dilute solutions. That this value is approached more nearly by the zinc chloride than by the cadmium chloride indicates that zinc chloride is dissociated to a higher degree. Conductance ratios also show zinc chloride to be the more highly dissociated.

The author takes this opportunity to acknowledge the helpful suggestions of, and to express his indebtedness to, Dr. Gilbert N. Lewis, in whose laboratory this work was conducted.

Summary.

Previous work by the author, in which mercurous sulfate was used in a reference electrode, is discussed and the reason for the inaccuracy noted. From the electromotive force of the cell $\underline{\text{Zn}}; \text{ZnSO}_4; \text{Hg}_2\text{SO}_4; \text{Hg}$, the normal electrode potential of zinc was calculated to be 0.76 volt, with a probable accuracy of only 0.01 volt.

In the present work the e. m. fs. of the following cells have been measured:



In the first cell the concentrations of the zinc chloride solutions ranged from 0.0003 M up to 0.01 M . In the second, the concentrations of cadmium chloride ranged from 0.0001 M up to saturation (6.61 M). All measurements were carried out at a temperature of 25°.

The normal electrode potentials of zinc and cadmium were found to be (zinc) 0.758 \pm 0.002 volt and (cadmium) 0.3992 \pm 0.0010 volt, the normal potential of the hydrogen electrode being taken equal to zero.

The free energy of dilution of zinc chloride and cadmium chloride solutions was obtained.