

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF REED COLLEGE]

STUDIES IN THE MEASUREMENT OF ELECTROMOTIVE FORCE IN DILUTE AQUEOUS SOLUTIONS. I. A STUDY OF THE LEAD ELECTRODE

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The only method of determining electrode potentials and activity coefficients from electromotive-force measurements depends upon some form of an extrapolation to infinite dilution of the experimental values obtained. This method was first outlined by Lewis and Randall.¹ Experience has shown that the curve does not flatten into a straight line necessary for extrapolation until concentrations well below 0.01 *M* are attained. Therefore, measurements on solutions of low concentration are important for the accurate determination of electrode potentials and activity coefficients.

As a general rule investigators have been unable to check one another when dealing with solutions of high dilution. A recent summary by Randall and Young² of the electromotive force measurements involving the silver chloride electrode illustrates the varied results obtained in dilute solutions by different investigators. The value of the normal potential of the silver chloride electrode obtained by several investigators varies from 0.2221 to 0.2234, although their measurements agree very well in the concentrated solutions.

The difficulties of electromotive force measurements in dilute solutions depend upon the relatively high percentage effect of small factors which may be negligible in the more concentrated solutions. Such slight changes in concentration may be caused by a reaction of the solution with electrodes or containing vessel or by absorption of the solution by the container or electrodes. The usual method to avoid large percentage variations due to these slight changes in concentration has been to use a cell of large proportions, containing a liter or more of solution.³ Such cells require long periods of time, sometimes several days, to reach equilibrium. It has been the writer's experience that checks on solutions below 0.005 *M* are very difficult if not impossible to obtain when the large cell is used, even when the same solution and the same electrodes are used in two separate measurements.

Method and Apparatus.—The use of a small cell of 20-cc. capacity (shown in Fig. 1) designed to be emptied and refilled without the electrodes being disturbed has been

¹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Company, Inc., New York, 1923, p. 334.

² Randall and Young, *THIS JOURNAL*, 50, 989 (1928).

³ (a) Linhart, *ibid.*, 41, 1175 (1919); (b) Nonhebel, *Phil. Mag.*, [7] 2, 1085 (1926).

found to yield reproducible results on solutions well below 0.001 *M*. The method of operation is as follows.

The cell, with electrodes in position, and reservoir are filled with the solution and seasoned by standing for several hours, when the solution is drawn off and the reservoir filled with a new supply. The cell is washed with this new solution from the reservoir at frequent intervals for a period of an hour or more, the time depending upon the concentration of the solution used.

After the final filling, the solution is stirred with a stream of nitrogen for a half hour. The cell is then allowed to attain equilibrium without further change of solution or stirring. After the cell has reached equilibrium and the electromotive force has been measured, a second measurement can be made readily by filling the cell with a new supply of solution from the reservoir and repeating the operation.

This method is designed to eliminate the effect of slight variations by using a sufficiently large volume of solution and at the same time it takes advantage of the short time necessary for the small cell to attain equilibrium. The cells described in the second half of this paper usually came to equilibrium within two hours after the nitrogen was turned off and the e.m.f. remained constant for several hours. As for the volume of the solution the writer has found it difficult to obtain checks when less than 0.001 mole of the electrolyte has been used in making up the solution. When working with concentrations approximately 0.0002 *N*, five liters of solution were prepared, two liters of which were passed through the cell

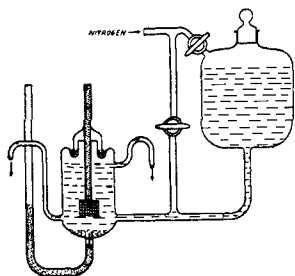


Fig. 1.

before constant and reproducible voltages were obtained.

In the second part of this paper this method has been applied to the study of the lead electrode. A similar application of the method to the study of the silver chloride electrode in dilute solutions is planned.

The Lead Electrode

No accurate determination of the normal potential of the lead electrode has been made. Several measurements have been made that involve the potential of the lead electrode, but, since the activity coefficients of the lead salts used in these measurements are uncertain, no exact calculation of the normal potential can be made from them. Measurements of Getman,⁴ Henderson and Stegeman⁵ and Lewis and Brighton⁶ were made on cells containing liquid junction potentials and salts of uncertain activity coefficients. Lewis and Randall⁷ have roughly calculated the activity coefficient of lead chloride from the measurements of Brönsted⁸ on the cell Pb, PbCl₂, AgCl, Ag, in which "Jahn" type silver chloride electrodes were used, by extrapolating to infinite dilution the values obtained from three measurements. Applying the activity coefficient for the saturated solution of lead chloride thus obtained to the measure-

⁴ Getman, *THIS JOURNAL*, **38**, 792 (1916); **40**, 611 (1918).

⁵ Henderson and Stegeman, *ibid.*, **40**, 84 (1918).

⁶ Lewis and Brighton, *ibid.*, **39**, 1906 (1917).

⁷ Lewis and Randall, *ref. 1*, p. 424.

⁸ Brönsted, *Z. physik. Chem.*, **56**, 645 (1906).

ment of Gerke⁹ on the cell $\text{Pb}, \text{PbCl}_2(\text{s}), \text{KCl} + \text{PbCl}_2, \text{HgCl}, \text{Hg}, E = 0.5357$, they obtain the value $\text{Pb}, \text{Pb}^{++}, E_0 = 0.122$.

This value can be considered as approximate only, since it depends upon an extrapolation to infinite dilution of measurements made in relatively concentrated solutions.

Gerke also compared the potential of the two-phase saturated lead amalgam electrode with that of electrolyzed crystals and with stick lead, obtaining 0.00580 and 0.00567, respectively.

Results from the experimental work outlined below indicate that 0.0058 is a better value than 0.0057 for the potential of the lead amalgam electrode against the lead electrode. The normal electrode potential of lead is shown to be 0.1263, a value 0.0043 higher than that accepted at the present time.

Experimental

I. Electrodes and Materials

1. The silver chloride electrodes were prepared according to the method outlined by Carmody,¹⁰ and were protected at all times from exposure to sunlight. They were prepared in groups of four, the electrodes in each group checking always within 0.02 mv.

2. The lead amalgam electrodes were prepared by heating mercury with freshly scraped stick lead (J. T. Baker's c. p.) in an atmosphere of nitrogen to form approximately a 5% solution. This was cooled to 80° and the liquid phase allowed to run into the cell through a capillary tube. The amalgam electrode so formed presented a liquid surface that was found to give more reproducible results than an amalgam that is rich in the solid phase. Repeated experiments showed it to be reproducible well within 0.01 millivolt.

3. The mercury used in the lead amalgam electrodes was purified by distilling three times in a current of air under reduced pressure as recommended by Hulett.¹¹

4. Conductivity water used in preparing all solutions was the product of a laboratory still made according to the specifications given by Bengough, Stewart and Lee.¹²

5. Lead chloride (J. T. Baker's c. p.) was recrystallized three times from hot water.

6. Nitrogen for stirring cells and removing oxygen from solutions was purified by being passed in order through potassium permanganate, alkaline cuprous chloride, alkaline pyrogallol, water and finally through a solution of the same concentration as used in the cell.

II. Potential of Lead Amalgam Electrode

The Cell: $\text{Pb}(\text{Stick}), \text{PbCl}_2, \text{Pb}(\text{Hg})$.—A small cell of 20-cc. capacity was used. The freshly scraped stick electrode and the amalgam electrode were put in position in the nitrogen-filled cell. Oxygen-free lead chloride solution was allowed to run into the cell from an attached reservoir, the solution stirred with a stream of nitrogen for ten minutes and the cell then sealed. Usually the cell came to equilibrium in less than ten minutes and the potential remained constant for about two hours. After this

⁹ Gerke, *THIS JOURNAL*, **44**, 1684 (1922).

¹⁰ W. R. Carmody, *ibid.*, **51**, 2901 (1929).

¹¹ Hulett, *Phys. Rev.*, **33**, 307 (1911).

¹² Bengough, Stewart and Lee, *J. Chem. Soc.*, **131**, 2156 (1927).

time a gray coating formed on the surface of the lead stick and the potential slowly lowered without again reaching a constant value.

Five different sticks (carefully selected to be free from physical defects) were used. The results, shown in Table I, are more comparable with Gerke's results from electrolyzed lead crystals than his results from lead sticks. It would appear therefore that 0.0058 is a better value for the potential than 0.0057 obtained as an average by Gerke.

TABLE I
E.M.F. VALUES OF ELECTRODES

Electrode	1	2	3	4	5	Av.
E.m.f.	0.00580	0.00585	0.00586	0.00586	0.00582	0.00584

III. The Cell: Pb(Hg), PbCl₂, AgCl, Ag

The electrode vessel is shown in Fig. 1. The methods of operation have already been described. Equilibrium was obtained usually within two hours after the nitrogen had been shut off. No measurement on dilutions below 0.01 *M* was considered until it had been checked to within

0.1 millivolt by a second reading on the same solution. Results appear in Col. 2 of Table II.

The electromotive force of the cell is given by the equation:

$$E = E'_0 - \frac{0.05915}{2} \log 4 (m\lambda)^3 \quad (1)$$

where E'_0 is the normal potential of the cell. Following the method outlined by Randall,¹³ this may be transformed into the equation

$$\log \lambda - \frac{E'_0}{0.08873} = - \left[\frac{E}{0.08873} + 0.2007 + \log m \right] \quad (2)$$

In Fig. 2 the quantity in the parenthesis is plotted against the square root of the ionic strength. By extrapolation to infinite dilution the

following result is obtained: $E'_0 = 0.3426$ v. Taking the potential of the silver chloride electrode to be 0.2221,² and the lead-lead amalgam potential to be 0.0058, the result obtained is

$$\text{Pb, Pb}^{++}, E_0 = 0.1263$$

Using this value in Equation 2, the activity coefficients of lead chloride have been calculated. They appear in Col. 3 of Table II.

¹³ Randall, *Trans. Faraday Soc.*, 23, 498 (1927).

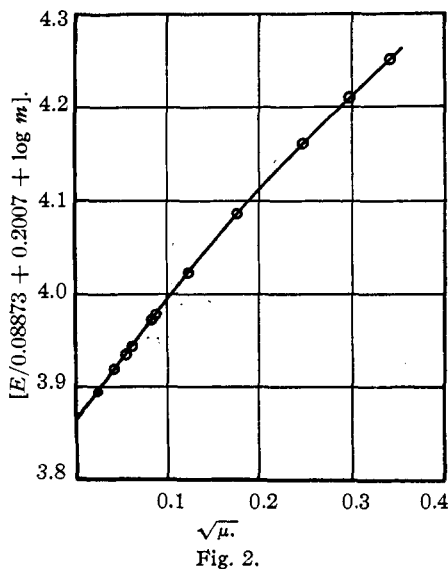


TABLE II

CELL: Pb(Hg), PbCl₂, AgCl, Ag

M^a	E , observed	λ , PbCl ₂	M^a	E , observed	λ , PbCl ₂
0.03905	0.4842	0.408	0.002348	0.5677	0.778
.02955	.4913	.449	.001337	.5870	.830
.02048	.5012	.502	.001034	.5960	.847
.01039	.5205	.598	.0006197	.6143	.881
.005160	.5419	.692	.0002116	.6537	.927
.002620	.5639	.771			

^a The effect of the solubility of the silver chloride electrode and the hydrolysis of the lead chloride have been considered. The effects are negligible except in the most dilute solution, where they are small, approximately equal and of opposite sign.

The activity coefficient of lead chloride in saturated solution (0.03905 M) is found to be 0.408. Applying this result and the value of the potential of the calomel electrode obtained by Randall and Young² to the measurement of Gerke,⁹ we obtain $Pb, Pb^{++}, E_0 = 0.1264$. This checks well with the value 0.1263 obtained by extrapolation to infinite dilution.

The writer is pleased to acknowledge his indebtedness to the Chemistry Department of Stanford University for apparatus and materials and for the privileges of their laboratory, in which the experimental work described in this paper was completed.

Summary

1. A new method of electromotive-force measurement in dilute solutions is described.
2. Electromotive-force measurements have been made on the cell Pb(Hg), PbCl₂, AgCl, Ag.
3. From the results of these measurements the normal electrode potential of lead and the activity coefficients of lead chloride have been calculated.

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