

ACTIVITY COEFFICIENTS AND DISSOCIATION OF LEAD CHLORIDE IN AQUEOUS SOLUTIONS¹

ROBERT M. GARRELS AND FRANK T. GUCKER, JR.

*Department of Geology, Northwestern University, Evanston, Illinois, and Departments of
Chemistry, Northwestern University, Evanston, Illinois, and Indiana University,
Bloomington, Indiana*

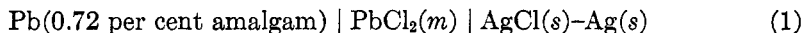
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The study of lead chloride is taken as an example of the experimental techniques and theoretical methods which may be applied to all moderately strong electrolytes. The deviation of the behavior of lead chloride from that of a strong electrolyte has been explained on the basis of the Gronwall-LaMer-Sandved extension of the Debye-Hückel theory for small highly charged ions, and also on the basis of incomplete dissociation. The second interpretation is strengthened by the discovery of ultraviolet absorption bands identified with the PbCl^+ ion, a quantitative investigation of which affords one method of determining the dissociation constant of this ion. Study of the conductance of lead chloride solutions also gives evidence of incomplete dissociation and allows an evaluation of the dissociation constant.

Finally, a great deal of information can be obtained from the E.M.F. of cells containing lead chloride alone and in the presence of other electrolytes, from which its activity coefficients have been determined. We present some new experimental data for the E.M.F. of cells with added sodium chloride, over a wide range of temperature and concentration. The plot of the usual extrapolation function $E^{\circ'}$ against the square root of the stoichiometric ionic strength approaches the Debye-Hückel limiting law from above rather than below, thus making extrapolation to find E° difficult. The results with added barium nitrate lie along a different curve from those with added alkali chlorides, showing that ionic strength is not the only variable to be considered. Nearly all of the E.M.F. data may be correlated, however, if we assume a secondary dissociation constant of about 0.03, calculate the ionic concentrations, and plot a suitably defined function against the actual ionic strength rather than the stoichiometric ionic strength. The same dissociation constant fits the conductance data, but a considerably larger value of the constant is obtained from the absorption spectra, which emphasizes the difficulties often involved in dealing with moderately strong electrolytes.

INTRODUCTION

There have been several studies of the activities of lead chloride in aqueous solution. In 1906 J. N. Brönsted (5) made a series of measurements from 0° to 90°C., using the cell:

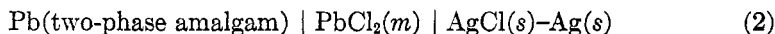


Subsequent workers have found that the silver-silver chloride electrodes of the type devised by Jahn, which Brönsted used, are not adequately reproducible, and that the lead amalgam electrode is only stable between 1.4 and 66 per cent lead.

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Later, A. J. Allmand and E. Hunter (3) measured the same cell at 25°C. over a wide range of concentration. They used amalgamated lead sticks for the lead electrodes, and carefully excluded oxygen from the system. They found a value of $E^0 = 0.3396$ v. for the cell, and obtained activity coefficients for lead chloride which agreed fairly well with those of Brönsted.

W. R. Carmody (6) carried out a careful set of measurements of the cell:



He also worked at 25°C. and varied the lead chloride concentration from saturation (0.039 *m*) to 0.0002 *m*. He found a value of $E^0 = 0.3426$ v. for the cell by linear extrapolation.

In 1936 M. C. Hannan (14) studied the same cell at concentrations from 0.01 to 0.0005 *m*, at 12.5° intervals from 0° to 50°C. She used two-phase lead amalgam electrodes prepared by electrolysis with a mercury cathode, silver-silver chloride electrodes of the type used by Carmody, and an atmosphere of nitrogen in the cell. Her work was done to test the Debye-Hückel theory as extended to unsymmetrical electrolytes by LaMer, Gronwall, and Grieff (19). Using their extended equation she found a value of $E^0 = 0.3435$ at 25°C.

A number of studies have been made of the activities of lead chloride in the presence of other electrolytes, at 25°C. Most of these (1, 2, 4, 20, 18, 17), dealing with the behavior of lead chloride in the presence of lithium, sodium, or potassium chloride, were carried out in connection with phase-rule studies of these systems. The last article, by E. R. Hounsell and H. N. Parton (17) summarizes the work on E.M.F. and activity coefficients, based on a value of $E^0 = 0.3432$ v. The authors point out that much of the previous work in the series was vitiated by dissolved oxygen in the solutions dilute in lead chloride. They used an atmosphere of hydrogen instead of nitrogen, and found that duplicate cells remained constant for 12 hr. or more.

E. Güntelberg (13) also measured the E.M.F. of cells containing lead chloride alone and in the presence of hydrochloric acid and potassium chloride. Unfortunately his work is available to us only in abstract, and we do not have the details of experimentation or his experimental results. His conclusions will be discussed in a later section.

H. D. Crockford and H. O. Farr, Jr., (7) studied the E.M.F. of cells containing lead chloride in the presence of barium nitrate, in order to determine the value of the *a* parameter (distance of closest approach of the ions) in mixed electrolytes.

Our work extends the measurements on lead chloride in the presence of sodium chloride from 25° to 65°C. The E.M.F. data are used to calculate the activity coefficient of lead chloride in these solutions. Its abnormally low value in these solutions is interpreted in terms of ionic association.

Elsewhere, one of us (12) has discussed the geological implications of these results, in connection with the interesting geological problem which started us upon this work and which was posed by the fact that, in vertical vein deposits, galena (PbS) frequently is found farther from the place of origin than sphalerite (ZnS), despite the lower solubility of the lead sulfide in most solutions. Since

primary liquid inclusions in galena crystals contain high concentrations (up to 4 *m*) of soluble chlorides, we investigated the effect of added sodium chloride upon the activity coefficient of lead chloride over the temperature range of geologic interest. The results were used to explain the increased solubility of lead sulfide in relation to zinc sulfide in vein solutions.

EXPERIMENTAL METHODS AND RESULTS

We used materials similar to those which Hounsell and Parton (17) found satisfactory except that tank nitrogen (Linde) instead of hydrogen was used to provide an oxygen-free atmosphere, since none of our solutions was extremely dilute in lead chloride. This nitrogen was purified by passing it through a series of gas-washing bottles containing successively potassium permanganate, alkaline

TABLE 1

*E.M.F. of cell: Pb (two-phase amalgam) | PbCl₂(*m*₁), NaCl(*m*₂) | AgCl(s)-Ag(s), from 25° to 65°C.; corresponding values of *E*⁰ and mean activity coefficients*

<i>m</i> ₁ (PbCl ₂)	<i>m</i> ₂ (NaCl)	$\frac{\mu}{3m_1 + m_2}$		25°C.	35°C.	45°C.	55°C.	65°C.
0.000	0.000	0.000	<i>E</i> ⁰	0.3434	0.3404	0.3368	0.3229	0.3287
0.0018	0.020	0.0254	<i>E</i>	0.5418	0.5447	0.5474	0.5502	0.5526
			γ_{\pm}	0.581	0.591	0.597	0.595	0.595
0.0036	0.100	0.1108	<i>E</i>	0.5054	0.5088	0.5114	0.5140	0.5164
			γ_{\pm}	0.432	0.422	0.414	0.404	0.394
0.0018	0.200	0.2054	<i>E</i>	0.5075	0.5124	0.5161	0.5195	0.5221
			γ_{\pm}	0.336	0.316	0.304	0.291	0.284
0.0018	0.400	0.4054	<i>E</i>	0.5025	0.5067	0.5099	0.5130	0.5161
			γ_{\pm}	0.243	0.231	0.224	0.215	0.206
0.0018	0.600	0.6054	<i>E</i>	0.5004	0.5038	0.5073	0.5103	0.5136
			γ_{\pm}	0.196	0.190	0.182	0.176	0.167

pyrogallol, and cuprous nitrate, and then over copper turnings heated to 300–400°C.

The cell was designed according to principles used by Carmody (6), with the addition of a second cell unit so that the *E.M.F.* readings could be checked. Cell operation followed Carmody's procedure.

Lead amalgam electrodes were prepared within the cell to avoid oxidation. The air in the cells was displaced with nitrogen; then the mercury and lead successively were dropped in against a strong current of nitrogen, and the amalgam was heated to 80°C. to insure saturation at all experimental temperatures.

Silver chloride electrodes were prepared according to the directions of M. Dole (9). They were white when fresh and gradually turned brown after use. They were reproducible within 0.1 mv., and the change in color did not affect the potential.

Temperature was controlled within 0.1°C. by immersion in an oil bath heated by a resistance coil and controlled by a mercury thermoregulator. Closer control was not necessary because of the small temperature coefficient of the cell.

E.M.F. readings were taken to 0.1 mv. on a Type K potentiometer, made by Leeds and Northrup Company, balanced against a recently calibrated standard cell. The experimental E.M.F. values of the two cells always checked within 0.6 mv., and usually within 0.2 mv.

Our experimental results are given in table 1.

E^0 AND MEAN ACTIVITY COEFFICIENTS

In cells of the type discussed here, either in pure lead chloride solutions or in mixtures of lead chloride and other salts, the reaction is:



The E.M.F. of this cell E in terms of the standard potential E^0 and the activity a of lead chloride is given by the equation:

$$E = E^0 - \frac{RT}{nF} \ln a_{\text{PbCl}_2} \quad (1)$$

or

$$E = E^0 - \frac{1}{2}k \log a_{\text{PbCl}_2} \quad (2)$$

where $k = 2.3029 RT/F$. This also can be written:

$$E = E^0 - \frac{1}{2}k \log m_{\text{Pb}^{++}} \cdot m_{\text{Cl}^-}^2 \cdot \gamma_{\text{Pb}^{++}} \cdot \gamma_{\text{Cl}^-}^2 \quad (3)$$

In terms of the mean activity coefficient of the lead chloride, the equation may be rearranged as follows:

$$E + \frac{1}{3}k' \log m_1(2m_1 + m_2)^2 = E^0 - k' \log \gamma_{\pm} \quad (4)$$

where m_1 is the concentration of lead chloride, m_2 is the concentration of added chloride, and $k' = \frac{3}{2}k$.

The left-hand member of equation 4, usually designated E^0' , is used in extrapolation to find E^0 and $\log \gamma_{\pm}$. In solutions of lead chloride alone, this equation becomes:

$$E + \frac{1}{3}k' \log 4 + k' \log m_1 = E^0 - k' \log \gamma_{\pm} \quad (5)$$

We have used equations 4 and 5 to calculate E^0' from our results and those of the other investigators included in table 2. In the sixth column are given values of E^0'/k' which in figures 1 and 2 are plotted as ordinates instead of E^0' in order to separate the curves for the different temperatures. The abscissas are $\mu^{1/2}$. Here μ is the usual ionic strength, defined as:

$$\mu \equiv \frac{1}{2} \sum_i m_i z_i^2 \quad (6)$$

where m_i is the stoichiometric molality and z_i the charge of the i^{th} ion. We have

included on the 25°C. curve the results of Carmody (6) and of Hannan (14) for cells containing lead chloride alone, and representative values of Hounsell and Parton (17) for cells with added lithium, sodium, or potassium chloride. The results show that, in all these solutions, the value of $E^{\circ'}$ depends chiefly upon the

TABLE 2

*E.M.F. of cell: Pb (two-phase amalgam) | PbCl₂(m₁), MCl(m₂), Ba(NO₃)₂(m₃) | AgCl(s)-Ag(s) at 25°C., with various extrapolation functions**

$m_1(\text{PbCl}_2)$	$m_2(\text{MCl})$	$m_3(\text{Ba}(\text{NO}_3)_2)$	μ	$E(\text{EXPTL.})$	$E^{\circ'}/k'$	$E^{\circ''}/k'$	$E^{\circ'''}/k'$	μ'
0.0002116			0.000635	0.6537	3.893	3.867	3.864	0.000629
0.0006197			0.001859	0.6143	3.916	3.872	3.863	0.001817
0.001034			0.003102	0.5960	3.932	3.876	3.861	0.002994
0.001337			0.004011	0.5870	3.942	3.878	3.861	0.003839
0.002348			0.007044	0.5677	3.969	3.884	3.857	0.006574
0.002620			0.007860	0.5639	3.974	3.884	3.855	0.007293
0.005160			0.01548	0.5419	4.020	3.894	3.848	0.01370
0.0018	0.0200		0.0254	0.5418	4.106	3.945	3.887	0.02427
0.01039			0.03117	0.5205	4.083	3.904	3.837	0.02575
0.02048			0.06144	0.5012	4.160	3.909	3.819	0.04656
0.019037		0.00503	0.07220	0.50426	4.1632	3.891	3.805	0.05939
0.02955			0.08865	0.4913	4.208	3.907	3.804	0.06366
0.0036	0.100		0.1108	0.5054	4.235	3.898	3.771	0.1066
0.03905			0.11715	0.4842	4.249	3.903	3.793	0.08253
0.019037		0.03030	0.14801	0.50872	4.2135	3.824	3.745	0.1369
0.0018	0.171		0.1764	0.5089	4.315	3.890	3.731	0.1740
0.0018	0.200		0.2054	0.5075	4.344	3.886	3.715	0.2029
0.0072	0.201		0.2226	0.4896	4.359	3.882	3.710	0.2125
0.019037		0.06069	0.23918	0.51223	4.2530	3.758	3.684	0.2291
0.019037		0.08027	0.29792	0.51430	4.2764	3.724	3.653	0.2882
0.0018	0.342		0.3474	0.5032	4.448	3.852	3.642	0.3446
0.019037		0.10025	0.35786	0.51543	4.2891	3.684	3.615	0.3486
0.0018	0.400		0.4054	0.5025	4.485	3.841	3.619	0.4025
0.0072	0.469		0.4906	0.4851	4.542	3.833	3.600	0.4790
0.0018	0.600		0.6054	0.5004	4.578	3.791	3.535	0.6024
0.0009	0.697		0.6997	0.5110	4.640	3.793	3.523	0.6982
0.0072	0.697		0.7186	0.4867	4.672	3.815	3.547	0.7064

* Data of Carmody (6) for lead chloride alone; results of this research and of Hounsell and Parton (17) for added alkali halides, and of Crockford and Farr (7) for added barium nitrate. For definitions of $E^{\circ'}$, $E^{\circ''}$, $E^{\circ'''}$, μ , and μ' see, respectively, equations 4, 12, 31, 6, and 34.

ionic strength. However there are some deviations, particularly for the solutions with a high concentration of added potassium chloride.

Our measurements did not extend to low enough concentrations to fix the dilute end of the curve with certainty. For this purpose we used the results of Hannan, which covered the range from 0° to 50°C. She had calculated E° at each temperature by means of the Debye-Hückel equation as extended by LaMer, Gronwall, and Grieff (19). She found that the results over the whole

range of temperature were represented by a single value of the parameter $\delta = 1.75 \text{ \AA}$. Although this value is too small to have much physical significance, these results were the most reliable ones available over a range of temperature.

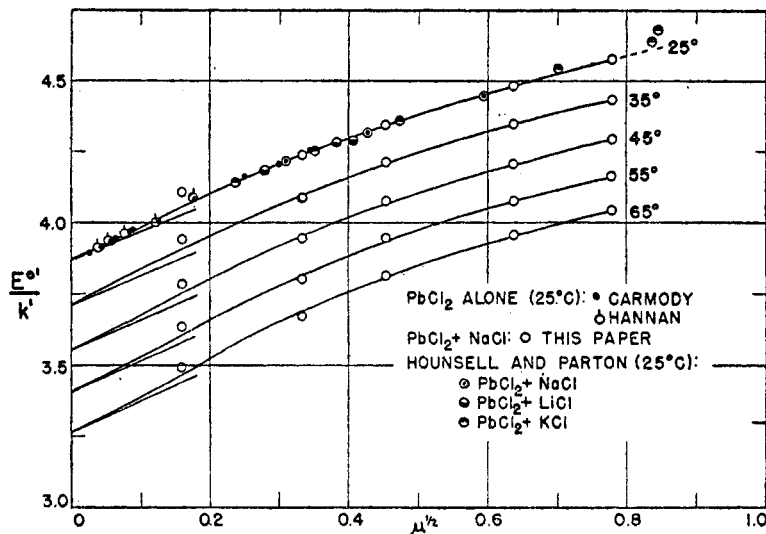


FIG. 1. (E^0/k') vs. $\mu^{1/2}$ for lead chloride alone and with added alkali halides at 25–65°C.

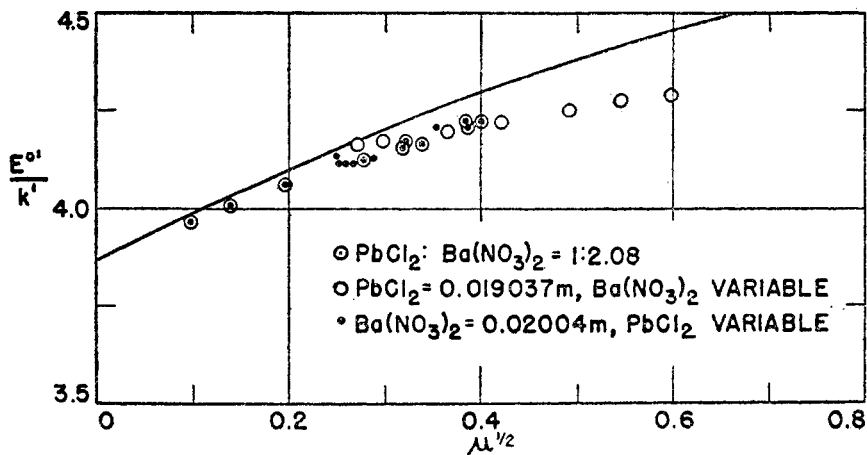


FIG. 2. (E^0/k') vs. $\mu^{1/2}$ for lead chloride with added barium nitrate at 25°C.

We found that the E^0 values she tabulated at 0°, 12.5°, 25°, 37.5°, and 50°C. could be represented within ± 0.04 mv. by a slight modification of the equation she had proposed to relate E^0 to the Centigrade temperature, namely:

$$E^0 = 0.34790 - 6.77 \times 10^{-5}t - 4.990 \times 10^{-6}t^2 + 2.270 \times 10^{-8}t^3 \quad (7)$$

This equation could be extended to 65°C. with no great loss of reliability. The

E^0 values given in table 1, calculated from this equation, probably are reliable to within about 0.5 mv. This limit is imposed by the discrepancies between different methods of extrapolation, which will be discussed later. The values of the mean activity coefficients listed in table 1 are calculated from E and E^0 by means of equation 4.

The Debye-Hückel limiting law slopes are shown at each temperature. It will be seen that the experimental curves do not approach these from below, as in the case of typical strong electrolytes. Instead, they lie above the limiting law until an ionic strength of about 0.7 is reached. The shape of the curve makes the usual extrapolation for E^0 uncertain.

Figure 1 does not include the results of Crockford and Farr (7) for lead chloride in the presence of barium nitrate solutions. When these are plotted on the same scale, they deviate widely from the results obtained in the presence of added chlorides. To avoid confusion of the experimental points, the results of Crockford and Farr are plotted separately in figure 2, together with the solid line of figure 1 at 25°C. Three series of experiments were carried out. In the first, the ratio of the molalities of lead chloride to barium nitrate was kept constant; in the second, the concentration of lead chloride was held constant and that of the barium nitrate was changed; while in the third the barium nitrate molality was fixed and that of the lead chloride was varied. The three series agree fairly well among themselves, but at high concentration they fall far below the results obtained in the presence of added chloride.

Crockford and Farr interpreted their results in terms of the change in the distance of closest approach of the ions in these mixtures. They used the equation derived by H. D. Crockford and H. C. Thomas (8) for the mean distance of closest approach \bar{a} in a mixture of two salts:

$$\bar{a} = \frac{a_1 f_1 + a_2 f_2}{f_1 + f_2} \quad (8)$$

Here a_1 and a_2 are the ionic diameter parameters for the individual salts and f_1 and f_2 are the respective collision frequencies, assumed to be proportional to the squares of the concentrations of the two salts. They used $a_1 = 1.75 \text{ \AA.}$ for lead chloride, calculated by LaMer, Gronwall, and Grieff (19), and $a_2 = 2.68 \text{ \AA.}$ for barium nitrate. This was computed from the value of $a = 2.50 \text{ \AA.}$, determined for the first series of experiments by the method of LaMer, Gronwall, and Grieff. This is appreciably less than might be expected. The crystal ionic radius given by L. Pauling (21) for Ba^{++} (1.35 \AA.) is about that for K^+ (1.33 \AA.) and G. Scatchard, S. S. Prentiss, and P. T. Jones (26), from their studies of freezing points of alkali nitrates, conclude that the nitrate ion is intermediate between the bromide and iodide ions in size in solution. The values for potassium bromide and iodide are given by H. S. Harned and B. B. Owen (16) based on calculations from Hückel's equation:

$$\log \gamma_{\pm} = -\frac{z_1 z_2 A \sqrt{\mu}}{1 + aB\sqrt{\mu}} + C\mu \quad (9)$$

where A and B are the constants of the Debye-Hückel theory and C is an empirical constant. Taking the mean of these values gives for barium nitrate the figure $\delta = 3.9 \text{ \AA}$. This is so near the values of 4.2, 4.0, and 3.8 given by Harned and Owen for lithium, sodium, and potassium chloride, respectively, that the strikingly different effect of barium nitrate upon lead chloride hardly can be due to the δ parameter.

THE ACTIVITY OF LEAD ION: COMPLEX FORMATION

As many previous workers have pointed out, the activity coefficients of lead chloride are unusually low in solutions of increasing ionic strength. Normal

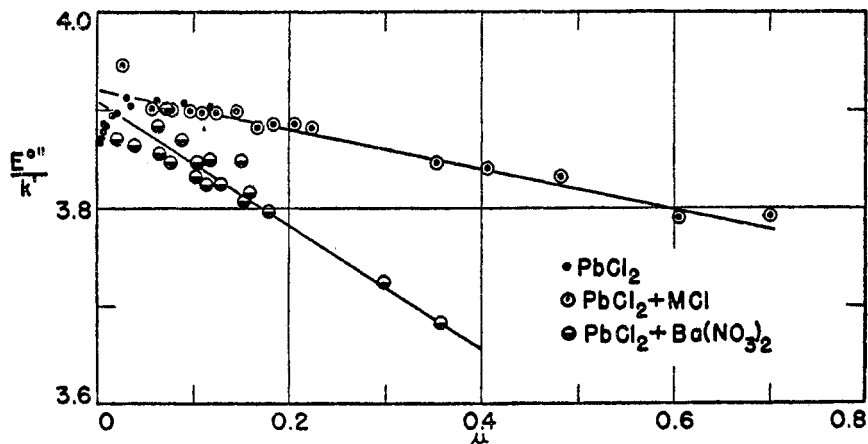


FIG. 3. (E''/k') vs. μ for lead chloride alone and with added electrolytes at 25°C.

strong 2-1 electrolytes in very dilute solution obey the Debye-Hückel equation which, in terms of ionic strength, is:

$$\log \gamma_{\pm} = -\frac{2A\sqrt{\mu}}{1 + \delta B\sqrt{\mu}} \quad (10)$$

This is sometimes divided out to give approximately:

$$\log \gamma_{\pm} = -2A\sqrt{\mu} + B'\mu \quad (11)$$

where $B' = 2AB\delta$. Substituting for $\log \gamma_{\pm}$ from equation 11 into equation 4 and rearranging terms gives:

$$E + \frac{1}{2}k' \log m_1(2m_1 + m_2)^2 - 2k'A\sqrt{\mu} = E^0 - k'B'\mu \quad (12)$$

The left-hand member of this equation, designated E'' , should decrease nearly linearly with μ and frequently is used in extrapolating data to obtain E^0 . In the case of lead chloride, however, a very different result is obtained, as shown in figure 3, which is a plot of the values of E''/k' given in the seventh column of table 2. Our results and those of Hounsell and Parton on mixtures of lead chloride and alkali chlorides fall nearly together along a reasonable line, while

the results of Crockford and Farr in mixtures of lead chloride and barium nitrate cluster around a different line with about three times as great a slope. Both of these lines would extrapolate to a value of E^0 about 5 mv. too high. The results for lead chloride alone approach the origin with a positive instead of the predicted negative slope. The graph of the $E^{0'}$ function clearly indicates divergence from the behavior of a typical strong electrolyte. It shows that the ionic strength alone does not determine this deviation, and suggests that the results may be treated in terms of ionic association to form one or more complexes. This was suggested sometime ago on the basis of E.M.F. data by G. Scatchard and R. H. Tefft (25), and later by E. Güntelberg (13), while additional evidence has been obtained along two very different lines. E. C. Righellato and C. W. Davies (24) have studied the anomalous conductance of lead chloride solutions, and they have interpreted the results in terms of formation of PbCl^+ complex ion. Independently, H. Fromherz and K. H. Lih (11) have studied the ultraviolet absorption spectra of these solutions, and also have obtained evidence for the formation of PbCl^+ in dilute solutions.

K FOR PbCl^+ FROM CONDUCTANCE

Righellato and Davies found that, over a considerable range of concentration, all strong electrolytes obeyed the equation:

$$\Lambda^0 - \Lambda\eta^{1/2} = a \cdot f(c) \quad (13)$$

Here Λ^0 and Λ are the equivalent conductances at concentrations zero and c , η is the viscosity at concentration c , a is the constant of the Debye-Hückel-Onsager equation, calculable from ionic mobilities, and $f(c)$ is the same function for all salts of the same valence type. Weak electrolytes, including lead chloride, do not obey this equation.

Righellato and Davies assumed that the conductance of the lead chloride solution is the sum of the conductances of the Pb^{++} , Cl^- , and PbCl^+ ions, and that the conductance of the first two ions is the same as in other (unassociated) solutions in which they are present at the same ionic strength. The conductance of the PbCl^+ ion they assumed to be 40 mhos, like that of all the other univalent complex ions they considered. They then determined the degree of ionic association, β , required to yield the observed conductance. The ionic concentrations in the solution are:

$$m_{\text{Pb}^{++}} = (1 - \beta)m; \quad m_{\text{Cl}^-} = (2 - \beta)m; \quad m_{\text{PbCl}^+} = \beta m$$

The actual ionic strength of the solution will be:

$$\mu' = (3 - 2\beta)m \quad (14)$$

This differs from the stoichiometric value $\mu = 3m$, which is also the actual ionic strength in a solution of a strong electrolyte. The value of β was determined by successive approximations, and the authors consider it accurate to better than 10 per cent.

Righellato and Davies then calculated the thermodynamic dissociation constant for the complex ion, given by the equation:

$$K = \frac{m_{\text{Pb}^{++}} \cdot m_{\text{Cl}^{-}}}{m_{\text{PbCl}^{+}}} \cdot \frac{\gamma_{\text{Pb}^{++}} \cdot \gamma_{\text{Cl}^{-}}}{\gamma_{\text{PbCl}^{+}}} \quad (15)$$

They used a form of the Debye-Hückel equation analogous to equation 11 for the individual ionic activities, namely:

$$\log \gamma_i = -Az_i^2 \sqrt{\mu'} + B_i \mu' \quad (16)$$

Converting equation 15 to logarithmic form they substituted for $\log \gamma_i$ from 16 to obtain:

$$\log K = \log K' - A \Sigma z_i^2 \sqrt{\mu'} + \Sigma B_i \mu' \quad (17)$$

TABLE 3
K for PbCl^{+} from conductance at 18°C.

<i>m</i>	0.001	0.0025	0.005	0.01	0.025
$10^3 \mu'$	2.944	6.980	13.34	24.74	53.34
$-\log K'$	1.165	1.389	1.338	1.313	1.291
$-\log K$	1.260*	1.525	1.510	1.518	1.516
<i>K</i>	0.0550*	0.0299	0.0309	0.0303	0.0305

Here K' is the classical (concentration) constant. In this case Σz_i^2 is 4, and $A = 0.50$ at 18°C.; hence rearranging gives:

$$\log K' - 2.0 \sqrt{\mu'} = \log K - \Sigma B_i \mu' \quad (18)$$

A plot of the quantity on the left against μ' gives a straight line with a slope of $\Sigma B_i = 4.44$, which is larger than the corresponding value for most other salts. Comparison with equation 11 shows that $2AB\bar{a} = \Sigma B_i$. Substituting the numerical values for the constants A and B , as tabulated by Harned and Owen (16, p. 119), we find $\bar{a} = 6.66 \text{ \AA}$. This is considerably larger than 2.75 \AA , the sum of the crystal ionic radii for lead chloride (21), but somewhat more plausible than the value of 1.75 \AA required by the extended equations of LaMer, Gronwall, and Grieff. Of the fifteen a values of the alkali halides tabulated by Harned and Owen (16, p. 381) twelve exceed the sum of the crystal radii by 0.5–2 \AA . and only three alkali halides fail to equal it.

Knowing ΣB_i and K' at various concentrations, Righellato and Davies calculated corresponding values of K , which are summarized in table 3. The average value of K , neglecting the uncertain starred figure at 0.001 m , is 0.0304.

K FROM ABSORPTION SPECTRA

Fromherz and Lih (11) studied the absorption spectra of lead chloride solutions from 2000 to 2750 \AA . The smoothed curves of their results are shown in figure 4, where the optical density, or logarithm of the extinction coefficient, is plotted

against the wave length. The extinction coefficient is defined by the Beer-Lambert law:

$$I/I_0 = 10^{-\epsilon cd} \quad (19)$$

Here I_0 and I are the initial and final intensities of light which passes through a solution of molarity c for a distance of d cm., and ϵ is the extinction coefficient, measured to 2 to 4 per cent. The curves all intersect in a single point, corresponding to an optical density of 3.740 at 2159 Å. This indicates a system of two absorbing species which they identified as Pb^{++} (hydrated) and PbCl^+ , which probably absorbs by what E. Rabinowitch (22) calls an electron-transfer mechanism:



The Cl^- does not absorb appreciably in this region. Measurements on lead perchlorate solutions showed that the optical density is independent of concentration, indicating no ionic association in solutions of this salt. Since the ClO_4^- is transparent in this region, the absorption peak with a maximum optical density of 3.990 at 2085 Å. must be due to the Pb^{++} . The extinction coefficient of any dilute lead chloride solution then will be:

$$\epsilon = \beta\epsilon_{\text{PbCl}^+} + (1 - \beta)\epsilon_{\text{Pb}^{++}} \quad (21)$$

In this equation both β and ϵ_{PbCl^+} are unknowns. However, Fromherz and Lih assumed that the absorption curve for PbCl^+ is symmetrical, like those of PbBr^+ and PbI^+ which they had calculated by difference, and that it obeys the Beer-Lambert law on dilution. The curves of the two most concentrated chloride solutions were analyzed, assuming values for β_1 and β_2 over a reasonable range. Comparison of the optical density curves for PbCl^+ showed that the dashed curve of figure 4 was consistent with both series of measurements, giving maxima at 2270 and 2265 Å., respectively, with half-widths of 232 and 226 Å. This yielded values of $\beta_1 = 0.320$ and $\beta_2 = 0.178$. The calculated curve for PbCl^+ was used with the observed curves of the dilute solutions to calculate the corresponding values of β from equation 21. The results are summarized in table 4, where the maximum error in β estimated by the authors is also included.

The value of β being known, the classical ionization constant was calculated by Fromherz (10) as:

$$K' = \frac{(1 - \beta)(2 - \beta)}{\beta} c \quad (22)$$

A plot of K' against c gives the thermodynamic constant K by extrapolation and also the activity coefficient ratio. Fromherz found $K = 0.0775$ at about 22°C., with an estimated uncertainty of ± 10 per cent.

Fromherz and Lih also studied solutions of lead chloride in concentrated alkali chloride solutions, and found absorption bands which they attributed to the PbCl_4^{--} ion. These merge imperceptibly into the Pb^{++} - PbCl^+ system in dilute solution, whence they conclude no intermediate ions are formed. Rabi-

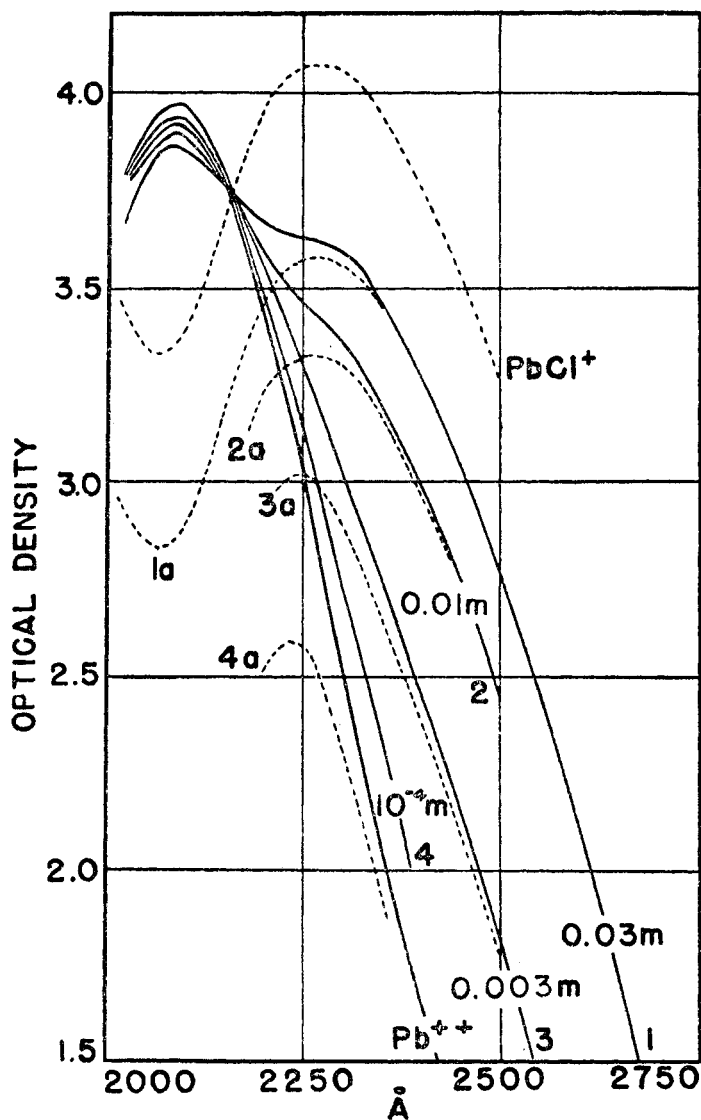


FIG. 4. The optical density of solutions of lead chloride according to Fromherz and Lih

TABLE 4

Degree of association of PbCl⁺ in dilute solutions of lead chloride, according to Fromherz and Lih

10^3c	27.69	1.108	2.769	0.9220
β	0.320	0.178	0.087	0.033
$\Delta\beta$	± 0.03	± 0.02	± 0.02	± 0.008

witch (22) thinks, however, that such ions might exist, with absorption bands in the same general region as the others. In a solution 0.000167 *M* in lead chloride

and 0.0167 M in potassium chloride they found 80 per cent Pb^{++} , 10 per cent PbCl^+ , and 10 per cent higher complexes.

K FROM E.M.F. DATA

The large disagreement in the value of the dissociation constant of PbCl^+ obtained from these two methods aroused our interest in evaluating it independently from E.M.F. data. Scatchard and Tefft (25) had already stated that it was approximately 0.03, and we used their method, as modified by H. S. Harned and M. E. Fitzgerald (15). The method has been summarized by Harned and Owen (16, p. 414 *et seq.*). The E.M.F. of the cell may be expressed in terms of the degree of dissociation of the PbCl^+ ion, α , and the true mean activity coefficient γ'_{\pm} of the lead chloride as:

$$E = E^0 - \frac{1}{2}k \log \alpha(1 + \alpha)^2 m^3 \gamma'_{\pm}{}^3 \quad (23)$$

Following Harned and Fitzgerald, we assumed that γ'_{\pm} was the same as that of the typical strong electrolyte barium chloride, as determined by E. A. Tippets and R. F. Newton (27). We transformed their Hückel-type equation for $\log f$ into the following:

$$\log \gamma_{\pm} = -\frac{1.0117\sqrt{\mu}}{1 + 1.3436\sqrt{\mu}} + 0.0388\mu \quad (24)$$

which reproduced their tabulated values of γ_{\pm} with an average deviation of ± 0.0004 up to 1.2 m . Substituting equation 24 into equation 23, we can assume values of K and solve for E^0 by successive approximations or, somewhat more simply, assume values of E^0 and solve for K by successive approximations. The appropriate equation is:

$$\begin{aligned} -\log \alpha(1 + \alpha)^2 = & \left[3 \log m + 2 \frac{(E - E^0)}{k} \right] \\ & - \frac{3.0350m^{1/2}\sqrt{2\alpha + 1}}{1 + 1.3436m^{1/2}\sqrt{2\alpha + 1}} + 0.1166m(2\alpha + 1) \quad (25) \end{aligned}$$

From this α is determined to 0.1 per cent by two or three successive approximations. The classical dissociation constant then is calculated as:

$$K' = \alpha \frac{(1 + \alpha)}{(1 - \alpha)} m \quad (26)$$

Harned and Fitzgerald assumed that the activity coefficients of PbCl^+ and Cl^- are equal, and that the activity coefficient of Pb^{++} is given by the Debye-Hückel equation:

$$\log \gamma_{\text{Pb}^{++}} = -\frac{2.0234\sqrt{\mu'}}{1 + 0.3283 a \sqrt{\mu'}} \quad (27)$$

where μ' is the actual ionic strength in the solution, given by equation 14, and a is assigned the value of 5 Å., comparable to that found for barium chloride and

large enough to make the extended terms of the Debye-Hückel theory negligible. Then:

$$K = K'\gamma_{\text{Pb}^{++}} \quad (28)$$

We used the data of Carmody to determine K in this way, taking several values of E^0 and also varying \hat{a} . The most consistent values were: $E^0 = 0.3430$ v., $\hat{a} = 6 \text{ \AA.}$, and $K = 0.0293$. Estimating the uncertainty in E^0 as 0.1 mv. and that in \hat{a} as 1 \AA. , we weighted each value of K according to the reciprocal of the sum of the resulting errors in E . The results of calculations with two different values

TABLE 5
Differences in millivolts between *E.M.F.* found by Carmody for the cell
 $\text{Pb}(\text{two-phase amalgam}) \mid (\text{PbCl}_2(m) \mid (\text{AgCl}(s) - \text{Ag}(s)$
and that calculated by various equations

Values of constants	E^0	0.3430	0.3429	0.3429	0.34325
\hat{a}	6	6	7	6	1.75
K	0.0293	0.0293	0.0280	0.0275	∞
m	$\Delta E = E$ (calculated) - E (observed) in millivolts				
0.0002	0.05	-0.04	-0.02	-0.25	-0.25
0.0006	0.02	-0.04	-0.03	-0.05	-0.05
0.0010	0.03	-0.02	0.02	-0.05	-0.05
0.0013	0.01	-0.02	0.00	0.05	0.05
0.0023	-0.02	0.02	0.07	0.15	0.15
0.0026	0.11	0.14	0.16	0.05	0.05
0.0052	0.00	0.09	0.14	0.05	0.05
0.0104	-0.13	0.11	0.09	0.05	0.05
0.0205	-0.43	0.00	-0.11		
0.0295	-0.61	-0.08	-0.24		
0.0391	-0.96	-0.36	-0.53		
Av. (1-8).....	± 0.05	± 0.06	± 0.07	± 0.09	± 0.09
(1-10).....	± 0.14	± 0.06	± 0.09		
(1-11).....	± 0.21	± 0.08	± 0.13		

of E^0 and \hat{a} are shown in table 5. The tabulated values of K are based upon the weighted values of the first eight experiments, up to and including the 0.01 m solution. Above this concentration the decreasing value of K , which can be compensated somewhat by increasing \hat{a} , probably is due to formation of higher complexes in addition to PbCl^+ , rather than to a decrease in $\gamma_{\text{Pb}^{++}}$. We have included also the deviations which LaMer, Gronwall, and Grieff calculated from these same data. A comparison shows that the assumption of complex ion formation is slightly more consistent with Carmody's data than the extended Debye-Hückel theory, although deviations below 0.05 mv. are not significant.

An analysis of Hannan's results at 25°C. showed that, over the range covered (0.0005-0.010 m), they were most consistent with values of $E^0 = 0.3433$, $\hat{a} = 6$, and $K = 0.0289$. The average deviation in E was ± 0.16 mv., chiefly because

the value at the highest concentration was 0.37 mv. low. The result for E^0 is consistent with Hannan's statement that Carmody's E^0 values were about 0.3 mv. higher than hers, a result which she attributed to his use of amalgams made from stick lead rather than electrolyzed amalgams.

The values of E^0 for the cell with lead chloride as electrolyte are summarized in table 6. The method of calculation based on the formation of PbCl^+ gives results about midway between those of direct linear extrapolation of E^0 against $\mu^{1/2}$ and the extended theory of LaMer, Gronwall, and Grieff.

Since the picture of incomplete ionization of PbCl^+ , with a constant of about 0.029 at 25°C., fitted the results of Carmody and Hannan for pure lead chloride solutions so satisfactorily, we tried to apply it also to the mixed solutions. If m_1 , m_2 , and m_3 are respectively the stoichiometrical concentrations of

TABLE 6
A comparison of E^0 values from various sources for the cell
Pb(two-phase amalgam) | $\text{PbCl}_2(m)$ | AgCl(s)-Ag(s)

METHOD OF EVALUATION	DATA	
	Carmody	Hannan
Linear vs. $\mu^{1/2}$ {	Graphical	0.3429
	Least squares	
K for PbCl^+ {	This article	0.3433
	Scatchard and Tefft	
LaMer, Gronwall, and Grieff	0.34325	0.3435

lead chloride, alkali chloride, and barium nitrate, the equation for the cell in terms of the degree of dissociation of the PbCl^+ , analogous to equation 23 is:

$$E = E^0 - \frac{1}{3}k' \log \alpha m_1 [(1 + \alpha)m_1 + m_2]^2 - k' \log \gamma'_{\pm} \quad (29)$$

where γ'_{\pm} is the true mean activity coefficient of the dissociated lead chloride. If we assume that this is the same as γ_{\pm} for barium chloride at 25°C., given by equation 24, we can substitute it into equation 29 and obtain:

$$E + \frac{1}{3}k' \log \alpha m_1 [(1 + \alpha)m_1 + m_2]^2 = E^0 + \frac{1.0117k' \sqrt{\mu'}}{1 + 1.3436 \sqrt{\mu'}} - 0.0388k' \mu' \quad (30)$$

However, for purposes of correlation, it is more convenient to substitute for γ'_{\pm} in equation 29 the limiting law for a 2-1 electrolyte, and define a function $E^{0'''}$ as:

$$E^{0'''} \equiv E + \frac{1}{3}k' \log \alpha m_1 [(1 + \alpha)m_1 + m_2]^2 - 1.0117k' \sqrt{\mu'} \quad (31)$$

The value of α is obtained by successive approximations from the equation:

$$\alpha = \frac{1}{2} \left[\sqrt{\left(1 + \frac{m_2}{m_1} + \frac{K}{m_1 \gamma'_{\text{Pb}^{++}}}\right)^2 + \frac{4K}{m_1 \gamma'_{\text{Pb}^{++}}}} - \left(1 + \frac{m_2}{m_1} + \frac{K}{m_1 \gamma'_{\text{Pb}^{++}}}\right) \right] \quad (32)$$

where $\gamma'_{\text{Pb}^{++}}$ is obtained from the Debye-Hückel equation (equation 27) putting $\bar{a} = 6$:

$$\log \gamma'_{\text{Pb}^{++}} = -\frac{2.0233\sqrt{\mu'}}{1 + 1.9699\sqrt{\mu'}} \quad (33)$$

and

$$\mu' = (2\alpha + 1)m_1 + m_2 + 3m_3 \quad (34)$$

The values of $E^{0'''}/k'$ thus obtained, setting $K = 0.029$, are listed in the eighth column of table 2. When plotted against the values of μ' listed in the ninth

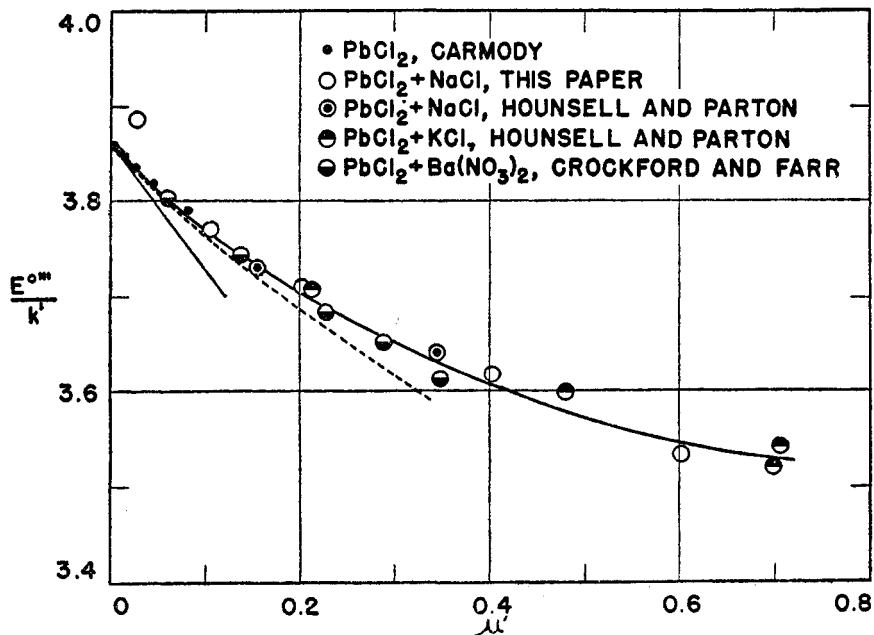


FIG. 5. $E^{0'''}/k'$ (based on $K = 0.0290$ for PbCl^+ and $\bar{a} = 6$) for lead chloride alone and with added electrolytes at 25°C .

column of the same table, they all fall close to a single line, as shown in figure 5. Comparison of equations 30 and 31 shows that, if the mean activity coefficient of the dissociated lead chloride is the same as that of barium chloride:

$$E^{0'''}/k' = E^0/k' - \frac{1.3593\mu'}{1 + 1.3436\sqrt{\mu'}} - 0.0388\mu' \quad (35)$$

The straight line of figure 5 indicates the limiting slope of this curve and the dashed line shows its further course. The calculated curve agrees quite well with the experimental in dilute solution, showing that the value of γ'_{\pm} is about that of barium chloride, but the divergence is appreciable above 0.1μ . This is not surprising, considering the assumptions involved. Thus the neglect of higher complexes in the more concentrated solutions would tend to make the values of α

from equation 32 too large and may explain some of the systematic deviations. The fact that the results for added chlorides fall slightly above those for added barium nitrate also may be explained in the same way, or may be due to incomplete dissociation of the latter salt, as suggested by Dr. Redlich. However, the differences are rather small, and this single plot serves to correlate all the experimental results. When it is used for extrapolation to obtain E_0 , the value

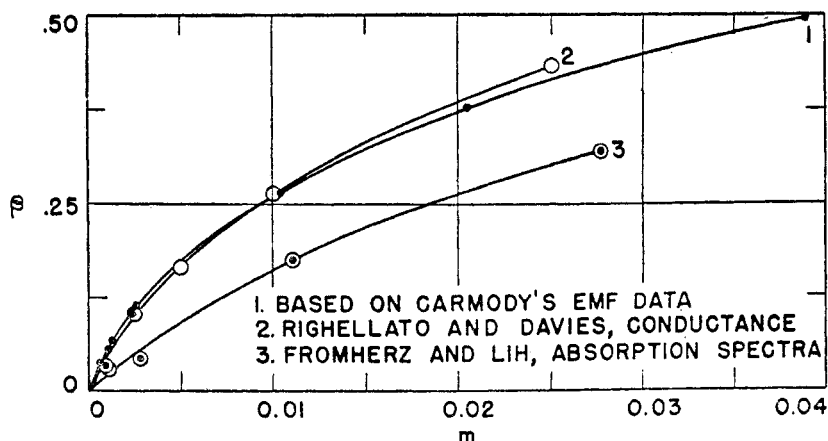


FIG. 6. Fraction (β) of lead chloride associated to form $PbCl^+$ at $25^\circ C.$, calculated by three independent methods.

TABLE 7

The dissociation constant of $PbCl^+$ calculated by various methods

AUTHOR	METHOD	K
This paper	Carmody's E.M.F. data	0.0293
This paper	Hannan's E.M.F. data	0.0289
Righellato and Davies	Conductance	0.0304
Redlich	von Ende's solubility data	0.06
Fromherz and Lih	Absorption spectra	0.08
Güntelberg	E.M.F. data	0.10

thus obtained agrees within 0.3 mv. with that of Hannan, so that it is much more suitable for extrapolation than $E^{0'}$.

SUMMARY OF VALUES OF K

The results of the calculations of the dissociation constant of $PbCl^+$ based on E.M.F. measurements show excellent agreement with the analysis of conductance data by Righellato and Davies, and wide divergence from the conclusions of Fromherz and Lih based on absorption spectra. This appears clearly in figure 6, where we have plotted the fraction of lead associated to form $PbCl^+$ at different concentrations. In table 7 we have listed the values of the dissociation constant of $PbCl^+$ discussed above, along with several others. C. L. von Ende (28) de-

terminated the freezing point of lead chloride solutions and calculated the concentration of Pb^{++} and PbCl^+ in the saturated solution at 25°C ., assuming that the ions are ideal solutes. Neglecting activity coefficients, O. Redlich (23) estimated the dissociation constant on the basis of these data, although he does not consider that the figure should carry any weight, because of the assumptions involved. The value given by E. Güntelberg (13) is based on his measurement of the E.M.F. of cells containing lead chloride alone and in the presence of hydrochloric acid or potassium chloride. Since we have seen only the abstract of his work we do not have the details of experimentation or computation, but his results seem at variance with the careful and concordant work of Carmody and Hannan. We have no explanation for the wide discrepancy between the results of about 0.03 based on these E.M.F. data and conductance data, and those of about 0.09, based upon absorption spectra and Güntelberg's data. Further work is needed to clear up this discrepancy.

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