

(In the remaining part of this paper surface tension, association, evaporation, freezing, melting, viscosity, solubility, and the internal structure of liquids will be briefly considered.)

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

## THE POTENTIAL OF THE LEAD ELECTRODE.

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On account of our almost complete ignorance as to the activity of bivalent ions, there are few cases where it has been possible to calculate even with moderate accuracy the electrode potentials of bivalent metals.<sup>1</sup> Numerous measurements<sup>2</sup> have been made, which involve the lead electrode, but there is none from which the normal electrode potential can be calculated with any certainty. Much of the former work has been done with solutions of lead nitrate. Aside from the difficulties due to the possible formation of nitrite from nitrate solutions there is no known method for determining the amount of intermediate ion in  $\text{Pb}(\text{NO}_3)_2$  or the activity of  $\text{Pb}^{++}$ .

We have investigated the potential of lead in the presence of solid  $\text{PbI}_2$ . This salt is so very insoluble in water that we may, without any serious error, estimate the activity of  $\text{Pb}^{++}$  in its saturated solution in pure water, and are thus enabled to calculate the normal electrode potential of lead. We have also investigated lead electrodes in the presence of  $\text{PbBr}_2$ ,  $\text{PbCl}_2$  and  $\text{PbSO}_4$ .

All measurements, unless otherwise stated, were made at 25°.

**Solid Lead Electrodes.**—It was found in a number of experiments that sticks of the best purchasable lead, scraped with a glass edge, gave the same potential as lead deposited by electrolysis, either upon lead or upon platinum, from a solution of lead perchlorate (containing for an accidental reason a certain amount of lead acetate). The electrodes of the three classes differed no more from one another than did several electrodes of the same class, the average deviation from the mean in both cases being less than 0.0001 volt.

This behavior is just what we should expect from a metal as soft as lead. It is our belief that the lack of reproducibility in electrodes of solid metal is due solely to conditions of strain in the solid surface. In the case of metals which flow readily, like lead or sodium or potassium,

<sup>1</sup> See Lewis and Lacey, *THIS JOURNAL*, 36, 804 (1914).

<sup>2</sup> Immerwahr, *Z. Elektrochem.*, 7, 477 and 625 (1900-01); Sackur, *Arbeits. k. Gesundheitsamt.*, 20, 539 (1903); Labendzinski, *Z. Elektrochem.*, 10, 77 (1904); Cumming, *Trans. Faraday Soc.*, Nov., 1908; Lewis, W. K., *Dissert.*, Breslau, 1908; Jaques, *Trans. Faraday Soc.*, 5, Nov., 1909; Getman, *THIS JOURNAL*, 38, 796 (1916); Fernau, *Z. physik. Chem.*, 17, 343 (1898); Brönsted, *Z. physik. Chem.*, 56, 645 (1906).

these accidental strains almost immediately disappear and the solid metals form entirely reproducible electrodes.

Our experiments furnish no evidence for the allotropic change of lead described by Getman.<sup>1</sup> The sticks of lead which we used were at least six years old and showed no difference in potential when measured against the lead tree freshly prepared by electrolysis.

**Lead Amalgam Electrodes.**—In order to take advantage of the greater convenience of an electrode of liquid metal, we have employed dilute lead amalgams, about 1% by weight, each of which was compared carefully with sticks of pure lead. The comparisons were made in the solution of lead perchlorate which we have just mentioned. The results with two different amalgams are given for illustration in Table I. The first row gives the average potentials of several electrodes of amalgam I against five scraped lead sticks, and the second row gives similar measurements for amalgam II, the first two being against lead electrolyzed upon platinum gauze, the second two against lead electrolyzed on lead, and the last against scraped stick lead.

TABLE I.

I.....	0.0077	0.0076	0.0077	0.0077	0.0076
II.....	0.0069	0.0069	0.0069	0.0068	0.0068

Altogether at various times five different amalgams were used, their potentials against solid lead being

I, 0.0077; II, 0.0069; III, 0.0077; IV, 0.0101; V, 0.0098.

These amalgams were stored and transferred in the absence of oxygen.

**Electrodes with Lead Iodide, Bromide and Chloride.**—The three lead halides, purified by recrystallization, were used in cells of the type Pb(amalg.), PbX<sub>2</sub>(solid), KX, N.E., all of which gave extremely satisfactory readings. The results with lead iodide are given in Table II, the first column showing the results for lead iodide in potassium iodide (0.1 *M*), with amalgam I; the second, the same electrode with amalgam II; the

TABLE II.

KI (0.1 <i>M</i> ) amalg. I.	KI (0.1 <i>M</i> ) amalg. II.	KI (0.01 <i>M</i> ) amalg. I.	KI (0.01 <i>M</i> ) amalg. II.
0.5737	0.5744	0.5201	0.5208
0.5736	0.5744	0.5200	0.5208
0.5736	0.5743	0.5203	0.5208
0.5735	0.5744	0.5201	0.5206
0.5736	0.5744	0.5202	0.5209
0.5735	0.5745	0.5201	0.5210
0.5736	0.5744	0.5199	0.5208
0.5736	0.5743	0.5201	0.5209
0.5735	0.5744	0.5202	0.5207
0.5736	0.5744	0.5199	0.5208
0.5738	0.5742	0.5201	0.5210
0.5734	0.5744	0.5201	0.5207

<sup>1</sup> Getman, THIS JOURNAL, 38, 792 (1916).

third, lead iodide in potassium iodide (0.01 *M*) with amalgam I, and the fourth the same with amalgam II. Each row shows the reading of a separate electrode about one hour after setting up.

Equally constant and reproducible values were obtained with lead bromide in potassium bromide (0.1 *M*) and lead chloride in potassium chloride (0.1 *M*) and we shall not take the space to give the detailed measurements, but shall give at once the final values for these cells and for those containing lead iodide, of which a part have been given in detail above. To each observed e. m. f. is added the difference in potential between the amalgam used and solid lead. We have then

$$\text{Pb, PbI}_2, \text{ KI}(0.01 \text{ } M), \text{ N.E.}; \text{ E} = 0.5812 \quad (1)$$

$$\text{Pb, PbI}_2, \text{ KI}(0.01 \text{ } M), \text{ N.E.}; \text{ E} = 0.5277 \quad (2)$$

$$\text{Pb, PbBr}_2, \text{ KBr}(0.1 \text{ } M), \text{ N.E.}; \text{ E} = 0.4979 \quad (3)$$

$$\text{Pb, PbCl}_2, \text{ KCl}(0.1 \text{ } M), \text{ N.E.}; \text{ E} = 0.4862. \quad (4)$$

**Measurements with Lead Sulfate.**—It seemed highly desirable to study electrodes of lead and lead sulfate in dilute sulfuric acid, not only for the sake of acquiring additional information regarding the normal potential of lead but also for the sake of determining the free energy of dilution of sulfuric acid by means of the cell  $\text{Pb, PbSO}_4, \text{ H}_2\text{SO}_4, \text{ H}_2$ . The free energy of dilution of sulfuric acid has been measured by Lewis and Lacey<sup>1</sup> by means of a similar cell, using mercury and mercurous sulfate, but at high dilutions this method fails on account of the solubility of mercurous sulfate. The greater insolubility of lead sulfate offers an opportunity of extending the measurements into more dilute solutions.

Unfortunately although we have attempted in a great variety of ways to utilize this electrode, we have had no success. Dissolved air which does not appreciably affect the cells which we have previously described, exerts here a great influence. For this reason measurements were made in entire absence of air but still without success. It occurred to us that the concentration in the neighborhood of the electrode might be changing because of the solution of the metal. For this reason a rather elaborate apparatus was devised, by which dilute sulfuric acid mixed with solid lead sulfate was allowed to flow over electrodes of solid lead amalgam. But in this case also irregularities of the order of 0.01 volt appeared. It seems that the solution of lead sulfate in dilute sulfuric acid is so slow a process that other factors which influence the concentration, such as the rate of reaction between lead and sulfuric acid, play a preponderating role.

**Solubility of Lead Iodide.**—Some of the lead iodide was shaken with doubly distilled water in the thermostat at 25°, and at the end of two days a liter of the solution was drawn through a filter and analyzed by precipi-

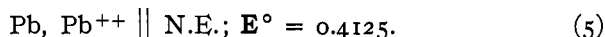
<sup>1</sup> Lewis and Lacey, *THIS JOURNAL*, 36, 804 (1914).

tating silver iodide and weighing. Three determinations gave, respectively, 0.00164, 0.00166, 0.00164 mol per liter. These results agree well with the value obtained by Lichty,<sup>1</sup> who found 0.00165, which we shall accept as correct.

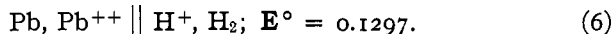
**The Solubility Product.**—From the measurements of Noyes and Woodworth,<sup>2</sup> who determined the conductivity of saturated lead iodide at 25°, the concentration of Pb<sup>++</sup> is 0.87 times the above value or 0.00144, provided that the only ions present are Pb<sup>++</sup> and I<sup>-</sup>. It certainly seems safe to assume that in this very dilute solution the amount of intermediate ion is very small, and moreover that the activity or corrected concentration of the ions is measured by the conductivity. We have therefore (Pb<sup>++</sup>)(I<sup>-</sup>)<sup>2</sup> = 0.00144 × (0.00288)<sup>2</sup> = 11.9 × 10<sup>-9</sup> as the true solubility product. Therefore in any solution whatever that is in equilibrium with solid PbI<sub>2</sub>, the product of the corrected concentration or activity of Pb<sup>++</sup> by the square of the activity of I<sup>-</sup> will be this same solubility product.

**The Normal Electrode Potential of Lead.**—Taking the corrected degree of dissociation<sup>3</sup> of potassium iodide (0.1 *M*) as 0.78 the concentration of I<sup>-</sup> is 0.078, and therefore from the solubility product given above we find for the corrected concentration of Pb<sup>++</sup> when potassium iodide (0.01 *M*) is saturated with lead iodide, the value 1.96 × 10<sup>-6</sup>.

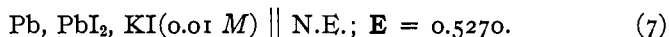
We may now calculate immediately E°, the normal potential of lead, from the equation E = E° - RT/2F ln 1.96 × 10<sup>-6</sup>. E is 0.5182 from Cell 1 and therefore, taking the liquid potential KI(0.1 *M*), KCl(0.1 *M*) as zero,



This is the value against the normal calomel electrode. Against the normal hydrogen electrode it is 0.4125 - 0.2828,<sup>4</sup> or



A similar calculation may be made from Cell 2. Here the measured e. m. f. contains a small liquid potential KI(0.01 *M*), KCl(0.1 *M*), which is undoubtedly equal to the potential KCl(0.01 *M*), KCl(0.1 *M*), namely 0.0007.<sup>5</sup> We have then



Taking the degree of dissociation of KI(0.01 *M*) as 0.93, the concentra-

<sup>1</sup> Lichty, *THIS JOURNAL*, 25, 469 (1903).

<sup>2</sup> Noyes and Woodworth, *Z. physik. Chem.*, 26, 152 (1898).

<sup>3</sup> The most recent values for the corrected degrees of dissociation which we shall use here will shortly be discussed in another paper.

<sup>4</sup> This value for the difference between normal hydrogen and normal calomel electrodes will be fully discussed in a paper about to appear by Lewis, Sebastian and Brighton.

<sup>5</sup> Lewis and Randall, *THIS JOURNAL*, 36, 1975 (1914).

tion of  $\text{Pb}^{++}$ , calculated from the solubility product is  $1.34 \times 10^{-4}$ . Hence

$$\text{Pb, Pb}^{++} \parallel \text{N.E.}; \mathbf{E}^{\circ} = 0.4125. \quad (5)$$

$$\text{Pb, Pb}^{++} \parallel \text{H}^+, \text{H}_2; \mathbf{E}^{\circ} = 0.1295. \quad (6)$$

The complete identity of the values of  $\mathbf{E}^{\circ}$  from Cells 1 and 2 is an extremely satisfactory check upon our experimental work, but it does not prove the correctness of the solubility product of lead iodide. The only chance of error in our value for the normal lead potential lies in the possibility that even in so dilute a solution as that of lead iodide in water the ordinary methods of calculating the solubility product may be slightly incorrect.

**The Solubility Products of Lead Bromide and Lead Chloride.**—Reversing the above procedure and using the value obtained for the normal potential of lead we may calculate from Cells 3 and 4 the true solubility products of lead bromide and lead chloride. Taking the degree of dissociation of potassium bromide and potassium chloride (0.1 *M*) as 0.78 we find for the concentration of  $\text{Pb}^{++}$  0.00129 in Cell 3 and 0.00322 in Cell 4. Adding to the concentration of halide ion from potassium halide twice the concentration of  $\text{Pb}^{++}$  we find for the true solubility products  $8.46 \times 10^{-6}$  for lead bromide and  $2.29 \times 10^{-5}$  for lead chloride.

If, however, we should proceed in the ordinary way to calculate these solubility products we should multiply the solubility<sup>1</sup> of  $\text{PbBr}_2$  (0.0264) and that of  $\text{PbCl}_2$  (0.0388) by the values of  $\lambda/\lambda_0$  (0.62 and 0.58) and take the products as equal to the concentration of  $\text{Pb}^{++}$  in the two cases. Then taking the concentration of halide ion as twice that of  $\text{Pb}^{++}$ , the solubility products are  $1.77 \times 10^{-5}$  and  $4.51 \times 10^{-5}$ , each of which is more than twice the true solubility product obtained above. It may be seen from these figures what enormous errors may appear in the activity of the ions of uni-bivalent salts when they are calculated from conductivity data on the assumption of no intermediate ions. We hope that it will be possible in the near future, with the aid of further data such as we have presented here, to calculate the activities of all the ions present in such solutions.

**Temperature Coefficients and Heats of Reaction.**—The heat of solution in mercury has been determined through measurements of e. m. f. for zinc,<sup>2</sup> cadmium,<sup>2</sup> sodium,<sup>3</sup> potassium,<sup>4</sup> and lithium.<sup>5</sup> To these we may add the heat of solution of lead from measurements of the difference

<sup>1</sup> Lichty, *THIS JOURNAL*, 25, 469 (1903); Von Ende, *Z. anorg. allgem. Chem.*, 26, 162 (1901); Noyes, *Z. physik. Chem.*, 9, 623 (1892).

<sup>2</sup> Richards and Lewis, *Proc. Amer. Acad.*, 34, 87 (1898).

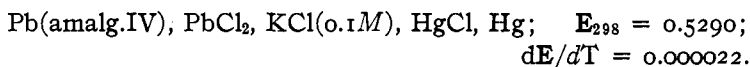
<sup>3</sup> Lewis and Kraus, *THIS JOURNAL*, 32, 1459 (1910).

<sup>4</sup> Lewis and Keyes, *Ibid.*, 34, 119 (1912).

<sup>5</sup> Lewis and Keyes, *Ibid.*, 35, 340 (1913).

in potential between lead and lead amalgam. A large number of measurements with solid lead and amalgam IV gave as the difference in potential 0.01016 at 25° and 0.00892 at 20°. Similar measurements with amalgam V gave 0.00979 at 25° and 0.00866 at 20°. From each set we may calculate the heat of solution of lead in mercury by means of the Gibbs-Helmholtz equation. The first gives 2940 and the second 2650 calories as the heat absorbed when one mol of lead dissolves in the dilute amalgam. The difference is probably not due to a difference in the concentrations of amalgams but to a magnification of small errors due to the unusually large temperature coefficient and the small temperature range. Since this calculation was made we find that Brönsted (*loc. cit.*) has made similar measurements and found the heat absorbed when one mol of lead dissolves in a dilute amalgam to be 2700 cal. This result is between the two just given, and since Brönsted used a much wider temperature range, we shall take his value as correct.

We have also measured the temperature coefficient of the cell



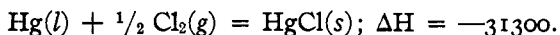
Hence, from the Gibbs-Helmholtz equation



We have found above



From the perfectly concordant calorimetric measurements of Nernst<sup>1</sup> and of Varet,<sup>2</sup>

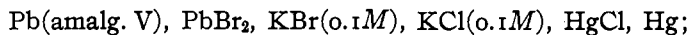


Combining these three equations we find,

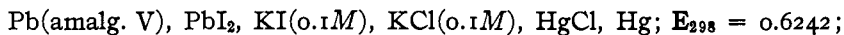


This is in complete accord with the value obtained by Berthelot, namely, -83900, while Thomsen obtained -82800.

For the sake of calculations which will be made in another place we have also determined the temperature coefficient of two cells involving lead bromide and lead iodide.



$$E_{298} = 0.5410; \quad dE/dT = -0.00024.$$



$$dE/dT = -0.00017.$$

### Summary.

An old sample of pure stick lead gives the same potential as lead freshly

<sup>1</sup> Nernst, *Z. physik. Chem.*, **2**, 23 (1888).

<sup>2</sup> Varet, *Ann. chim. phys.*, **8**, 102 (1896).

deposited by electrolysis either upon lead or upon platinum. A theory is offered for the non-reproducibility of certain solid electrodes.

The potential of solid lead in the presence of solid lead halides and solutions of the corresponding potassium halides was measured against the normal calomel electrode. From the measurements with lead iodide the normal electrode potential of lead is found to be 0.4125 against the normal calomel, and 0.1295 against the normal hydrogen electrode.

The solubility of lead iodide has been redetermined, and from the e. m. f. measurements the true solubility products of lead bromide and lead chloride are obtained and shown to differ greatly from those which would be calculated by ordinary methods.

From measurements of temperature coefficient of e. m. f. the heat of solution of lead in mercury and the heat of formation of lead chloride have been determined.

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[CONTRIBUTION FROM THE INSECTICIDE AND FUNGICIDE LABORATORY, MISCELLANEOUS DIVISION, BUREAU OF CHEMISTRY.]

### THE DECOMPOSITION OF DILEAD ARSENATE BY WATER.

By C. C. McDONNELL AND J. J. T. GRAHAM.

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Dilead arsenate, largely on account of the fact that it is very slightly soluble in water, is extensively employed as an insecticide for use on plants. Notwithstanding the fact that this lead arsenate is but very slightly soluble in water, its use often produces serious burning when applied to tender foliage. Although this is due in many cases, as shown by Headden,<sup>1</sup> and Haywood and McDonnell,<sup>2</sup> to the decomposition of the lead arsenate by dissolved salts in the water used in applying the material, still burning of the foliage has been noted even when the water employed was pure. Volck<sup>3</sup> states that lead hydrogen arsenate may be completely transposed to trilead arsenate by the prolonged action of fog, dew and rain. Tartar and Robinson,<sup>4</sup> however, were unsuccessful in their endeavor to verify Volck's statement. On account of the divergence of opinion on the subject, and in view of its economic importance, we were led to make this investigation.

Pure dilead arsenate, in the form of a fine amorphous powder, was prepared by adding to a solution of lead nitrate a solution of monopotassium arsenate in excess. The precipitate was separated by filtration and thoroughly washed.

Calc. for  $Pb_2HAsO_4$ :  $As_2O_5$ , 33.11%;  $PbO$ , 64.29%. Found:  $As_2O_5$ , 33.11%;  $PbO$ , 63.93%.

The first set of experiments was carried out in the following way: Eight

<sup>1</sup> Colo. Exp. Sta., *Bull.* 131, 21 (1908).

<sup>2</sup> Bur. Chem., *Bull.* 131, 46 (1910).

<sup>3</sup> *Science*, 33, 868 (1911).

<sup>4</sup> THIS JOURNAL, 36, 1850 (1914); Oregon Ag. Exp. Sta., *Bull.* 128, 15 (1915).