

the formation of a more electropositive group by combination of the trimethyl tin group with the solvent. It is pointed out that the properties of trimethyl tin chloride correspond closely to the properties of methyl iodide and more particularly to those of the halogen acids.

5. The properties of the trimethyl tin group and of its compounds may be accounted for on the basis of the electro-affinity of this group. The analogy which this group bears to hydrogen is pointed out.

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THE FREE ENERGY AND HEAT OF FORMATION OF LEAD MONOXIDE

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Introduction

The purpose of this investigation was to determine the change in the free energy and heat content when lead oxide (PbO) is formed from its elements at 25°.

Apparently no measurements have yet been made from which the free energy of lead oxide may be accurately obtained. High-temperature equilibria would doubtless be complicated by the formation of other oxides of lead and always involve a more or less unreliable extrapolation to standard temperature on account of inaccurate heat data. Lewis and Randall² have attempted to calculate the free energy of lead monoxide from solubility measurements and molal free energies but obtain a very uncertain value. As the results of Berl and Austerweil³ show, in solutions of lead monoxide there is considerable formation of complex ions such as PbOH⁺, so that the activity of the lead ion would be difficult to estimate even in very dilute solutions. Lewis and Randall² have also pointed out the probable uncertainty in the thermochemical value of the heat of formation of lead monoxide and the excessive discrepancy between their approximate value of its free energy and that obtained by using low-temperature specific-heat data, heats of reaction, and the constant entropy principle (the so-called "third law of thermodynamics").

Since lead oxide is only slightly soluble in dilute alkaline solutions, a measurement of the electromotive force of cells such as H₂(g) | dil. alkaline solution | PbO(s) + Pb(s) should give directly a measure of the free-energy change in the reaction H₂(g) + PbO(s) = Pb(s) + H₂O(l). A combina-

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² Lewis and Randall, "Thermodynamics," McGraw-Hill Co., New York, 1923, p. 497.

³ Berl and Austerweil, *Z. Elektrochem.*, **13**, 165 (1907).

tion of the electromotive-force measurements with the known value of the free energy of liquid water would give the free-energy content of $1\text{PbO}(s)$.

In view of the unreliability of the thermochemically determined heat of formation, we have obtained the heat of the above reaction from the temperature coefficient of the electromotive force of the above-mentioned cells. This, when combined with the known heat of formation of liquid water, gives the desired heat of formation. The possession of the requisite low-temperature specific data, together with the free energy and heat of formation of lead oxide permits a further test of the "third law."

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Preparation of Materials and Solutions

We prepared for use in our cells red lead monoxide, which is the stable form at ordinary temperatures.⁴ The yellow oxide and also the hydroxide, in contact with alkaline solutions, slowly change over to the stable red form. A fine, crystalline, dark red oxide was obtained by slowly adding crystals of pure lead acetate to a boiling, concentrated solution of sodium hydroxide from which the carbonate had been removed by the addition of a small amount of barium hydroxide. The oxide thus obtained was thoroughly washed with water and dried in a vacuum over sulfuric acid.

Lead was plated on platinum spirals from a solution of pure lead oxide in strong perchloric acid containing a small amount of Witte's peptone. This gave a light gray, closely-adhering deposit free from occlusions. Finely divided lead was prepared by fusing pure lead carbonate with pure sodium cyanide in a porcelain dish, and filing the button thus obtained.

Barium hydroxide solution was used as electrolyte, since it is more easily obtainable pure than are the alkali hydroxides and also because it remains free from dissolved carbonate. The solution was made from a high grade of the pure crystallized salt of commerce.

Air was carefully excluded from all solutions and from the cell by the use of glass flasks fitted with sealed-on outlet tubes and connected to a supply of nitrogen.

Apparatus

One of the chief difficulties experienced with cells which depend upon the saturation of a solution with a solid lies, we believe, in the slowness of the approach to saturation and of the removal of oxygen. This can, however, be obviated by efficient stirring of the solution. We have, therefore, used an automatic pump which saturates and stirs the solution di-

⁴ For a discussion of the relative stabilities of the various forms of lead oxide, their solubilities, etc., see Abegg, "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, 1909, III [2] 673 ff. and 677 ff.

rectly in the cell without contact of the solution with air or with other than glass apparatus.

The complete cell, with the circulating pump attached, is shown in Fig. 1.

Referring to the diagram, the glass tube CC is fitted with an inner tube BB in which slides a loosely-fitting plunger P consisting of strips of transformer iron completely enclosed in a glass tube. When the electromagnet AA is energized (by an automatic current-interrupter not shown in the figure) the glass plunger P rises rapidly, forcing the liquid which completely fills the interior of the apparatus, up through the inner tube and down the annular space between CC and BB, out at D, through the glass wool plug E, through the mass of lead and lead oxide at F, out again through the glass wool plug at the top and side of the lead cell T, opening the float valve H which is ground to a seat

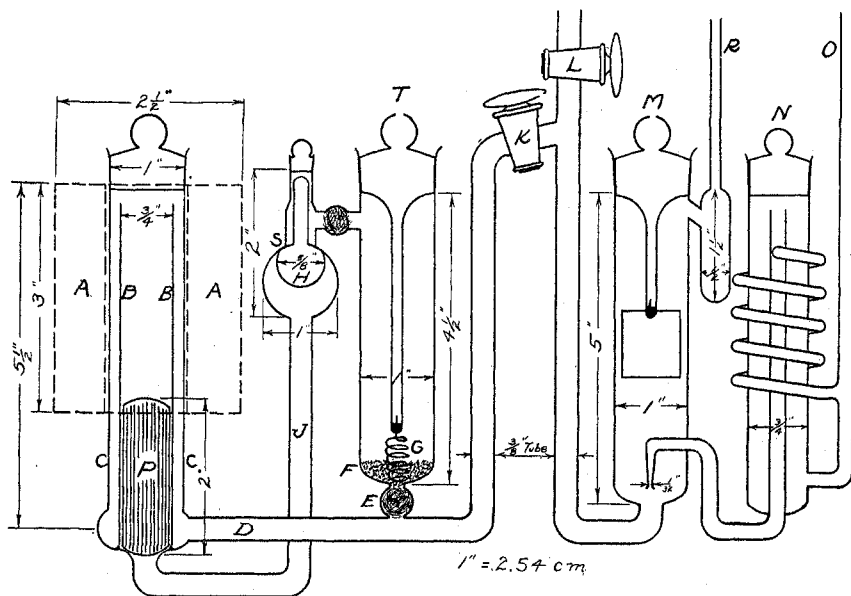


Fig. 1

at S, down the tube J and back to the bottom of the plunger P. The current through the electromagnet having been broken, the plunger P slowly sinks to the bottom of the tube BB allowing the solution to pass between it and the walls of the tube, the reseating of the float valve H preventing backward flow of the liquid. The cycle is repeated at intervals of 5 or 6 seconds, pumping about 6 cc. of solution per stroke. In a short time this whole section of the apparatus is filled with a fine silt of the oxide which exposes a large surface and quickly saturates the solution.

The hydrogen saturator and half-cell are shown at the extreme right of the figure. The hydrogen, entering at O, passes around the spiral in small bubbles which emerge from the top of the spiral, the solution returning to the reservoir N and the gas passing through the central tube and into the hydrogen cell M. This type of saturator gives long contact of the gas with the liquid, avoids spray, circulates the solution in the reservoir, and offers little back pressure to the hydrogen generator. The trap at the bottom of the outlet tube R prevents moisture condensed from the escaping hydrogen from flowing back into the cell.

The hydrogen for the cell was generated by electrolysis of a potassium hydroxide solution contained in a U-tube, the oxygen electrode of which was placed well up in the side arm to prevent diffusion of oxygen over to the hydrogen side. The hydrogen passed over a platinum coil electrically heated to redness to remove traces of oxygen, and over phosphorus pentoxide to remove water, then through a fine capillary tube which regulated the flow of hydrogen through the saturator and cell.

The cells were kept in a bath of light oil (commercially known as "Transil Oil"), the temperature remaining constant to 0.02° as determined by a thermometer calibrated by the Bureau of Standards.

The electromotive forces were measured with a potentiometer of a modern type against a Weston standard cell.

Measurement of the Electromotive Forces

We were careful to avoid the use of the lead obtained by electrolysis in the form of "lead tree," since this type of deposit is hard to wash free from traces of impurities and doubtless contains much occluded salt from the electrolyzing bath. The presence of carbonate is also undesirable, for although lead carbonate is very slightly soluble in water, it is doubtless somewhat soluble in alkaline solutions. Thus, when lead acetate solution was added to a solution of commercial sodium hydroxide there was no precipitate of lead carbonate, while barium carbonate precipitated in considerable amount when a solution of barium hydroxide was added.

The individual cells were run for a period of several days. They showed variations of less than 0.1 mv. for many hours after the cells had come to equilibrium. Each cell was alternately pumped out and allowed to stand until finally further pumping produced no change in the measured electromotive force.

The lead half-cell contained an excess of solid lead oxide mixed with finely divided lead, contact with which was made through platinum leads plated with lead as previously described.

Final values of the measured electromotive forces are presented in Table I. The headings are for the most part self-explanatory. The

TABLE I
OBSERVED ELECTROMOTIVE FORCES

Cell	Temp. $^\circ\text{C}.$	Moles $\text{Ba}(\text{OH})_2$ per kg. H_2O	Pressure of hydrogen	E.m.f. obs.	E.m.f. when H_2 is 1 atm.	Best value
1	25	0.2242	722	0.2487	0.2494	
2	25	.0766	722	.2487	.2494	
3	25	.2478	721	.2487	.2494	
4	25	.1488	724	.2486	.2492	0.2494
5	45	.2242	673	.2414	.2431	
6	45	.0766	674	.2412	.2429	
7	45	.2478	672	.2416	.2433	
8	45	.1488	676	.2414	.2430	0.2430

hydrogen pressure given has been corrected for the observed barometer reading, the vapor-pressure of water at the respective temperatures, and a head of 1 or 2 cm. of water above the electrodes in the hydrogen half-cell. Each value of "e.m.f. observed" is the value obtained for a separate filling of the cell with new solution and materials.

Calculations

From the "best values" of our electromotive forces we find for the reaction $\text{PbO(s)} + \text{H}_2(1 \text{ atm.}) = \text{H}_2\text{O(l)} + \text{Pb(s)}$ the following free energy values: at 298.1° K. , $-\Delta F = 11,509 \text{ cal.}$; at 318.1° K. , $-\Delta F = 11,214 \text{ cal.}$ Taking the free energy of $\text{H}_2\text{O(l)}$ at 298.1° K. as $-56,560 \text{ cal.}$,⁵ we calculate the free energy of PbO(s) at this temperature to be $-45,050 \text{ cal.}$ The difference between the free energy of pure water and that of water in the barium hydroxide solutions is hereby neglected; but this is permissible, since the vapor pressure of even a 0.25 molal solution certainly does not differ from that of water by more than 2%; and this corresponds to a free-energy difference of only 12 calories.

This free energy of lead oxide differs by about 4000 cal. from the value ($-41,000 \text{ cal.}$) previously derived by Lewis and Randall from available solubility data for lead oxide and the electrode potentials of lead and oxygen.

Using the integrated Gibbs-Helmholtz equation, $\frac{E_2}{T_2} - \frac{E_1}{T_1} = \frac{\Delta H}{NF} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

whereby ΔH is assumed constant over the temperature interval involved (ΔC_p is only 6.0 cal. per degree), and substituting our measured electromotive forces, and the temperatures 318.1° and 298.1° , we calculate ΔH for the above reaction to be equal to $-15,910 \text{ cal.}$ Taking the heat content of liquid water at 25° C. to be $-68,270 \text{ cal.}$,⁶ we calculate the heat of formation of PbO(s) from its elements at 25° C. to be $-52,360 \text{ cal.}$

To obtain ΔH as a temperature function, this value of the heat of formation of 1 PbO at 25° may be combined with the following expressions for the heat-capacities at constant pressure: for 1 Pb , $6.01 + 0.00085 T + 0.00000154 T^2$; for 1 PbO , 11.58; for $\frac{1}{2}\text{O}_2$, $3.25 + 0.0005 T$. The expression for 1 Pb is derived from the values of the specific heats, 0.03083 at 18° and 0.03155 at 100° , obtained by Jaeger and Diesselhorst⁷ and the value 0.03380 at 300° obtained by Naccari.⁸ The expression for 1 PbO is derived from the value of the specific heat 0.0519 at 23° obtained by Russel,⁹ and that for $\frac{1}{2}\text{O}_2$ is taken from Lewis and Randall.¹⁰ These lead to the following expressions for the heat-content and free-energy increases ac-

⁵ Ref. 2, p. 485.

⁶ Ref. 2, p. 477.

⁷ Jaeger and Diesselhorst, *Wiss. Abh. Phys.-Techn. Reichsanst.*, **3**, 269 (1900).

⁸ Naccari, *Atti acad. sci. Torino*, **23**, 107 (1887-88).

⁹ Russel, *Phys. Z.*, **13**, 59 (1912).

¹⁰ Ref. 2, p. 80.

companying the formation of 1 PbO from its elements at temperatures between 0°C., and the melting point of lead (327°C.):

$$\begin{aligned}\Delta H &= -52,980 + 2.32 T - 0.000675 T^2 - 0.000000257 T^3 \\ \Delta F &= -52,980 - 2.32 T \ln T + 0.000675 T^2 + 0.000000128 T^3 + 39.62 T\end{aligned}$$

Lewis and Randall (Ref. 2, p. 497) give the value of $T \Delta S$, calculated from low-temperature specific-heat data with the aid of the constant-entropy principle for the reaction $\text{Pb} + \frac{1}{2}\text{O}_2 = \text{PbO}$ at 25°C. as -6900 cal. Subtracting this value from our value for the heat of formation of lead oxide we calculate the free energy of lead oxide at 25° to be -45,460. This value is 410 cal. less than the more accurate value based upon our electromotive-force measurements; but this is about the usual order of agreement between the free-energy value calculated upon the assumption of the constant-entropy principle and that obtained by chemical methods.¹¹

Summary

1. An apparatus has been described for effectively saturating and stirring the electrolyte in a cell, thereby decreasing greatly the time taken for a cell containing a solid salt to come to equilibrium.

2. Electromotive-force measurements upon the cell, $\text{H}_2(\text{g}) \mid \text{Ba}(\text{OH})_2 (0.0766-0.2242 M) \mid \text{PbO}(\text{s}) + \text{Pb}(\text{s})$, give the free energy of PbO(s) as -45,050 cal. at 25°, when the free energy of liquid water at this temperature is taken as -56,560 cal.

3. From the temperature coefficient of the electromotive force of this cell the heat of formation of PbO(s) at 25° is calculated to be -52,360 cal. when the heat of formation of liquid water at 25° is taken as -68,270 cal. Temperature-functions for its heat-content and free energy have been derived.

4. From the above value for the heat of formation of PbO(s) and the value of its entropy of formation derived by Lewis and Randall from the constant-entropy principle, the free energy of PbO(s) at 25° is found to be -45,460 cal., which is as close to our more accurate experimental value as are most of the free energies computed by this method.

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¹¹ See Lewis and Gibson, *THIS JOURNAL*, **39**, 2554 (1917).