2. The lattice parameter was found to vary linearly with the mole per cent. of the components.

3. Ôtani's curve is believed to be the correct equilibrium solidus for this system.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

The Potentials of the Lead Oxide Electrodes in Alkaline Solution[1]

BY LYLE VERNON ANDREWS AND D. J. BROWN

Glasstone,[2] who measured the lead oxide–lead dioxide electrode, worked with normal solutions of sodium hydroxide only. Since lead oxide acts as an acidic oxide in concentrated alkaline solution, the activity of the sodium hydroxide in the two half cells would be different. It has been shown by Glasstone[2] and Milbauer[3] that lead dioxide in contact with an alkaline solution of lead oxide reacts to form the oxide commonly called red lead, Pb_3O_4 which has also been shown by Glasstone to be lead orthoplumbate, Pb_2PbO_4.

In view of these facts it would seem impossible to obtain a standard potential using lead oxide and lead dioxide in the alkaline half cell. It should, however, be possible to make the measurement in two steps, using lead orthoplumbate as the intermediate product and calculate the oxidation potential.

For a reference electrode, we decided upon the $Hg–HgO(s)–OH^-$ electrode.[4] The two cells proposed are

$$\text{Hg-HgO(s)-PbO(s)-KOH-PbO(s)-Pb}_3\text{O}_4\text{(s)-Pt} \quad (1)$$
$$\text{Hg-HgO(s)-KOH-PbO}_2\text{(s)-Pb}_3\text{O}_4\text{(s)-Pt} \quad (2)$$

When an electron current passes through the cells from right to left, the following reactions take place

$$Hg + Pb_3O_4 \rightleftharpoons HgO + 3PbO$$
$$2Hg + 3PbO_2 \rightleftharpoons 2HgO + Pb_3O_4$$

These equations indicate that the electromotive force of the cells should be independent of the concentration of the alkali.

Lead dioxide was deposited on platinum foil, made rough either by coating with platinum black and then heating in a blast lamp, or by treating the smooth foil with hot aqua regia for a few minutes. The roughened platinum was cleaned with hot concentrated nitric acid, followed by a half hour treatment with hot half normal potassium hydroxide solution. The solution from which the lead dioxide was deposited, contained about 0.5% of lead nitrate and was about 2 normal in nitric acid. A current density of approximately 0.003 amp./sq. cm. was used.[5]

Lead orthoplumbate was prepared by treating lead dioxide, deposited on platinum foil, with a solution 0.5–1.0 normal in potassium hydroxide and almost saturated with lead oxide, for ten to fifteen hours at about 80°. These conditions have been shown by Glasstone[2] and Milbauer[3] to give lead orthoplumbate. The deposit adheres firmly, and forms a coating over the lead dioxide.

Lead oxide, red variety, was precipitated from a hot 12 normal solution of potassium hydroxide[6] by adding powdered lead acetate to the hot alkali. The oxide was washed by decantation with hot 10 normal potassium hydroxide, then washed thoroughly and repeatedly with hot distilled water and dried over sulfuric acid in a vacuum desiccator. Analysis for lead[7] gave 99.7% PbO. A small amount of water was evolved when the oxide was heated strongly.

Potassium hydroxide solution was prepared as described by Ming Chow.[4] Doubly distilled water, distilled in an all-Pyrex still, first from alkaline permanganate and then redistilled from the clean still, was used to prepare all solutions.

Saturated solutions of the oxides were made in 200-ml. round-bottomed, long-necked flasks, fitted with ground-glass stoppers and provided with rubber caps to prevent carbon dioxide from working past the ground-glass stoppers. These flasks were almost filled with solvent, an excess of the solid oxide added and then shaken in a constant temperature air-bath at 25.0 ± 0.2°.

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(1) Original manuscript received January 3, 1933.

(2) Glasstone, *J. Chem. Soc.*, **121**, 1456 (1922); 1469 (1922).

(3) Milbauer, *Chem. Zeit.*, **38**, 587 (1914).

(4) Ming Chow, THIS JOURNAL, **42**, 488 (1920).

(5) Smith, THIS JOURNAL, **27**, 1287 (1905); Fischer and Schleicher, "Elektroanalytisch Schnellmethoden," zweite Auflage, 1926, p. 243.

(6) Smith and Woods, *ibid.*, **45**, 2632 (1923).

(7) Brown, Moss and Williams, *Ind. Eng. Chem., Anal. Ed.*, **3**, 134 (1931).

All potentials were measured with a Leeds and Northrup type K potentiometer. The standard cell was checked frequently against a new cell, checked by the Bureau of Standards. Electrode vessels were kept in a thermostat bath at 25.00 ± 0.05°.

The experimental half cell for the measurement of the lead oxide–lead orthoplumbate electrode was made by dipping a platinum foil coated with electrolytic lead dioxide into a solution of 0.5–1.0 normal potassium hydroxide almost saturated with lead oxide and allowing it to stand at a temperature of 80° for ten to fifteen hours. The lead oxide reacts with the exposed lead dioxide to form lead orthoplumbate. The electrode becomes distinctly red in color. It was allowed to stand in a solution similar to the one to be used in the half cell. It was then transferred to the half cell which contained a dilute solution of potassium hydroxide which had previously been saturated with lead oxide. In a very few minutes such an electrode reached a value within one or two millivolts of its final value. Sometimes the initial value was a little below and sometimes a little above the final value. The final value was usually reached in less than twenty-four hours. It then remained practically constant for a number of days.

Two reference and two experimental half cells were used in each set of cells. In some cases a duplicate set of cells was made up and measured so as to give four values. All actual measurements are included. The same solution was used throughout the cell so as to eliminate junction potentials.

This electrode was very satisfactory in the range of concentration shown in Table I. In concentrations of potassium hydroxide 0.01 molal and greater potentials showed a greater variation and in general gave a lower value.

Data for this series are given in Table I.

TABLE I

E. M. F. OF CELLS Hg–HgO(s)–PbO(s)–KOH–PbO(s)–Pb_3O_4(s)–Pt

Molality of KOH	E_1^a	E_1^b	E_1^c	E_1^d	E_1
0.0010	0.1502	0.1503	0.1504	0.1508	0.1504
.0025	.1505	.1506			.1506
.0050	.1504	.1495	.1507	.1502	.1502
.0100	.1505	.1480	.1495	.1495	.1495

From Table I the value of the cell is given as 0.1504 ± 0.0005 volt. The reference electrode as measured by Ming Chow is 0.0984 volt. The value of the PbO(s)–Pb_3O_4(s)–OH^- electrode is therefore +0.2488 ± 0.0005 volt.

The best results for the lead orthoplumbate–lead dioxide electrode were obtained by saturating the dilute alkaline solutions with the solid oxides by shaking in a flask containing the orthoplumbate deposited on large sheets of platinum foil, and powdered electrolytic lead dioxide which did not tend to form a suspension. When electrodes coated with lead orthoplumbate were inserted in a half cell containing powdered electrolytic lead dioxide and a solution prepared as described above, E rose from an initial value of about 0.18 volt to a value slightly above the final one, and then dropped back. In the case of the solutions more concentrated than 0.01, a large surface of orthoplumbate was necessary or the results were high. The data of this series are in Table II.

TABLE II

E. M. F. OF CELLS Hg–HgO(s)–KOH–PbO(s)–Pb_3O_4(s)–Pt

Molality of KOH	E_2	E_2	E_2	E_2	E_2
0.0010	0.1940	0.1963			0.1951
.0025	.1968	.1957			.1963
.0050	.1965	.1960	0.1994	0.2000	.1980
.0100	.1990	.1975	.1950	.1938	.1963

From the values in Table II the value of the cell is 0.1964 ± 0.001. The potential of the lead dioxide–lead orthoplumbate electrode is therefore equal to +0.295 ± 0.001.

The value E_3° of the cell

Hg–HgO(s)–PbO(s)–KOH–PbO(s)–PbO_2(s)–Pt

may be calculated from E_1° and E_2° by means of the equation

$$E_3^\circ = \frac{E_1^\circ + 2E_2^\circ}{3} = \frac{0.1504 + (2 \times 0.1964)}{3} = 0.1811 \pm 0.001 \text{ volt}$$

The potential of the electrode PbO_2(s)–PbO(s)–OH^- ($\alpha = 1$) is therefore +0.280 ± 0.001 volt.

The free energy changes of the following reactions may be calculated (a) from the measured values of the cells

$$Hg + Pb_3O_4 = HgO + 3PbO$$

$$\Delta F_{298}^\circ = -NE_1^\circ F = \frac{-2 \times 0.1504 \times 96{,}500}{4.183} = -6940 \text{ cal.} \quad (1)$$

$$2Hg + 3PbO_2 = Pb_3O_4 + 2HgO$$

$$\Delta F_{298}^\circ = -NE_2^\circ F = \frac{-4 \times 0.1964 \times 96{,}500}{4.184} = -18{,}120 \quad (2)$$

$$PbO_2 + 2PbO = Pb_3O_4$$

$$\Delta F_{298}^\circ = \frac{-18{,}120 - (2 \times 6940)}{3} = -1400 \quad (3)$$

(b) Using the above values and that accepted by Spencer and Mote[8] for the reaction

$$\begin{aligned}
&HgO = Hg + {}^1/_2O_2 && \Delta F_{298} = 13{,}850 \\
&3PbO + {}^1/_2O_2 = Pb_3O_4 && = -6{,}910 && (4) \\
&Pb_3O_4 + O_2 = 3PbO_2 && = -9{,}580 && (5) \\
&PbO + {}^1/_2O_2 = PbO_2 && = -5{,}500 && (6)
\end{aligned}$$

(c) Using the preceding values and that calculated by Spencer and Mote[8] for the reaction

$$\begin{aligned}
&Pb + {}^1/_2O_2 = PbO && \Delta F_{298} = -\ 45{,}100 \\
&3Pb + 2O_2 = Pb_3O_4 && = -142{,}210 && (7) \\
&Pb + O_2 = PbO_2 && = -\ 50{,}600 && (8)
\end{aligned}$$

Summary

1. The potentials of two electrodes have been measured and the potential of a third electrode calculated from these. The values are

$PbO(s)–Pb_3O_4(s)–OH^-$ $+\ 0.2488 \pm 0.0005$ volt
$Pb_3O_4(s)–PbO_2(s)–OH^-$ $+\ 0.1295 \pm 0.001$ volt
$PbO(s)–PbO_2(s)–OH^-$ $+\ 0.280 \pm 0.001$ volt

2. The free energy changes have been calculated from the measured values of the cells.

LINCOLN, NEBR.

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[8] Spencer and Mote, THIS JOURNAL, **54**, 4618 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Compressibility of Aqueous Solutions

BY EDITH H. LANMAN AND BEVERIDGE J. MAIR

Introduction

The compressibility coefficients of many aqueous solutions of both electrolytes and nonelectrolytes have been determined during the past fifty years, and the data obtained in this field, prior to the year 1919, have been summarized by Cohen and Schut in "Piezochemie." Since that time, accurate determinations of the compressibility of aqueous solutions of various organic substances have been determined at Harvard, but, at the time this work was undertaken, no further work had been done on solutions of electrolytes. The existing data in this field had been obtained at different temperatures over varying pressure ranges, and at random concentrations. It therefore seemed worth while to redetermine the compressibility coefficients of certain inorganic salts and their acids and bases, all at the same temperature, over the same pressure range, and at equivalent concentrations.

The substances chosen were the chlorides and hydroxides of lithium, sodium and potassium, hydrochloric and acetic acids, and potassium acetate. The compressibility of glacial acetic acid was also determined. Determinations were made at three concentrations for each substance: *i. e.*, one mole of substance to twenty-five moles of water, one to fifty, and one to one hundred. All measurements were made at 25° and between 100 and 300 megabars.

Preparation of Materials and Analysis of Solutions.—The salt solutions were made up from Baker analyzed chemicals. It was not considered worth while to recrystallize these substances, since an impurity of several tenths of a per cent. could not cause a change in compressibility which could be detected (*e. g.*, the difference in compressibility of $NaCl\cdot25H_2O$ and $KCl\cdot25H_2O$ is only 0.78×10^{-6}). The concentrations of the chloride solutions were determined by precipitation with silver nitrate, and the more dilute solutions were made up by adding the calculated amount of water to a weighed portion of the standard solution.

The hydrochloric acid was prepared by distilling one to one C. P. acid, and noting the pressure during distillation. The concentration was then computed from the pressure,[1] and verified by precipitation with silver nitrate. This was then diluted by adding the calculated amount of water to give $HCl\cdot25H_2O$ (and $HCl\cdot50H_2O$ and $100H_2O$).

The sodium hydroxide solution was prepared by dissolving the C. P. base in water in a gold dish to prevent contamination by silica. Only a small amount of water was used in order that the less soluble carbonate might remain undissolved. The solution was then filtered, diluted to the approximate concentration desired, and stored in a Pyrex bottle. Carbonate was then tested for by adding definite amounts of barium chloride solution (of known concentration) to samples of the solution. The precipitates were allowed to settle, the supernatant liquids decanted and Ba^{++} tested for by sulfuric acid. The amount of Ba^{++} necessary to precipitate the carbonate was then calculated and added to the sodium hydroxide solution. After allowing the precipitate to settle, the solution was siphoned into a bottle containing carbon dioxide-free air. The solution was at all times protected from contamination with carbon dioxide by means of soda lime. Solutions of potassium hydroxide and lithium hydroxide were prepared in a similar manner.

The concentrations were determined by titrating against the hydrochloric acid, using phenolphthalein as an indicator. Weight burets were used. The more dilute solutions were made up accurately by addition of the calcu-

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[1] Hulett, THIS JOURNAL, **31**, 390 (1909).