has been the basis of forthcoming studies on different aspects of the problem of catalysis of ester saponification in water solution.

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[Contribution from the Eppley Laboratory]

CELLS OF THE STANDARD CELL TYPE WITH LOW ELECTROMOTIVE FORCES

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A standard cell with a low electromotive force would have some advantages over the ordinary standard cell in the measurement of small electromotive forces. Obata[1] has investigated the possibility of using for this purpose the cells

$$\mathrm{Cd(Hg)} \mid \mathrm{CdCl_2.2.5H_2O,\ sat.} \mid \mathrm{CdCl_2.2.5H_2O + PbCl_2,\ sat.} \mid \mathrm{Pb(Hg)} \qquad (1)$$

$$\mathrm{Cd(Hg)} \mid \mathrm{CdI_2,\ sat.} \mid \mathrm{CdI_2 + PbI_2,\ sat.} \mid \mathrm{Pb(Hg)} \qquad (2)$$

Taylor and Perrott[2] set up and measured some cells similar to Cells 1 and 2, the only difference being that they used an unsaturated lead amalgam, 0.72% lead. By combining the electromotive forces of their cells with the electromotive force of the cell

$$\mathrm{Pb} \mid \mathrm{Pb^{++}} \mid \mathrm{Pb\ amalgam,\ 0.72\%};\ E_{25} = 0.0109 \qquad (3)$$

which was measured by Brönsted,[3] and that of the cell

$$\mathrm{Pb} \mid \mathrm{Pb^{++}} \mid \mathrm{Pb(Hg),\ sat.};\ E = 0.0057 + 0.000016\ (t-25) \qquad (4)$$

which was measured by Gerke[4] the electromotive forces of Cells 1 and 2 can be calculated. For Cell 1 at 25° the value 0.1432 volt is obtained from the results of Taylor and Perrott, while Obata found 0.1408 volt. Similarly for Cell 2 at 25° the value 0.1020 volt is obtained from the results of Taylor and Perrott, while Obata found 0.0996 volt. Thus, there is a difference of about 2.2 mv. between the results of Taylor and Perrott and those of Obata for both cells.

Van Ginneken and Kruyt[5] have given as the requirement for a standard cell that, with temperature and pressure constant, both electrode systems must be invariant systems of the same components. The cells of Taylor and Perrott did not conform to this specification because the lead amalgam was not a two phase amalgam. One electrode system, therefore, was not an invariant system. Also, the other electrode system contained no lead. The cells of Obata were not true standard cells because the cadmium-amalgam electrode system contained no lead.

[1] Obata, *Proc. Phys. Math. Soc. Japan* [3], **3**, 64, 136 (1921).

[2] Taylor and Perrott, This Journal, **43**, 486 (1921).

[3] Brönsted, *Z. physik. Chem.*, **56**, 668 (1906).

[4] Gerke, This Journal, **44**, 1697 (1922).

[5] Van Ginneken and Kruyt, *Z. physik. Chem.*, **77**, 744 (1911).

To make Cells 1 and 2 into true standard cells, according to the specification of Van Ginneken and Kruyt, the cadmium amalgam must be replaced by an amalgam saturated with both cadmium and lead. The system cadmium-lead-mercury has been studied by Kremann, Prammer and Helly,[6] who found that within a certain range of compositions the cadmium activity was constant. The author[7] has tried replacing the cadmium amalgam of the Weston standard cell with a cadmium-lead amalgam having a composition within the constant cadmium activity range. The cells were as reproducible as true Weston cells and had an electromotive force 1.13 mv. higher at 25°.

The work described below was undertaken to study the effect of replacing the cadmium amalgam of Cells 1 and 2 with cadmium-lead amalgam.

Preparation of Materials

Two lots of lead amalgam were prepared, both containing 10% of lead. The first was prepared by electrolysis of a saturated lead chloride solution with a mercury cathode and a platinum anode. The lead chloride was prepared by adding redistilled hydrochloric acid solution to a solution of twice-recrystallized lead nitrate. The mercury was passed through a column of mercurous nitrate solution and redistilled at low pressure in a current of air.

The second lead amalgam was prepared by dissolving the required amount of lead in some of the above-described mercury. The lead was prepared by the method of Richards and Wadsworth[8] from the twice-recrystallized nitrate.

The cadmium-lead amalgam was prepared by depositing cadmium by electrolysis in some of the first lead amalgam. By adding small amounts of the above-described mercury and lead, the composition was adjusted to 11% lead, 9% cadmium and 80% mercury, or 10, 15, and 75 atomic per cent., respectively. This composition is within the range in which the cadmium activity is constant.

The cadmium chloride and the cadmium iodide were both recrystallized twice.

The lead chloride and the lead iodide were prepared by precipitation from a solution of the twice-recrystallized nitrate, the first with redistilled hydrochloric acid solution and the second with a solution of recrystallized potassium iodide. Both were recrystallized.

Preparation of the Cells

The cells were set up in glass H-vessels of the type used for Weston cells.[9] The amalgams were melted by heating, and cadmium-lead amalgam was placed in one leg of the vessel and lead amalgam was placed in the other. For the chloride cells some lead chloride was ground in a mortar with some cadmium chloride and was made into a paste with cadmium chloride solution. The paste was placed on top of the lead amalgam to a depth of at least 1 cm. Cadmium chloride crystals ground with some of the saturated solution were placed above the paste and also above the cadmium-lead amalgam. More crystals were then added, and the cells were filled to a point above the cross-arm with saturated cadmium chloride solution. The iodide cells were set up similarly. The

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[6] Kremann, Prammer and Helly, *Z. anorg. Chem.*, **127**, 306 (1923).

[7] Vosburgh, This Journal, **47**, 2531 (1925).

[8] Richards and Wadsworth, *ibid.*, **38**, 223 (1916).

[9] Vosburgh and Eppley, *ibid.*, **45**, 2269 (1923).

cells were usually evacuated to remove air bubbles, and the tops were flushed out with nitrogen and then sealed.

In the preparation of the first group of chloride cells, Cells 407–409, and the first group of iodide cells, Cells 340–342, the precautions previously described[10] for the exclusion of oxygen in the preparation of Weston cells were taken. In the others no attempt was made to protect the materials from the air while the cells were being set up. In the case of the chloride cells this omission seemed to make no difference in the electromotive force, but it might have been the cause of the 0.2 mv. difference between the two groups of iodide cells.

In the first group of chloride cells the electrolyte contained a small amount of hydrochloric acid. The solution was made by saturating a 0.001 *M* hydrochloric acid solution with cadmium chloride. In the other cells the electrolyte was a saturated solution of cadmium chloride, or cadmium iodide, in redistilled water.

The first lead amalgam was used in all except Cells 456–459, in which the second lead amalgam was used.

Electromotive-Force Measurements

The electromotive forces were measured by means of a Leeds and Northrup thermocouple potentiometer. The potentiometer was accurate to 0.02% according to the data of the manufacturer. It was not checked. The standards were the Weston cells used as standards in previous investigations.[11] They were probably accurate to 0.01%. The standards were maintained in an oil thermostat at 25 ± 0.02° throughout the investigation. The experimental cells were kept in an oil thermostat capable of being maintained within 0.01° of the desired temperature. They were always maintained at constant temperature for a period of at least three days before important measurements. Tables I and II give the electromotive forces at 25° over a period of 8 and 9 months, respectively.

Table I

$Cd(Pb, Hg) \mid CdCl_2.2.5H_2O,\ sat. \mid CdCl_2.2.5H_2O + PbCl_2,\ sat. \mid Pb(Hg)$

	Electromotive force, 25°				
Cells	1 month v.	2 v.	4 v.	6 v.	8 v.
407–409	0.13866	0.13869	0.13871	...	0.13807
429–430	.13870	.13869	...	...	.13822
456–459	...	.13873	0.13870	0.13865	...

Table II

$Cd(Pb, Hg) \mid CdI_2,\ sat. \mid CdI_2 + PbI_2,\ sat. \mid Pb(Hg)$

	Electromotive force, 25°				
Cells	1 month v.	3 v.	5 v.	7 v.	9 v.
340–342	0.10082	...	0.10088	0.10088	0.10082
427–428	.10065	0.10065	...	.10056	...

The chloride cells were quite reproducible. The average variation of the nine cells from the mean was about ±0.03 mv., and the maximum variation was 0.13 mv. They were quite constant for a period of 4 to 6 months at least. The first two groups decreased somewhat in electromotive force after a change in temperature to 40° and back to 25°, as indicated by the values in the column of Table I headed 8 months. They

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[10] Vosburgh, This Journal, **47**, 1258 (1925).

[11] See Ref. 10, p. 1256.

became variable after this and one showed definite signs of deterioration.

The iodide cells were not as reproducible as the chloride cells. They did not give evidence of permanent change in electromotive force during the time they were under observation. The average variation from the mean of the 5 cells, when they were 1 month old, was ± 0.08 mv., and the maximum variation was 0.3 mv. The two groups differed by about 0.2 mv.

After constancy was assured at 25°, the temperature of the thermostat was changed successively to 20, 15, 20, 25, 30, 35, 40, 35, 30 and 25°, the cells being maintained at each temperature for 3 days to 2 weeks. The temperatures were measured by means of two platinum resistance thermometers and a mercury thermometer which had been checked by the Bureau of Standards. Temperatures were probably accurately measured to ±0.01°.[12] Several electromotive-force measurements were made at each temperature. The chloride cells showed little hysteresis. After a temperature change, particularly after a decrease, the electromotive force usually changed a few hundredths of a millivolt over a period of 3 or 4 days. The iodide cells showed much more hysteresis. After an increase in temperature the electromotive force became too high. It decreased very slowly and never came to equilibrium in the time allowed before the next temperature change. With a decrease in temperature the effect was the opposite. The hysteresis was more pronounced in Cells 340–342 than in Cells 427–428.

The results of the measurements at different temperatures are given in Table III. Each value is the average of two measurements, one after an increase in temperature and the other after a decrease, except the values at 25, 15 and 40°. At 25° the equilibrium value before the temperature was changed is given, and at 15 and 40° there was only one measurement at each temperature.

Table III

Electromotive Forces at Different Temperatures

	Electromotive force					
Cells	15° v.	20° v.	25° v.	30° v.	35° v.	40° v.
407–409	0.14030	0.13955	0.13872	0.13914	0.13997	0.14082
429–430	.14030	.13953	.13871	.13913	.13998	.14082
340–342	...	.09934	.10082	.10195	.10329	...
427–428	.09800	.09934	.10064	.10192	.10323	.10456

In the case of the iodide cells there was always a difference between the two values at the same temperature because of the hysteresis. In the case of Cells 340–342 this usually amounted to 0.3 mv. to 0.4 mv., but it was less than 0.1 mv. for Cells 427–428. It was obvious that neither of the two values represented the equilibrium condition, but it was assumed that the mean of the two would be approximately the equi-

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[12] See Vosburgh, *J. Optical Soc. Am.*, **12**, 513 (1926).

librium value. Calculated in this way the results for the two groups of iodide cells agreed very well.

Discussion

The Chloride Cell.—If the electromotive force of the cell

$$Cd(Pb, Hg) \mid CdCl_2.2.5H_2O, \text{ sat.} \mid CdCl_2.2.5H_2O + PbCl_2, \text{ sat.} \mid Pb(Hg) \qquad (5)$$

be plotted against temperature, the graph shown in Fig. 1 is obtained. The graph consists of two branches, one of which is a straight line, and the other, the one on the left, is nearly so. The two branches meet at about 26.2°. Below 26.2° the cell has a negative temperature coefficient, and above 26.2° it has a positive one. This is an indication of a transition point of some substance in the cell. According to Dietz[13] and Cohen and Bruins[14] the substance $CdCl_2.2.5H_2O$ is stable between —5 and 34°. Above 34° the monohydrate is the stable form. Fig. 1 gives no evidence of this transition point, the curve being a straight line between 26.2 and 40°.

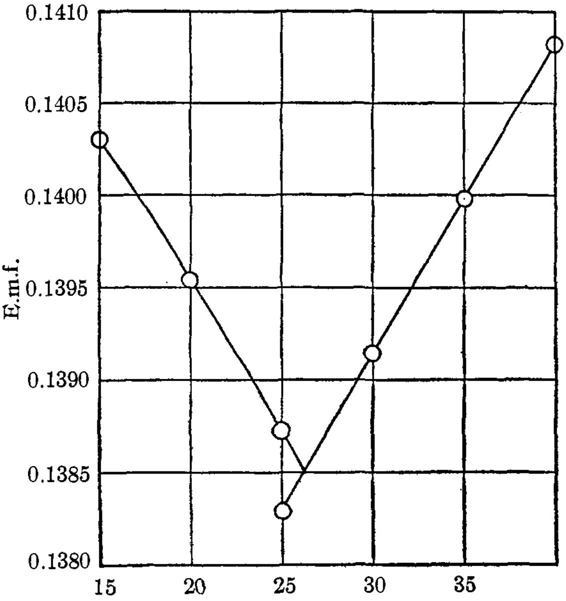

Fig. 1.—Relation between the electromotive force of the cell $Cd(Pb, Hg) \mid CdCl_2.2.5H_2O$, sat. $\mid CdCl_2.2.5H_2O + PbCl_2$, sat. $\mid Pb(Hg)$ and the temperature.

Evidently as the temperature was raised from 25 to 30° transition took place. After the temperature had decreased from 30 to 25°, the

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[13] Dietz, *Z. anorg. Chem.*, **20**, 257 (1899).

[14] Cohen and Bruins, *Verslag Akad. Wetenschappen Amsterdam*, **25**, 739 (1917).

last change in the series of measurements, the electromotive force at the latter temperature did not agree with the former values at 25°, but was abnormally low. It fell on the straight line representing the temperature-electromotive force relation above 26.2°, indicating that transition had not taken place when the temperature decreased from 30 to 25°. The electromotive force remained low for a considerable period and was somewhat erratic for several months after the temperature change. No abnormal behavior was noticed after any of the other temperature changes.

Between 15 and 26.4° the electromotive force of the chloride cell is given by the equation

$$E = 0.13872 - 0.000168\ (t - 25) - 0.0000010\ (t - 25)^2$$

This can be combined with the equation for the electromotive force of the cell

$$\mathrm{Cd(Pb, Hg)} \mid \mathrm{Cd^{++}} \mid \mathrm{Cd(Hg)}^{15} \qquad (6)$$

namely,

$$E = 0.00113 + 0.000025\ (t - 25) + 0.0000002\ (t - 25)^2$$

giving for Cell 1

$$E = 0.13759 - 0.000193\ (t - 25) - 0.0000012\ (t - 25)^2$$

Obata found a value 3 mv. higher at 25°, while a value 5.6 mv. higher can be calculated from the results of Taylor and Perrott.

If the electromotive force of Cell 1 is combined with the electromotive force of Cell 4 and that of the cell[16]

$$\mathrm{Cd} \mid \mathrm{Cd^{++}} \mid \mathrm{Cd(Hg)};\ E = 0.0505 - 0.000244\ (t - 25) \qquad (7)$$

the electromotive force of the cell

$$\mathrm{Cd} \mid \mathrm{CdCl_2.2.5H_2O,\ sat.} \mid \mathrm{CdCl_2.2.5H_2O + PbCl_2,\ sat.} \mid \mathrm{Pb} \qquad (8)$$

is found to be

$$E = 0.1824 - 0.000453\ (t - 25) - 0.0000012\ (t - 25)^2$$

Therefore, for the reaction

$$\mathrm{Cd + PbCl_2 + 2.5H_2O\ (from\ sat.\ solution) \longrightarrow CdCl_2.2.5\ H_2O + Pb}$$

$\Delta F_{25} = -8417$ cal., $\Delta S_{25} = -20.9$ and $\Delta H_{25} = -14{,}650$ cal.

Thermochemical data determined at temperatures of 18 to 20° are available for the calculation of the heat of reaction of this cell. Thomsen found $\Delta H_{18} = -93{,}240$ cal. for the heat of formation of cadmium chloride, and Braune and Koref[17] found $\Delta H_{20} = -85{,}700$ cal. for the heat of formation of lead chloride. Cohen and Bruins[18] found $\Delta H_{18} = -7110$ cal. for the heat change accompanying the formation of the hydrate of cadmium chloride in the saturated solution. Combining the thermochemical data, $\Delta H_{18} = -14{,}650$ cal., while from the data for Cell 8, $\Delta H_{18} = -14{,}420$ cal.

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[15] Ref. 7, p. 2534.

[16] Gerke, *Chem. Reviews*, **1**, 377 (1925).

[17] Braune and Koref, *Z. anorg. Chem.*, **87**, 183 (1914).

[18] Cohen and Bruins, *Verslag Akad. Wetenschappen Amsterdam*, **26**, 587 (1917).

The chloride cell would not make a good standard cell. Its temperature coefficient is large, and on account of the peculiar nature of the temperature-electromotive force relation, the discovery of another cell which could be combined with it to eliminate the temperature coefficient over a sufficient range of temperature is improbable. The formation of a metastable state after a decrease in temperature from 30 to 25° is a serious disadvantage. One of the cells failed toward the end of the temperature coefficient determination, and the others were in a metastable state and erratic after this determination was completed, making the constancy of the cells over long periods of time questionable.

The Iodide Cell.—The cell

$$\mathrm{Cd(Pb, Hg)} \mid \mathrm{CdI_2,\ sat.} \mid \mathrm{CdI_2 + PbI_2,\ sat.} \mid \mathrm{Pb(Hg)} \qquad (9)$$

has a practically linear temperature-electromotive force relation between 15 and 40°. It does not show any irregularity such as the chloride cell does. The temperature formula is not of the highest degree of accuracy on account of the hysteresis. The following should give the electromotive force within ± 0.1 mv.,

$$E = 0.1007 + 0.00026\ (t - 25)$$

If the electromotive forces of Cells 6 and 9 are combined, the electromotive force of Cell 2 is found to be

$$E = 0.0996 + 0.000235\ (t - 25) - 0.0000002\ (t - 25)^2$$

This agrees within 0.1 mv. with the value found by Obata.

If the electromotive forces of Cells 2, 7 and 4 are combined, the electromotive force of the cell

$$\mathrm{Cd} \mid \mathrm{CdI_2,\ sat.} \mid \mathrm{CdI_2 + PbI_2,\ sat.} \mid \mathrm{Pb} \qquad (10)$$

is found to be

$$E = 0.1444 - 0.000025\ (t - 25) + 0.0000002\ (t - 25)^2$$

Therefore, for the reaction $\mathrm{Cd + PbI_2 \longrightarrow CdI_2 + Pb}$, $\Delta F_{25} = —6664$ cal., $\Delta S_{25} = —1.15$ and $\Delta H_{25} = —7008$ cal.

The heat of reaction can be calculated from thermochemical data. Braune and Koref[19] found $\Delta H_{20} = —41{,}850$ cal. for the heat of formation of lead iodide. Gerke[20] found a value in close agreement with this electrochemically. For the heat of formation of cadmium iodide, Thomsen found $\Delta H = —48{,}830$, while Taylor and Perrott[21] found $\Delta H = —48{,}440$. The heat of reaction for Cell 10 on the basis of Thomsen's heat of formation is $\Delta H = —6980$ cal., and on the basis of Taylor and Perrott's heat of formation is $\Delta H = —6590$ cal. The agreement of the former with the value $\Delta H_{20} = —7034$ cal. calculated from the electromotive force and temperature coefficient of Cell 10 is very good.

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[19] Ref. 17, p. 180.

[20] Gerke, Ref. 4, p. 1703.

[21] Ref. 2, p. 492.

The large and persistent hysteresis of Cell 10 and its large temperature coefficient are disadvantages to its use as a standard cell.

Other Cells.—A few cells were set up similar to Cells 5 and 9 but with bromide or sulfate electrolytes. Neither the cells with the bromide electrolyte nor those with the sulfate electrolyte were reproducible, and both groups of cells were variable. It is to be noted that Mellon and Henderson[22] found that lead standard cells which contained a lead-amalgam-lead-sulfate electrode, were not constant when the electrolyte was a cadmium sulfate solution and were not as reproducible as the cells in which some other salts were used as the electrolyte.

Summary

The cells

$$\mathrm{Cd(Pb, Hg)} \mid \mathrm{CdCl_2.2.5H_2O, sat.} \mid \mathrm{CdCl_2.2.5H_2O + PbCl_2, sat.} \mid \mathrm{Pb(Hg)}$$

$$\mathrm{Cd(Pb, Hg)} \mid \mathrm{CdI_2, sat.} \mid \mathrm{CdI_2 + PbI_2, sat.} \mid \mathrm{Pb(Hg)}$$

were set up and their electromotive forces were measured over a period of several months at 25°, and also at 5° intervals from 15 to 40°.

The electromotive force of the first cell was not in agreement with the values of similar cells measured by Obata and by Taylor and Perrott. The electromotive force of the second cell agreed well with that of a similar cell measured by Obata.

The temperature-electromotive force relation of the cell with the chloride electrolyte indicated a transition point at a temperature between 26 and 27°.

Neither of these cells seems to be especially well adapted for use as a low-voltage standard cell, the chloride cell having a transition point which would interfere, while the iodide cell shows marked and persistent hysteresis. Both have large temperature coefficients.

The heats of reaction were calculated and compared with the heats of reaction calculated from thermochemical data.

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[22] Mellon and Henderson, THIS JOURNAL, **42**, 680 (1920).