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OXIDE CELLS OF CADMIUM, COPPER, TIN AND LEAD[1]

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In the course of a program of investigation of the thermodynamic properties of oxides, the Bureau of Mines at its Berkeley Station carried out a series of measurements upon certain galvanic cells involving oxide electrodes. Work upon zinc oxide previously reported[3] had furnished very satisfactory values of the free energy of formation of the oxide as compared to results by other methods. The results of further measurements were in no case as satisfactory as those upon zinc, for reasons which will appear, and publication was withheld until substantiation by entropy determinations was accomplished. These entropies have now been determined.[4] Enough work was done to indicate the limitations of the cell measurement method for free-energy determination upon oxide materials. Only the briefest outline of methods, and data from the most satisfactory of nearly a hundred cells which were set up in the course of the work, will be recorded here.

Apparatus and Methods

The types of cells used were of three sorts: the ordinary H-type cell with and without a stopcock in the cross arm, unstirred cells with hydrogen electrode and circulating cells with automatic magnetic pump, such as were used by Smith and Woods.[5] The H-cells were used exclusively for measurements in which the oxide electrode was compared to the mercury oxide half-cell in dilute barium hydroxide solution. These cells were completely sealed from the atmosphere, and the contents were stirred to a slight degree by slow rocking upon an oscillating support under the cross arm. Early measurements showed that the transfer of solid oxides between the legs of the H seriously affected the electromotive force when only a glass wool plug was used, so that all measurements recorded here were made in cells with a stopcock, which was opened only during the time of making a voltage measurement. The unstirred cells with hydrogen electrode were similar to the cells with magnetic pump, with the omission of the latter. The cells will not be further described here. When the latter type was used, it is designated below by the symbol $H_2(p)$. All hydrogen cell values recorded have been corrected for barometric pressure and for the effect of water vapor in the saturator, which decreases the partial pressure of hydrogen.

The electrical measuring device was a modern type of potentiometer, with galvanometer sensitive to better than 0.01 millivolt, properly shielded, and whose standard cell was frequently checked against another of a different manufacture. In all cases the

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[3] Maier, Parks and Anderson, THIS JOURNAL, **48**, 2564 (1926).

[4] Millar, *ibid.*, **51**, 207, 215 (1929).

[5] Smith and Woods, *ibid.*, **45**, 2632 (1923).

accuracy of the measurement was considerably beyond the limiting deviations of electromotive force involved in the inherent fluctuations of the cell value.

Thermostats were of an automatic oil type, controlled to about 0.03°. The true temperature of the first thermostat nominally at 25° was 24.83°, as determined by a sensitive thermometer with Bureau of Standards calibration, and the second thermostat nominally at 45° had a true temperature of 44.92°.

Barium hydroxide solution was used throughout as electrolyte. The material was purified by recrystallization before the solution was made up, was stored in large bottles with atmospheric vent through a long column of soda lime, and was repurified just before use by boiling with shavings of pure zinc in a flask with a trap to prevent re-access of air. Various concentrations were made by aliquot dilution with air-free and carbon dioxide-free distilled water. The solutions were standardized against benzoic acid (Bureau of Standards calorimetric standard).

The sign of the electromotive force given in the tables is such that a spontaneous reaction has a positive e.m.f. and negative free-energy change. In the case of the HgO cells, we have assumed the reaction to be $M + HgO = MO + Hg$, and for the hydrogen cells $M + H_2O = MO + H_2$.

I. Cadmium Oxide

The first cadmium oxide cells were made of a C. P. grade of reddish brown, "amorphous" oxide, which had been further purified of traces of electronegative metals by boiling with C. P. cadmium metal shavings in dilute barium hydroxide solution. The cadmium electrodes were of 8.00 and 12.46% cadmium amalgam, made electrolytically from carefully purified materials. The usual purifications for the preparation of the mercury and mercury oxide for the mercury oxide half-cell were carefully made. The results of the first cells are shown in Table I.

TABLE I

EARLY CADMIUM OXIDE CELLS AT 24.83°

8.00% Cadmium Amalgam

Cell no.	Ref. electrode	Molality of $Ba(OH)_2$	No. of readings averaged	Duration of period of readings, days	E.m.f.	Av. dev. of mean
A	HgO(red)	0.2426	22	11	+0.8649	±0.0005
B	HgO(red)	.1213	21	11	+ .8551	± .0011
C	HgO(red)	.0809	15	8	+ .8569	± .0017
D	HgO(yellow)	.2426	22	10	+ .8616	± .0019
				Average	+ .8596	± .0037
1	H_2(p)	.1213	11	7	− .0667	± .0017
2	H_2(p)	.2308	10	8	− .0925	± .0024
3	H_2(p)	.1154	7	4	− .0911	± .0063
4	H_2(p)	.0231	7	6	− .07260	± .0014

The considerable fluctuation of the values for the cells in Table I seemed ascribable to changes in the cadmium oxide. It was noted that the color of the oxide became slightly lighter when the purification was carried out by boiling with cadmium shavings. This phenomenon could be explained by the slow hydration of the oxide. A sample of the oxide was then boiled for about one week in a flask with reflux condenser, using a small amount of barium hydroxide (about 0.0002 *M*), and protecting from the atmosphere with a barometric mercury trap. At the expiration of this time the color of the oxide had nearly disappeared, indicating that a considerable amount of hydration had occurred. The gradual change with time of electromotive force observed in the first cells may have been due to this action.

Further samples of cadmium oxide were prepared by calcining the purified C. P. "amorphous" oxide and by the ignition of precipitated cadmium oxalate. Material prepared by ignition becomes markedly crystalline, ranging in color from dark brown to blue black, depending on the time and temperature of calcination. A temperature of 750° was found to slow up the hydration without producing too large crystals, which were to be avoided because of the length of time required for the electrolyte to become saturated with oxide. Results for cells with the new materials are given in Table II. Since the presence of the barium hydroxide seemed to increase the rate of hydration, lower concentrations were used.

TABLE II

CADMIUM CELLS AT 24.83°

With Ignited Oxide and 12.46% Amalgam

Cell no.	Oxide form	Ref. electrode	Molality of $Ba(OH)_2$	No. of readings averaged	Time, days	E.m.f.	Av. dev. of mean
E	Oxalate, ign.	HgO	0.0210	8	10	+0.86162	±0.00065
F	Oxalate, ign.	HgO	.0105	4	5	+ .85624	± .00004
G	C. P. ign.	HgO	.0210	4	5	+ .85625	± .0011
H	C. P. ign.	HgO	.0070	8	7	+ .85656	± .0008
"Best" Cells							
I	C. P. ign.	HgO	.0210	7	8	+ .85864	± .00020
I	Duplicate C. P. ign.	HgO	.0210	5	5	+ .85815	± .00006
J	C. P. ign.	HgO	.0105	6	7	+ .85885	± .00040
K	C. P. ign.	HgO	.0070	7	7	+ .85867	± .00053
		Average of "Best" cells				+ .85858	± .00021
5	C. P. ign.	H_2(p)	.0105	5	5	− .07806	± .0025
6	C. P. ign.	H_2(p)	.0210	4	5	− .06810	± .0011
			"Best" H_2 cell			+ .06810	

A preliminary calculation of the free energy of formation of the oxide from the data of Table II showed practically identical results to be obtained with the mercury or hydrogen reference electrode. When Cells I, J and L, which had been at 24.83° for several weeks, were brought to 44.92°, the results shown in the first part of Table III were obtained, but similar calculations did not give results consistent with *new* Cells 7 and 8 compared to the hydrogen electrode.

In order to determine whether this discrepancy was caused by peculiarities of the cadmium amalgam, new Cells Nos. 25 to 28, inclusive,

TABLE III

FURTHER CADMIUM CELLS WITH IGNITED OXIDES

Description of cell	No. of cell	Ref. electrode	Molality of $Ba(OH)_2$	No. of readings	Time, days	E.m.f.	Av. dev. of mean
Old Cells	I	HgO	0.0210	14	16	+0.85138	±0.00042
Raised to 44.92°	J	HgO	.0105	5	6	+ .85133	± .00056
	L	HgO	.0052	5	6	+ .85159	± .00043
			Average			+ .85143	± .00010
New Cells:	7	H_2(p)	.0070	4	4	.05747	± .0000
With 12.46%	8	H_2(p)	.0035	4	4	− .05880	± .0043
amalgam at 44.92°			Average			− .05813	
New Cells:	25	H_2(p)	.2170	7	9	− .01225	± .00050
With electro-	26	H_2(p)	.1085	4	4	− .01239	± .00060
deposited Cd	27	H_2(p)	.2170	10	13	− .01227	± .00026
44.92° electrodes	28	H_2(p)	.0723	9	9	− .01237	± .00017
			Average			− .01232	± .00006
Old Cells brought	I	HgO	.0210	9	12	+ .84670	± .00034
back to 24.83°	I, dupl.	HgO	.0210	4	4	+ .84721	± .00085
	J	HgO	.0105	9	12	+ .84617	± .00072
	K	HgO	.0070	7	8	+ .84620	± .00014
	L	HgO	.0052	9	12	.84668	± .00016
			Average			+ .84659	± .00033

were set up, using electrodeposited cadmium in place of amalgam. Getman[6] has shown that the electromotive force of electrodeposited metallic cadmium compared to amalgam in cells of the type

$$\mathrm{Cd} \left| \tfrac{1}{2}\ \mathrm{Sat.\ Sol.\ CdSO_4} \right| 8\%\ \mathrm{Cd\ Amal.}$$

depends on the history of the cells, and that cells "stabilized" above 40° have an electromotive force of $E = 0.04280 + 0.000170\ (t - 25)$, or 0.04619 volt at 44.92°. If this figure be subtracted from −0.01232 volt found for new oxide cells using electrodeposited cadmium, the result, −0.05851 volt, is obtained, a fair check with −0.05813 found from Cells 7 and 8.

In view of the above, old cells which had been at 24.83° for several weeks, and subsequently at 44.92° for several weeks longer, were brought back to 24.83°, with the results shown in the last part of Table III. The satisfactory constancy thus achieved failed to substantiate the original values of these cells.

Some explanation of the behavior of these cells may be found in an accessory experiment. Cadmium amalgam was anodically polarized by a continuous current of 0.5 micro-ampere per square centimeter in barium hydroxide solution for a period of several months. There was produced not cadmium oxide but a hydrated mixture of cadmium and mercury oxides. Although amalgam gives reversible electrodes in neutral or acid solutions, it is certain that such electrodes are not immediately and completely reversible in these basic solutions, where the solubility

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[6] F. H. Getman, THIS JOURNAL, 39, 1806 (1917).

of the mercury oxide is apparently so low that cadmium cannot precipitate mercury ions at these concentrations, or at best can do so only with extreme slowness.

The amalgam cell equivalent to the measurements on Cells 25 to 28, inclusive, may be calculated from Getman's results, as above, and from the free energies of water and mercuric oxide given by Lewis and Randall,[7] to be +0.86235 volt. The data may be summarized as follows

$$\text{New Amalgam Cells}\begin{cases} E_{24.88} = +0.85858 \text{ volt} \\ E_{44.92} = +0.86235 \text{ (equivalent)} \end{cases}$$

$$\text{Old Amalgam Cells}\begin{cases} E_{24.88} = +0.84659 \\ E_{44.92} = +0.85143 \end{cases}$$

A plausible assumption concerning these discrepancies may be that one set represents a cell reaction forming hydroxide and the other oxide. Getman's results for α-cadmium, the supposed stable form, are represented by the equation $E = 0.04742 - 0.000200\ (t - 25)$, from which, for the reaction $Cd_\alpha + Hg = Cd$ amalgam, $\Delta F_{298} = -2188$ cal., and $\Delta H_{298} = -4940$ cal. (from the differential Gibbs-Helmholtz equation). From the summarized measurements above, we have for the reaction Cd amalgam + HgO = CdO + Hg, or, alternatively, Cd amalgam + HgO + $H_2O = Cd(OH)_2 + Hg$

$$\text{New Cells}\begin{cases} \Delta F_{298} = -39{,}622 \\ \Delta H_{298} = -37{,}044 \end{cases} \qquad \text{Old Cells}\begin{cases} \Delta F_{298} = -39{,}068 \\ \Delta H_{298} = -35{,}756 \end{cases}$$

Combining the results of Getman's work with these values, and taking the free energies of mercury oxide and liquid water as −13,808 and −56,560, respectively, from Lewis and Randall, if the new cells represent oxide formation, $\Delta F^{\circ}_{298}(CdO) = -55{,}618$: $\Delta H_{298} = -63{,}584$. From these figures, ΔS for the formation of CdO from its elements is −26.73. Lewis and Randall give for the entropy of solid cadmium, $S_{298} = 11.80$; but instead of their value for oxygen, $S_{298}(^1/_2O_2) = 24.0$, we shall use 24.47, based on recent unpublished determinations of the entropy of oxygen at the boiling point and 1 atmosphere (40.57), and the data of Scheel and Heuse[8] (8.37) from thence to room temperature. From these quantities, $S_{298}(CdO) = 9.54$.

From the data of the old cells, similar calculations lead to the result for the formation of cadmium oxide: $\Delta F^{\circ}_{298} = -55{,}064$; $\Delta H_{298} = -62{,}305$; $S_{298} = 11.98$. The data of Millar[9] lead to a value for cadmium oxide, $S_{298} = 13.17$, indicating that the old cells more nearly represent the cell reaction involving CdO. Recalculating the results for the new cells on the basis of cell reaction to form $Cd(OH)_2$, for the formation of this substance from its elements, $\Delta F^{\circ}_{298} = -112{,}178$; $\Delta H_{298} = -131{,}850$; and

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[7] G. N. Lewis and Merle Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, pp. 484–485.

[8] Scheel and Heuse, *Ann. Physik*, **4**, 40, 484 (1913).

[9] Millar, This Journal, **50**, 2653 (1928).

for the reaction $CdO + H_2O = Cd(OH)_2$, $\Delta F^\circ_{298} = -554$; $\Delta H_{298} = -1288$ (based on cell coefficients).

Thermal values for the heat of formation of cadmium oxide are Berthelot,[10] 66,400; J. Thomsen,[11] 65,780; Ditte,[12] 60,800; Mixter,[13] 57,000 for "amorphous" and 63,000 for crystalline, and Moose and Parr,[14] 65,200; whereas the free energy from the old cells, combined with Millar's direct entropy determination, leads to 61,950. For the hydroxide, Thomsen's value of the heat of formation from metal, oxygen and water was 65,680, which combined with Lewis and Randall's average for water, 68,270, gives 133,950 for the formation from the elements. However, Berthelot's figure for the heat of neutralization for cadmium hydroxide is 20,290 which, combined with Richards and Burgess'[15] heat of solution, 17,200, gives for the hydroxide −133,450.

The assumption of an oxide cell reaction for old cells implies that the oxide is the stable form at 25°, whereas according to the free-energy calculations, the hydroxide should be stable at this temperature. In view of this anomalous condition, no accuracy greater than perhaps 500 calories may be claimed for the free energy of the oxide.

II. Cuprous Oxide

The cuprous oxide electrode has been investigated by Allmand,[16] first against a hydrogen reference electrode in sodium or potassium hydroxide, later against the calomel electrode. Allmand found the hydrogen electrode in his solutions, to be unsatisfactory but this may have been due, in part at least, to his use of caustic alkali. Experience in this Laboratory has shown that with care the hydrogen electrode in barium hydroxide solution is fairly satisfactory. The calculated values of e.m.f. corresponding to the reaction $Cu_2O + H_2 = 2Cu + H_2O$ at 17° are given by him as 0.473 volt in 0.1 N alkali and 0.466 volt in normal alkali; part of this divergence may have been due to the uncertain liquid potentials involved in the use of the calomel reference electrode.

In the first cells of the present investigation, cuprous oxide made by dissociating a supposedly C. P. grade of cupric oxide (from nitrate) was used, with the results against the mercury oxide reference electrode of 0.4395 and 0.4479 volt, but these cells were quite unstable and maintained a steady progressive decrease of voltage. It seemed possible that this was caused by the presence of impurities in the oxide; therefore, a further

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[10] Berthelot, *Ann. chim. phys.*, [5] **4**, 189 (1875).

[11] J. Thomsen, *Ber.*, **16**, 2163 (1883).

[12] A. Ditte, *Bull. soc. chim.*, [2] **16**, 227 (1871).

[13] Mixter, *Am. J. Sci.*, **36**, 55 (1913); **40**, 20 (1915).

[14] J. C. Moose and S. W. Parr, THIS JOURNAL, **46**, 2656 (1924).

[15] Richards and Burgess, *ibid.*, **32**, 431, 1176 (1910).

[16] A. F. Allmand, *J. Chem. Soc.*, **95**, 2151 (1909); **99**, 840 (1911).

preparation was made by first oxidizing electrolytic copper wire in a muffle at 700° to a depth of about 0.1 mm., heating in an evacuated silica container at 1000°, and at a pressure of 0.002 mm., until no further oxygen was evolved, sealing off and permitting the contents to cool slowly. In setting up the cells, connection to the copper electrode was made through a platinum spiral upon which a dense, coherent and non-crystalline copper deposit had been electroplated.

The most satisfactory of the cells measured are shown in Table IV. Because of lack of thermostat capacity, no cells against the hydrogen reference electrode were measured at 25°. Although the cells are regarded as somewhat more satisfactory than Allmand's, previous experience had shown that the *accurate* calculation of heats of formation from cell coefficients is somewhat unsatisfactory with most oxide cells, and is barely worth while for these cells, unless gross errors exist in the thermal data, as in the previously reported case of zinc, or where it is a question of deciding between several possible cell reactions.

TABLE IV

CUPROUS OXIDE CELLS

Cell no.	Temp., °C.	Ref. electrode	Molality of $Ba(OH)_2$	No. of readings	Time, days	E.m.f.	Av. dev. of mean
M	24.83	HgO	0.2130	13	15	+0.45201	±0.00038
N	24.83	HgO	.1065	21	24	+ .45335	± .00085
O	24.83	HgO	.0532	6	7	+ .45184	± .00057
P	24.83	HgO	.0426	9	11	+ .45146	± .00046
Q	24.83	HgO	.0426	5	6	+ .45182	± .0011
				Average		+ .45210	± .00050
9	44.92	H_2(p)	.1065	6	7	− .46270	± .00030
10	44.92	H_2(p)	.0426	4	5	− .46298	± .00090
				Average		− .46284	

From the values of e.m.f. given in Table V, we calculate for Cu_2O, $\Delta F_{318} = -34{,}426$, $\Delta F_{298} = -34{,}672$, while Allmand's results give $\Delta F_{290} = -34{,}920$. From calculated free energies of mercuric oxide and water at 44.92, as derived from Lewis and Randall's free energy equation for these materials, the equivalent mercury oxide reference cell value of

TABLE V

CUPRIC OXIDE CELLS WITH HYDROGEN REFERENCE ELECTRODE

Cell no.	Temp., °C.	Molality $Ba(OH)_2$	No. of readings	Time, days	E.m.f.	Av. dev. of mean
11	24.83	0.2120	9	10	−0.64267	±0.00018
12	24.83	.1075	6	7	− .64276	± .00019
13	24.83	.0504	3	3	− .64225	± .0010
13	24.83	.0504	5	6	− .64086	± .0021
Duplicate				Average	− .64213	± .00046
14	44.92	.2170	13	15	− .64158	± .00050
15	44.92	.1075	7	9	− .63763	± .00038
				Average	− .6396	

hydrogen cells at 44.92° is calculated to be +0.45806 volt. The value of ΔH for the formation of Cu_2O is then calculated to be $-38,400$ cal. Thomsen[17] gave 40,800, and Berthelot[18] 43,800. It is perhaps not to be expected that values for the heat of reaction calculated in this way from two different types of cells could give much better agreement.

Millar[19] has given a preliminary value for the entropy of cuprous oxide as 21.7 ± 1.0. Taking the entropy of copper as 8.18, in accordance with Lewis and Randall, and 24.47 for $^1/_2O_2$ as previously, ΔS for the formation of Cu_2O from its elements becomes -19.13 and ΔH is calculated from this and the free energy to be $-40,375$ cal., a fair substantiation of Thomsen's figure.

III. Cupric Oxide

Cupric oxide reacts with metallic copper in neutral or basic aqueous solutions, resulting in the formation of cuprous oxide. Two cells were set up, one consisting of copper in contact with CuO, with 0.0414 molal $Ba(OH)_2$, using the mercury oxide reference electrode, and the second cell Pt | CuO | 0.0414 *M* $Ba(OH)_2$ | Cu_2O | Pt. The first cell had an initial voltage of 0.1820 and the second of 0.1889, but the electromotive force of the first showed a rapid and continuous increase until at the end of two weeks 0.394 volt had been reached. It seemed apparent that it would ultimately increase to an amount corresponding to Cu_2O *vs.* HgO. The second cell was highly polarizable and showed plus and minus variations between the initial value and a maximum of about 0.244 volt.

Despite these preliminary experiments, it was decided to try the Cu | CuO electrode against a hydrogen reference electrode. It was realized that such a cell could not become completely stabilized, but might show a "steady state" value over a period of time corresponding to the reduction of CuO to Cu_2O.

Reference to Table V will show that this expectation was realized, at least in part, at 25°. At 45° the local action in the cell is so rapid that difficulty is experienced in maintaining an electroplated deposit of copper on platinum, even though copper itself (in the form of wire) was mixed with the cupric oxide. The copper oxide was of the same sample that was used in the preparation of cuprous oxide but consisted of completely oxidized wire prepared at 700°.

Assuming the cell reaction in this case to be $Cu_2O + H_2O = 2CuO + H_2$, and using the previously determined results for Cu_2O, the free energy of formation of CuO is calculated as $\Delta F^{0}_{298} = -30,800$, and from the integrated Gibbs-Helmholtz equation, $\Delta H = -38,652$. Thomsen's[17] thermal value was 37,160. Millar[19] gives for the entropy of CuO, 9.75 ±

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[17] Thomsen, *J. prakt. Chem.*, [2] **12**, 283 (1875).

[18] Berthelot, "Thermochemie," Vol. II, p. 317.

[19] Millar, This Journal, **51**, 215 (1929).

0.05, from which ΔS of formation is -22.90. Calculating ΔH from the cell value of free energy and the entropy as before, the result is $\Delta H = -37{,}626$, a result intermediate between Thomsen's thermal value and that from cell coefficients.

IV. Stannous Oxide

Stannous oxide was prepared by boiling a solution of freshly prepared stannous chloride with sodium carbonate in the absence of air. The stannous chloride, after recrystallization, had been boiled for some time with metallic tin (shavings of special electrolytic metal) to reduce traces of stannic chloride. The original tin from which the chloride was made was of especial purity from an electrolytic refining process and contained less than 0.1% of impurity.

The stannous oxide electrode was made through a platinum spiral with an electroplated deposit of tin. The plating solution was of stannous sulfate with aloin as addition agent. In all cases except the last three cells against the mercury oxide electrode, the deposit was dense, coherent and non-crystalline. In the last three cells of this set the deposit was spongy and the cells were arranged for comparison against the same HgO electrode as the previous set.

The cells against mercury oxide showed a slow rise in voltage for about a week's time, after which they were nearly constant for the same period, but later showed a progressive decrease. It is assumed that the initial increase was caused by the slow disappearance of traces of oxygen from

Table VI

Measurements of Stannous Oxide Cells

Cell no.	Temp., °C.	Ref. electrode	Molality of $Ba(OH)_2$	E.m.f.
R1	24.83	HgO	0.2120	+1.0221
R2	24.83	HgO	.0707	+1.0205
R3	24.83	HgO	.0424	+1.0179
S1	24.83	HgO	.2120	+1.0280
S2	24.83	HgO	.0848	+1.0314
S3	24.83	HgO	.0424	+1.0328
T1	24.83	HgO	.2030	+1.0297
T2	24.83	HgO	.1075	+1.0300
T3	24.83	HgO	.0508	+1.0281
T1 (spongy tin)	24.83	HgO	.2030	+1.0298
T2 (spongy tin)	24.83	HgO	.1075	+1.0291
T3	24.83	HgO	.0508	+1.0276
	Average of last 3 sets		1.0296	±0.0011
16	44.92	H_2(p)	.2030	+0.0930
17	44.92	H_2(p)	.1015	+ .0920
			Average	+ .0925

the cells and the slow attainment of saturation with oxide, and that the final decrease resulted from the gradual spoiling of the tin surface by traces of electronegative impurities. The values given in Table VI correspond to the average for a week's period in each case at the maximum voltage attained. Despite the apparent reproducibility of the hydrogen cells, they were still showing a rise of 0.3 millivolt per day after three weeks of life, and the results are considered to be too low. This is further indicated by the calculation of free energies and heats of formation for SnO, which are

$$\left.\begin{array}{l}\Delta F^{\circ}_{298} = -61{,}332 \\ \Delta F^{\circ}_{318} \quad\;\; -60{,}054\end{array}\right\} \Delta H = -80{,}000$$

Millar[20] has found the entropy of SnO to be $S_{298} = 13.56$. Using Lewis and Randall's figure for the entropy of white tin, $S_{298} = 11.17$, and 24.47 for $^1/_2O_2$, ΔS of formation is -22.08, and ΔH from this and the measured free energy is $-67{,}914$, a good check with Andrews'[21] thermal value, 67,600.

V. Stannic Oxide

Stannic oxide was made by the oxidation of electrolytically purified tin by nitric acid, with subsequent washing, and with final calcination at 400° of the metastannic acid so formed.

Cells of this material behaved in a manner similar to the cupric oxide cells, but changed even more rapidly. In one case a cell with an initial voltage of 0.11 had changed to 0.79 volt in ten days' time. The few results recorded below represent no very definite value but rather the order of magnitude of a constantly increasing voltage, beginning at the second day of the cell's life and extending for the time recorded. After this period a more rapid rate of increase occurred. Table VII shows the results.

TABLE VII

THE STANNIC OXIDE ELECTRODE AT 44.92°

HYDROGEN REFERENCE ELECTRODE

Cell no.	Molality of $Ba(OH)_2$	No. of readings	Time, days	E.m.f.	Av. dev. of mean
18 Mossy Sn	0.2170	5	5	+0.1161	±0.0008
19 Coherent Sn	.2170	5	5	+ .1155	± .0010
20 Coherent Sn	.1085	2	2	+ .1148	
			Average	+ .1155	

According to the value of e.m.f., the cell reaction should have a free-energy change of $\Delta F_{318} = -10{,}660$, or -5330 cal., depending upon whether the tin is reduced to metal or the lower oxide. If the reaction was $Sn + 2H_2O = SnO_2 + 2H_2$, the free energy of formation of SnO_2

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[20] Millar, THIS JOURNAL, **51**, 207 (1929).

[21] Andrews, *Phil. Mag.*, [3] **32**, 321 (1848).

becomes $-122{,}230$ at 318° K., but if the cell reaction was $SnO + H_2O = SnO_2 + H_2$, $\Delta F_{318}(SnO_2) = -122{,}115$. It is apparent that in this case it is impossible to distinguish between the cell reactions on the basis of the evidence available. For calculation the first case is assumed. Because of lack of definiteness of electromotive force and cell reaction, further experimental work was not attempted but tentative calculations will be made.

From the specific heats of white tin and oxygen, and Lewis and Randall's entropy at 298°, the entropies at 318° are estimated as follows: $S_{318}(Sn) = 12.2$, $S_{318}(O_2) = 49.4$. Similarly, from Millar's[20] specific heat data, $S_{318}(SnO_2) = 13.3$. Then ΔS_{318} for the reaction of formation of stannic oxide is -48.3, and since $(\partial \Delta F/\partial T)_P = -\Delta S$ which varies but little with the temperature, the value of $\Delta F^{\circ}_{318} = -122{,}230$ may be corrected to 298°K. by the subtraction of $20 \times 48.3 = 966$ cal. Then $\Delta F_{298}(SnO_2) = -123{,}200$ in round numbers.

Again, calculating the entropy change of formation at 298°K. from the data, $S_{298}(Sn) = 11.18$ (Lewis and Randall), $S_{298}(O_2) = 48.94$ (as previously), $S_{298}(SnO_2) = 12.51$, $\Delta S = -47.61$. From this latter, and the estimated free energy of $-123{,}200$ cal., $\Delta H = -137{,}392$—a satisfactory check with the figures of both Mixter[22] and Andrews,[21] who gave 137,800.

The work of Fraenkel and Snipischski[23] on the reduction equilibria of stannic oxide by carbon monoxide does not permit calculation of a definitive value of free energy of stannic oxide.

VI. Lead Dioxide

The monoxide of lead electrode has been investigated by Smith and Woods,[5] who found for the free energy of formation of PbO, $\Delta F^{\circ}_{298} = -45{,}050$ cal. Lead dioxide, lead sesquioxide and red lead have been studied by Glasstone,[24] who gave for the $Pt \mid PbO, PbO_2$ *N*–NaOH electrode potential 0.27 volt, and concluded that PbO and PbO_2 combine in the presence of *N* alkali to give Pb_3O_4.

In the present work we wished to ascertain whether these results were duplicable in barium hydroxide electrolyte. Lead dioxide was made electrolytically in a lead perchlorate solution which was hot and strongly acid. The lead electrode was made by deposition from a lead perchlorate solution with peptone as addition agent. Comparisons of the $Pb \mid PbO_2 \mid Ba(OH)_2$ electrode with the mercury oxide and hydrogen electrode are given in Table VIII.

If the cell reaction be assumed to be the reduction of lead dioxide to

[22] Mixter, *Silliman's J.*, [4] **27**, 231 (1909).

[23] Fraenkel and Snipischski, *Z. anorg. allgem. Chem.*, **125**, 235 (1923).

[24] Glasstone. *J. Chem. Soc.*, **121**, 1456 (1922).

TABLE VIII

MEASUREMENTS ON LEAD DIOXIDE CELLS

Cell no.	Ref. electrode	Temp., °C.	Molality of $Ba(OH)_2$	No. of readings	Time, days	E.m.f.	Av. dev. of mean
U	HgO	24.83	0.1015	10	12	+0.69140	±0.00037
V	HgO	24.83	.0508	9	11	+ .69148	± .00043
				Average		− .69144	
21	H_2(p)	44.92	.2030	7	8	− .1983	± .0009
22	H_2(p)	44.92	.1085	6	7	− .1924	± .0003
23	H_2(p)	44.92	.0543	6	7	− .1967	± .0009
24	H_2(p)	44.92	.2170	4	5	− .1977	± .0011
				Average		− .1962	

monoxide, these voltages lead to a free energy of the dioxide of approximately −90,000 cal., but if the cell reaction is assumed to be the complete reduction of the dioxide, the order of magnitude of the calculated free energy of the dioxide is not changed. Calculations from either type of cell are moderately concordant and it is obvious that the cell reaction could not involve a reduction of PbO_2. If, however, it is assumed that the cell reaction may be only the formation or reduction of monoxide, the free energy of formation of the monoxide calculated from the observed voltage is $\Delta F^\circ_{298} = -45{,}717$. This figure is sufficiently close to Smith and Woods' result of −45,050 to justify belief that the actual cell reaction was principally lead monoxide formation.

It is of interest to calculate for copper, tin and lead the free-energy change resulting from the reduction of the higher to lower oxide by the metal at 25°. The free energies used for copper and tin are taken from this work, but for lead dioxide the figure calculated by Millar[20] and for lead monoxide the result of Smith and Woods are used.

$$\begin{array}{lll}
\mathrm{Cu} + \mathrm{CuO} = \mathrm{Cu_2O} & & \\
\quad -30{,}800 \qquad -34{,}672 & \Delta F = -3872 & \\
\mathrm{Sn} + \mathrm{SnO_2} = 2\mathrm{SnO} & & \\
\quad -123{,}200 \qquad 2 \times (-61{,}332) & \Delta F = +536 & \\
\mathrm{Pb} + \mathrm{PbO_2} = 2\mathrm{PbO} & & \\
\quad -52{,}010 \qquad 2 \times (-45{,}050) & \Delta F = -38{,}090 &
\end{array}$$

The large negative free-energy change for the lead reaction is adequate explanation for the disappearance of the dioxide in contact with the lead electrode, and the rapid degeneration of the cell as made with dioxide to give only monoxide reactions. The degeneration of the cupric oxide cells noted in an earlier part of this paper is consistent with the calculation showing that cupric oxide is not stable in contact with copper, and in this case the reaction occurring was actually the transformation from one to the other oxide. Stannous oxide has been described by T. Maeda[25] as unstable with respect to tin and stannic oxide at 700–950°. The small calculated positive value of the reaction for tin as written above accounts

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[25] T. Maeda, *Bull. Japan Inst. Phys. Chem. Research*, **2**, 350 (1923).

for the lack of definiteness in the tin cells, since the formation or reduction of either oxide could not be expected to take place exclusively.

It is not probable that a lead monoxide electrode made up originally with lead dioxide could give results of sufficient accuracy to serve as criticism of Smith and Woods' figures, and their result is undoubtedly the accurate one.

VII. Comment Concerning Oxide Electrodes

In this work it was found that cells involving oxide electrodes were highly polarizable and very sensitive to the presence of traces of electronegative impurities in the oxide material and electrolyte. Much of the difficulty with oxide or electrolyte containing more electronegative elements as impurity and resulting in rapid deterioration of the cells because of strong local action is readily eliminated by treating the oxide in suspension in the electrolyte with turnings of the pure metal in question for some time before use (preferably at a boiling temperature). Such turnings added to the cell contents are not entirely satisfactory, since the electrodeposited metal of the electrode proper usually acts preferentially in replacing the electronegative elements. In spite of such precautions, it was found impossible to produce cells which were *permanently* stable, although it was often possible to produce cells having constant e.m.f.'s for several weeks. Because of the inherent variations and polarizability of the cells, the temperature coefficient of oxide cells is usually difficult to determine with sufficient accuracy to give satisfactory thermal data.

Entropy calculations have been of great use in determining the cell reaction and furnishing assurance of the validity of the measurements. It is thought that free-energy determinations combined with entropy values will make possible the calculation of heats of formation, in many cases much more accurately than any possible direct determination. Because of the difficulty of obtaining thermal data from these cells, the selection of the cell reaction is uncertain in some cases; for this reason the results have been found acceptable only when substantiated by check with other independent methods, especially entropy determinations.

TABLE IX

SUMMARY OF MEASUREMENTS AND CALCULATIONS

Subs.	ΔF°_{298} of formation	S_{298} (Millar)	ΔH_{298} (formation) from cell coef.	ΔH_{298} (formation) from ΔF and S
CdO	− 55,064 ± 500	13.17 ± 0.1	− 62,305 ± 500	− 61,950 ± 500
$Cd(OH)_2$	−112,178 ± 500	....	−131,850 ± 500	....
Cu_2O	− 34,672 ± 200	21.7 ± 1.0	− 38,400 ± 2000	− 40,375 ± 400
CuO	− 30,800 ± 200	9.75 ± 0.05	− 38,652 ± 1000	− 37,626 ± 200
SnO	− 61,332 ± 300	13.56	− 80,000 ± 15000	− 67,914 ± 300
SnO_2	−123,200 ± 400	13.51	....	−137,400 ± 400

Summary

1. Oxide electrodes of cadmium oxide, cuprous and cupric oxide, stannous and stannic oxide and lead dioxide have been compared to the hydrogen or mercuric oxide electrode in barium hydroxide solutions.

2. Free energies of formation from these results and calculated heats of formation are summarized in Table IX.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE HEAT CAPACITIES AT LOW TEMPERATURES OF THE OXIDES OF TIN AND LEAD[1]

BY RUSSELL W. MILLAR[2]

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In continuation of the general program of determination and compilation of thermal and equilibrium data concerning the oxides and sulfides of metals, the heat capacities of SnO, SnO_2, Pb_3O_4 and PbO_2 have been measured from about 70°K. to room temperature. The method and apparatus employed were those previously used by the author.[3]

Materials.—The stannous oxide was made by the precipitation of stannous hydroxide with ammonia from a boiling solution of pure stannous chloride. Dehydration was accomplished by boiling the solution. The addition of a few crystals of stannous chloride, as recommended by Ditte,[4] hastened the reaction. The oxide was at first dark red but soon changed to the stable bluish black modification. It was cooled, filtered, washed with cold water and dried *in vacuo* over fused potassium hydroxide to constant analysis. Air was excluded as well as possible during filtration and washing. Titration with standard iodine solution of two samples dissolved in hydrochloric acid showed 98.0% of SnO. The impurity was probably SnO_2. Metallic tin, determined by reduction with hydrogen, was 87.36 to 87.21%, whereas the theoretical percentage is 88.12.

Stannic oxide was made by the action of dilute nitric acid on pure electrolytic tin. The material, when washed and ignited at 400°, was analyzed by reduction with hydrogen. Two determinations gave 99.84 and 99.73% of the theoretical amount of tin.

Lead dioxide was prepared by the electrolysis of an acid solution of lead nitrate, according to the method of Palmaer.[5] Lead carbonate was added to maintain the lead-ion concentration and to prevent the hydrogen-ion concentration from rising. Crystalline lead was formed at the cathode and dense plates of lead dioxide, which attained a thickness of 2–3 mm., at the anode. The product was ground to pass a 14-mesh screen, washed with boiling water until the washings showed no trace of nitrate and dried at 120°. Analysis by oxidation of hydrochloric acid, absorption of the chlorine evolved

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[3] Millar, THIS JOURNAL, **50**, 1875 (1928).

[4] Ditte, *Compt. rend.*, **94**, 792, 864 (1882).

[5] Palmaer, *Medd. Kgl. Vetenskapsakad, Nobelinst.*, **5**, 1 (1919).