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.

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[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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[2] Associate chemist, Pacific Experiment Station, Berkeley, California.

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

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

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

in potassium iodide solution, and titration of the iodine with standard thiosulfate showed 99.8, 99.2 and 99.6% of the theoretical amount of active oxygen.

Lead orthoplumbate, or minium, was prepared by decomposition of electrolytic lead dioxide in a stirred bath of molten potassium nitrate at 460°, according to Milbauer.[6] The salt was washed out and the product was dried at 120°. Analysis by the method used for lead dioxide indicated only 98.7, 96.1, 96.5, 96.5 and 97.2% of the theoretical quantity of active oxygen. Reduction by hydrogen showed 90.62% lead, whereas the theoretical percentage is 90.66. Probably decomposition of the dioxide was carried too far by excessive heating of the sides of the nitrate bath, but an impurity of considerable lead monoxide cannot be serious, since the heat capacity of lead orthoplumbate is only slightly more than three times that of the monoxide throughout the range of temperature of the measurements.

In the following tables heat capacities are expressed in gram calories (15°) per mole. One calorie is equal to 4.185 absolute joules. The calculations were made on the basis of O = 16, Sn = 118.7 and Pb = 207.20.

Table I

The Molal Heat Capacity of SnO

T, °K.	69.6	73.0	81.7	93.3	108.1	125.0	140.8	156.9
C_p	4.067	4.300	4.910	5.432	6.251	6.975	7.594	8.145
T, °K.	181.7	193.5	209.7	230.2	251.3	268.3	284.3	292.5
C_p	8.856	9.172	9.536	9.917	10.17	10.24	10.51	10.52

Table II

The Molal Heat Capacity of SnO_2

T, °K.	71.8	75.2	79.3	84.8	93.8	103.6	118.2	126.0	
C_p	3.087	3.323	3.619	3.995	4.532	5.242	6.165	6.621	
T, °K.	142.2	154.6	181.8	202.7	215.5	271.6	273.4	287.2	289.4
C_p	7.442	8.103	9.319	10.18	11.05	12.02	12.15	12.30	12.41

Table III

The Molal Heat Capacity of Pb_3O_4

T, °K.	71.5	78.5	85.6	100.1	111.7	127.1	138.6	151.3	172.1
C_p	16.65	17.82	18.81	20.55	22.33	24.29	25.82	27.08	28.77
T, °K.	187.4	208.8	227.1	247.1	259.8	266.2	278.2	292.6	
C_p	30.34	31.66	32.73	34.24	33.00	34.44	34.37	34.46	

Owing to its low apparent density, only about 0.3 mole of lead orthoplumbate could be loaded into the calorimeter, so that the empty calorimeter had more heat capacity than the sample. The result was a loss in accuracy. Usually the heat capacity of the sample was 1.5 to 4 times that of the empty calorimeter. The large errors in Points 13, 14 and 15 can be explained only by poor contacts in the potentiometer switches, which were causing trouble at the time.

An uncertainty at the lower end of the temperature scale caused inaccuracy in the calculations for Points 1, 2 and 3 in Table IV.

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[6] Milbauer, *Chem.-Ztg.*, **38**, 477. 559. 566. 587 (1914).

TABLE IV

THE MOLAL HEAT CAPACITY OF PbO_2

T, °K.	69.9	73.1	84.5	89.8	98.9	111.6	126.0	140.7	151.8	166.9
C_p	5.430	5.688	6.345	6.866	7.484	8.337	9.160	9.971	10.46	11.23
T, °K.	183.4	198.4	212.9	227.9	242.0	261.6	270.5	298.1	297.2	
C_p	11.94	12.72	13.11	13.50	13.95	14.60	14.83	15.42	15.43	

As before, the entropy of the oxide at 25° was calculated by graphical integration in the range covered by the data, using the relation

$$S_{298} - S_T = \int_T^{298} C_p \mathrm{d} \ln T$$

and by extrapolation to the absolute zero by means of combinations of Debye and Einstein functions. The following equations indicate the values of $\beta\nu$ used in these functions, denoted by $D(\beta\nu/T)$ and $E(\beta\nu/T)$, for the substances named, and the maximum temperatures for which the combinations of theoretical curves reproduce the experimental values of C_p.

SnO, $D\left(\frac{215}{T}\right) + E\left(\frac{494}{T}\right)$ 0.5% to 178°K.

SnO_2, $D\left(\frac{305}{T}\right) + E\left(\frac{487}{T}\right) + E\left(\frac{968}{T}\right)$ 0.5% to 200°K.

Pb_3O_4, $3D\left(\frac{119}{T}\right) + E\left(\frac{?}{T}\right)$ ......

PbO_2, $D\left(\frac{183}{T}\right) + E\left(\frac{342}{T}\right)$ 0.5% to 94°K.

The curve for Pb_3O_4 follows closely that of $3PbO$ drawn from the data of Nernst and Schwers[7] and of Russell.[8] The difference decreases rapidly with decreasing temperature, and probably does not reverse sign, so that, at low temperatures, the two curves follow the same Debye curve. Although better agreement with C_v, if sufficient data for the calculation of this quantity existed, could doubtless be obtained if more complicated combinations of these two functions were devised, nothing would be gained, since the extrapolation gives the entropy with only a slight error in any case.

The entropies of these oxides at 25° are: SnO, 13.56; SnO_2, 12.51; Pb_3O_4, 60.53; PbO_2, 18.27.

In order to calculate the free energy according to the equation

$$\Delta F = \Delta H - T\Delta S \tag{1}$$

for the reaction metal + oxygen = oxide, we must know the entropies of metallic tin, lead and of oxygen. From Brönsted's[9] data, Lewis, Gibson and Latimer[10] have calculated for Sn (white), $S^\circ_{298} = 11.17$, and

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[7] Nernst and Schwers, *Sitzb. preuss. Akad. Wiss.*, 355 (1914).

[8] Russell, *Physik. Z.*, **13**, 59 (1912).

[9] Brönsted, *Z. physik. Chem.*, **88**, 479 (1914).

[10] Lewis, Gibson and Latimer, THIS JOURNAL, **44**, 1008 (1922).

from those of Griffiths and Griffiths[11] for Pb, $S^{\circ}_{298} = 15.53$. As before, for O_2, $S^{\circ}_{298} = 49.2$.

Stannous Oxide.—No reliable values of the heats of formation of the oxides of tin exist. For the reaction $Sn(s) + 1/2O_2(g) = SnO(s)$, Mixter[12] gives $\Delta H = -66{,}800$, Andrews[13] $-67{,}600$, Delephine and Hallopean[14] $-70{,}700$, and G. Chaudron[15] $-69{,}000$. The results of measurements made in this Laboratory of the e.m.f. of cells, which will soon be published, give an accurate value of the free energy of stannous oxide, from which will be calculated a value of its heat of formation more accurate than any of the above.

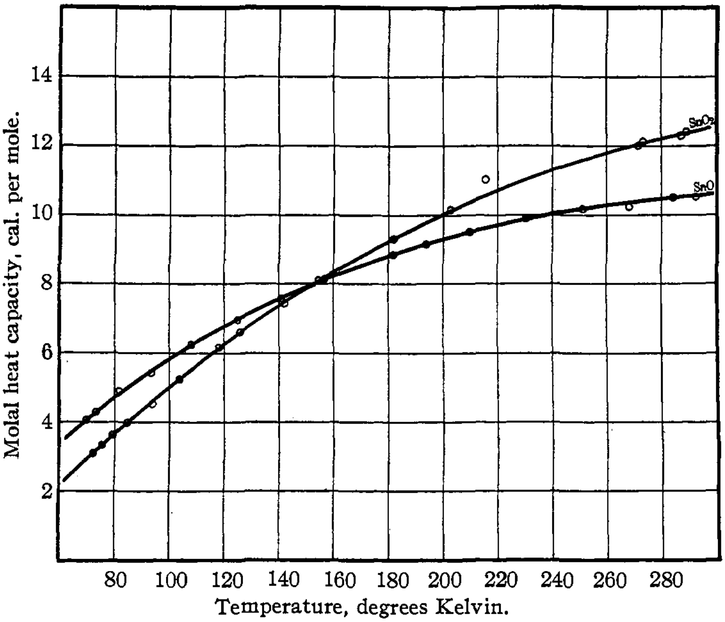

Fig. 1.—The molal heat capacities of SnO and SnO_2.

Stannic Oxide.—For the reaction Sn (white) + $O_2(g) = SnO_2(s)$, Mixter gives $\Delta H = -137{,}800$; Andrews $-137{,}800$; Moose and Parr[16] $-138{,}200$; and Maeda[17] $-130{,}260$. Mixter's value, $-137{,}800$, is probably but little in error. From the entropies of white tin, oxygen and stannic oxide, $\Delta S^{\circ}_{298} = -47.86$ and, finally, for $SnO_2(s)$, $\Delta F^{\circ}_{298} = -123{,}540$.

Lead Monoxide.—For the reaction $Pb(s) + 1/2O_2(g) = PbO(s)$,

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[11] Griffiths and Griffiths, *Proc. Roy. Soc., London*, **90A**, 557 (1914).

[12] Mixter, *Am. J. Sci.*, [4] **27**, 229 (1909).

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

[14] Delephine and Hallopean, *Compt. rend.*, **129**, 600 (1899).

[15] Chaudron, *Ann. chim. phys.*, [9] **16**, 220 (1921).

[16] Moose and Parr, THIS JOURNAL, **46**, 2656 (1924).

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

G. Chaudron[15] gives $\Delta H = -50{,}200$, Treadwell[18] $-50{,}400$, Berthelot[19] $-50{,}800$, Thomsen[20] $-50{,}300$, Günther[21] $-52{,}900$ and Smith and Woods[22] $-52{,}360$. With the exception of the last two, these values are exceptionally concordant and would ordinarily be accepted, but the cells of Smith and Woods,[22] which were of the form $Pb(s) + PbO(red) \mid Ba(OH)_2$ soln. $\mid H_2(g)$ were exceptionally reproducible at both 25 and 45°. Günther, who determined accurately the heat of formation of lead chloride by means of cell measurements, concluded that Thomsen's value for that quantity was too large by 2600 calories, and recalculated the latter's data for lead monoxide on that basis. Since Smith and Woods are the only investigators who definitely state that they used the red, tetragonal form, which is the stable one at room temperature, instead of the yellow, orthorhombic form, and since their measurements are undoubtedly accurate, their values of the free energy and the heat of formation are accepted and are quoted here for later reference.

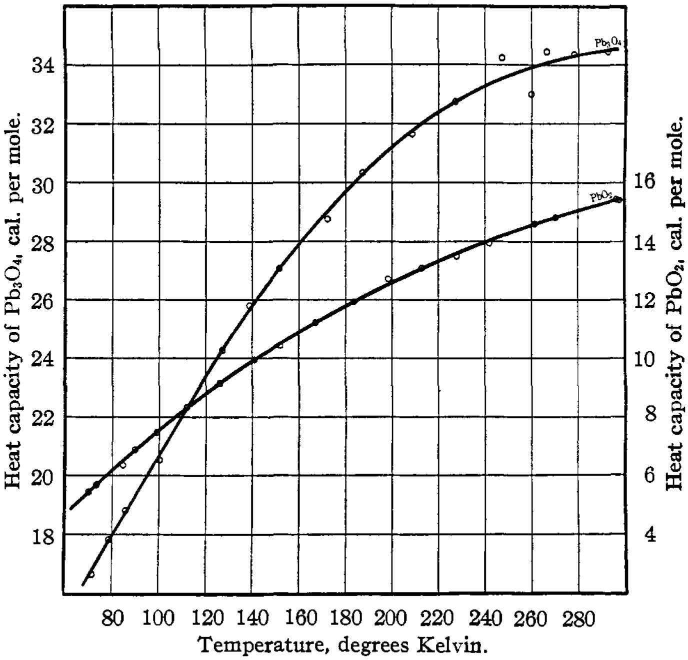

Fig. 2.—The molal heat capacities of Pb_3O_4 and PbO_2.

$$Pb(s) + 1/2O_2(g) = PbO(red);\quad \Delta F^\circ_{298} = -45{,}050;\quad \Delta H_{298} = -52{,}360 \qquad (2)$$

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[18] Treadwell, *Z. Elektrochem.*, **22**, 414 (1916).

[19] Berthelot, *Ann. chim. phys.*, [4] **30**, 191 (1873).

[20] Thomsen, "Thermochemische Untersuchung," Leipzig, **3**, 329 (1883).

[21] Günther, *Z. Elektrochem.*, **23**, 197 (1917).

[22] Smith and Woods, This Journal, **45**, 2632 (1923).

Randall and Spencer,[23] from measurements of the solubility of red and yellow lead monoxide in solution of sodium hydroxide, have calculated the difference in free energy of the two forms

$$\text{PbO(yellow)} = \text{PbO(red)};\quad \Delta F_{298} = -163 \tag{3}$$

Lead Dioxide.—For the reaction $PbO(s) + 1/2O_2(g) = PbO_2(s)$, Tscheltzow[24] gives $\Delta H = -12{,}140$, which added to Equation 2 gives for the reaction $Pb(s) + O_2(g) = PbO_2(s)$, $\Delta H = -64{,}500$. Mixter[25] gives $-65{,}600$.

Glasstone,[26] from cell measurements, has calculated the free energy changes at 17° of several reactions involving the oxides of lead. Apparently his lead monoxide was the red form. A recalculation of his two most reliable sets of measurements gives

$$PbO_2(s) + H_2(g) = \text{PbO(red)} + H_2O(l);\quad \Delta F^\circ_{298} = -49{,}600 \tag{4}$$

$$3PbO_2(s) + 2H_2(g) = Pb_3O_4(s) + 2H_2O(l);\quad \Delta F^\circ_{298} = -104{,}360 \tag{5}$$

From Equations 2 and 4 and the free energy of water

$$H_2(g) + 1/2O_2(g) = H_2O(l);\quad \Delta F^\circ_{298} = -56{,}560 \tag{6}$$

given by Lewis and Randall[27]

$$Pb(s) + O_2(g) = PbO_2(s);\quad \Delta F^\circ_{298} = -52{,}010 \tag{7}$$

Wescott,[28] from determinations of the equilibrium constant of the reaction $PbCl_2(s) + Cl_2(g) + 2H_2O = PbO_2(s) + 4HCl(\text{soln.})$ and the free energy of lead chloride, calculated for $Pb(s) + O_2(g) = PbO_2(s)$, $\Delta F^\circ_{298} = -52{,}330$, but he used an old value, $-56{,}620$, as the free energy of liquid water. When the more recent value given in Equation 6 is used, his results give $-52{,}210$ for the free energy of lead dioxide. The good agreement with Glasstone's value given in Equation 7 must, however, be considered as fortuitous, since the activity of the hydrochloric acid in Wescott's solution was somewhat uncertain. By combining Equations 1 and 7 with the entropies of lead, oxygen and lead dioxide, the heat of formation of lead dioxide can be calculated:

$$Pb(s) + O_2 = PbO_2(s);\quad \Delta H_{298} = -65{,}960 \tag{8}$$

in fair agreement with Mixter's value.

Lead Orthoplumbate.—By combining Equations 2, 4, 5 and 6

$$3Pb(s) + 2O_2(g) = Pb_3O_4(s);\quad \Delta F^\circ_{298} = -147{,}270 \tag{9}$$

a value which can be compared with one calculated from careful measurements of the decomposition pressure of lead orthoplumbate by Reinders

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[23] Randall and Spencer, This Journal, **50**, 1572 (1928).

[24] Tscheltzow, *Compt. rend.*, **100**, 1458 (1885).

[25] Mixter, *Am. J. Sci.*, [4] **27**, 396 (1909).

[26] Glasstone, *J. Chem. Soc.*, 121, 1456, 1469 (1922).

[27] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 485.

[28] Wescott, This Journal, **42**, 1335 (1920).

and Hamburger.[29] They showed that, at the temperatures of their measurements, yellow lead monoxide was formed, and that it did not form solid solutions with the lead orthoplumbate. Their data have been treated by the method described by Lewis and Randall,[30] whose equations and symbols will be used in what follows. The reaction is $2Pb_3O_4(s) = 6PbO(\text{yellow}) + O_2$. Reinders and Hamburger represent their results accurately by the equation

$$\log p_{\text{mm.}} = -\frac{35{,}926}{4.571T} + 11.8976$$

where it is evident that they have used for the gas constant, $R = 4.571/2.303$ instead of 1.9885, the value accepted here. If 1.9885 is used, their data may be equally well represented by

$$\log p_{\text{mm.}} = -\frac{35{,}987}{4.57877T} + 11.8976$$

Calculation by means of the approximation $d \ln p/d(1/T) = -\Delta H/R$ gives for their reaction, $\Delta H = -35{,}987$. Heat capacity equations for the substances involved are now required in order to calculate ΔH_0.

From the determinations of Regnault[31] and of Magnus[32] the heat capacity of lead monoxide is 11.4 at 330°K. and 11.7 at 417°K., whence for PbO, $C_p = 10.26 + 0.0034T$. At room temperature the heat capacity of lead orthoplumbate is 3.06 times that of lead monoxide. Assuming that this ratio holds through the region of Reinders and Hamburger's measurements, for Pb_3O_4, $C_p = 31.41 + 0.0106T$. For oxygen Lewis and Randall[33] give O_2, $C_p = 6.50 + 0.0010T$. For the decomposition of two moles of lead orthoplumbate, $\Delta C_p = 5.24 + 0.0005T$. Taking, at the average temperature of the measurements, $\Delta H_{823} = 35{,}987$, ΔH_0 becomes 31,505. The standard free energy change at the temperature of each of the 16 experiments was calculated by means of the equation $\Delta F^\circ = -RT \ln P$, where P is the experimentally determined pressure of the oxygen in atmospheres. By substitution of these values of ΔF°, ΔH_0, and the coefficients of the equation for ΔC_p in the free energy equation in the usual way, 16 values of the integration constant I were calculated which varied from -0.77 to -0.31, most of them being grouped closely about the average, $I = -0.52$. Then for

$$2Pb_3O_4(s) = 6PbO(\text{yellow}) + O_2;\quad \Delta F^\circ = 31{,}505 - 5.24T \ln T - 0.00025T^2 - 0.52T;$$
$$\Delta F^\circ_{298} = 22{,}430;\quad \Delta H_{298} = 33{,}090 \quad (10)$$

From Equations 1 and 10, $\Delta S^\circ_{298} = 35.76$, and by the use of the entropies of Pb_3O_4 and O_2, PbO(yellow), $S^\circ_{298} = 17.94$.

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[29] Reinders and Hamburger, *Z. anorg. Chem.*, **89**, 71 (1914).

[30] Lewis and Randall, ref. 27, p. 173.

[31] Regnault, *Ann. chim. phys.*, [3] 1, 129 (1841).

[32] Magnus, *Physik. Z.*, **14**, 5 (1913).

[33] Lewis and Randall, ref. 27, p. 80.

Combining Equations 2, 3 and 10

$$3Pb(s) + 2O_2(g) = Pb_3O_4(s);\ \Delta F^\circ_{298} = -145{,}870$$

and with the entropies of Pb_3O_4, Pb and O_2

$$\Delta H_{298} = -171{,}050 \quad (11)$$

On returning to Equations 10 and 11, it may be noted that

$$Pb(s) + 1/2O_2 = PbO(yellow);\ \Delta H_{298} = -51{,}500$$

and with 2

$$PbO(yellow) = PbO(red);\ \Delta H_{298} = -860;\ \Delta S^\circ_{298} = -2.35 \quad (12)$$

From Equations 1 and 2, PbO(red), $S^\circ_{298} = 15.62$. Smith and Woods in their paper noted the large discrepancy between their value of the entropy of red lead monoxide and the value of the entropy of lead monoxide, 16.3, which Lewis and Randall[34] calculated from measurements of its heat capacity by Nernst and Schwers.[7] The writer has recalculated the entropy from the same data and obtained 16.41, whereas Miething,[35] using the same data, obtained 17.04. Nernst and Schwers, although they say nothing concerning their sample, probably used the yellow form.

The entropy of yellow lead monoxide which was calculated from Reinders and Hamburger's results, 17.94, is undoubtedly too high, due probably to the assumptions regarding the heat capacities of lead monoxide and orthoplumbate above room temperature. For the present, then, the free energy of lead orthoplumbate which was calculated from Glasstone's data will be accepted, together with the corresponding heat of formation calculated from the entropies of this substance and of lead and oxygen. Thus

$$3Pb(s) + 2O_2(g) = Pb_3O_4(s);\ \Delta F^\circ_{298} = -147{,}270;\ \Delta H_{298} = -172{,}440$$

Likewise, from Equations 2 and 3, the entropy of yellow lead monoxide, 16.41, and the entropies of lead and oxygen

$$Pb(s) + 1/2O_2(g) = PbO(yellow);\ \Delta F^\circ_{298} = -44{,}887;\ \Delta H_{298} = -51{,}960$$

Summary

The heat capacities of stannous and stannic oxide, lead dioxide and lead orthoplumbate have been determined from 70 to 300°K. and their entropies at 25° have been calculated.

The following table contains the results of calculations from these data and others found in the literature.

	S°_{298}	ΔF°_{298}	ΔH_{298}
SnO(s)	13.56	....	....
SnO_2(s)	12.51	−123,540	−137,800
PbO(red)	15.62	− 45,050	− 52,360
PbO(yellow)	16.4	− 44,887	− 51,960
Pb_3O_4(s)	60.53	−147,270	−172,440
PbO_2(s)	18.27	− 52,010	− 65,960

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[34] Lewis and Randall, ref. 27, p. 498.

[35] Miething, *Abhand. deut. Bunsen-Ges.*, No. 9, 1920.