in the form of porous granules. The poorest catalysts have the finest grained structure. No explanation for the "mixture effect" is discovered.

6. An apparent anomaly in the results has been pointed out. In the region of true adsorption, all the sorption curves except that for Sample 1 coincide, indicating nearly equal surface exposure per unit pore volume for all these granules, in spite of great difference in pore size.

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[Contribution from the Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, California]

THE HEAT CAPACITY AT LOW TEMPERATURES OF ZINC OXIDE AND OF CADMIUM OXIDE[1]

By Russell W. Millar[2]

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Research on the heat capacities of the oxides of metals previously reported by the author[3] has been continued. For the sake of a comparison of results with those of Parks and his co-workers,[4] the heat capacity of zinc oxide was redetermined.

Materials.—The zinc oxide used was the Sample 2 described by Maier, Parks and Anderson. It had been kept in an evacuated silica flask at 1100° for sixty hours. The product was microcrystalline and contained, according to them, less than 0.1% of impurities.

The cadmium oxide used was prepared by heating pure cadmium oxide in an open platinum dish at 1100° for three days. The product was finely crystalline and of much higher apparent density than the original powder.

The values of C_p, the heat capacity in calories per mole per degree, are presented in Tables I and II and in Fig. 1 opposite the corresponding temperatures in degrees Kelvin.

The entropy was calculated, as described previously, by extrapolation to the absolute zero by means of the sum of suitable functions of the form of Debye and of Einstein. For zinc oxide a Debye function with $\beta\nu = 295.5$ and an Einstein function with $\beta\nu = 753$ fitted the data with an accuracy of 0.5% to 250°K., although C_v and C_p begin to deviate at much lower temperatures. At higher temperatures the experimental values fall below those given by the theoretical functions. Using C_p and log T as coördinates, the curve was extrapolated to 37.58°K., where it joined the Debye curve at $C_v = 0.860$. Below this temperature the tables of Mieth-

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[3] Millar, This Journal, **50**, 1875 (1928).

[4] (a) Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926); (b) Maier, Parks and Anderson, This Journal, **48**, 2564 (1926).

TABLE I

THE MOLAL HEAT CAPACITY OF ZINC OXIDE

T, °K.	C_p cal./mole	T, °K.	C_p cal./mole	T, °K.	C_p cal./mole
89.7	3.794	142.9	5.895	225.0	8.318
95.8	4.080	81.8	3.488	228.4	8.443
102.5	4.375	84.2	3.561	231.8	8.413
109.0	4.649	167.0	6.818	277.3	9.267
116.6	4.941	174.7	7.059	282.5	9.400
120.1	5.078	183.2	7.309	284.8	9.432
124.2	5.237	189.7	7.548	286.9	9.527
128.7	5.450	196.8	7.697	289.1	9.480
131.2	5.576	204.7	7.996	295.3	9.505
134.9	5.650	210.8	8.052	297.9	9.641
139.2	5.796	220.1	8.220		

TABLE II

THE MOLAL HEAT CAPACITY OF CADMIUM OXIDE

T, °K.	C_p cal./mole	T, °K.	C_p cal./mole	T, °K.	C_p cal./mole
71.3	4.078	136.1	7.460	151.9	8.045
77.9	4.495	148.0	7.945	177.1	8.774
90.5	5.286	160.9	8.309	194.9	9.165
101.1	5.843	288.0	10.35	232.5	9.879
112.2	6.402	289.2	10.35	253.5	10.06
124.2	6.942	290.4	10.30		

ing[5] give the entropy as 0.308 cal. per mole. The area above this temperature represents 9.97 entropy units, so that for ZnO, S°_{298} = 10.28. The error is probably not over 0.05 unit.

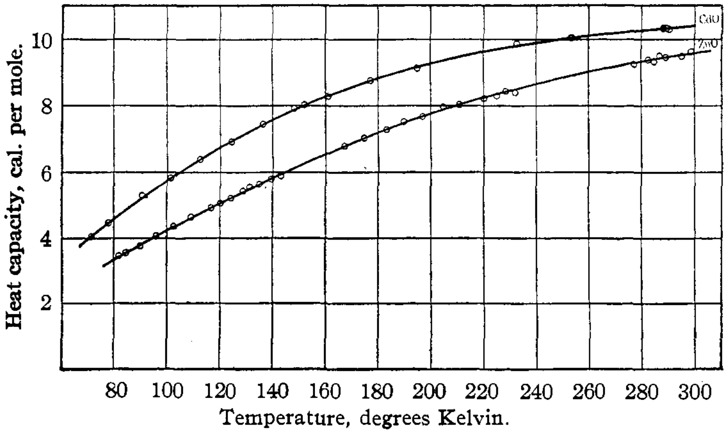

Fig. 1.—The molal heat capacities of cadmium oxide and zinc oxide.

A similar calculation for cadmium oxide, with $\beta\nu$ = 236 and 478.5 for the Debye and Einstein functions, respectively, gives 0.36 entropy unit

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[5] Published in Nernst, "Die theoretischen und experimenteller Grundlagen des neuen Wärmesatzes," Wilhelm Knapp, Halle, 1918.

at 31.84°K. and, by graphical integration, 12.81 units between 31.84 and 298°K. Thus for CdO, $S°_{298} = 13.17$. The sum of these functions agrees with the data within 0.2% to 160°K., and exceeds the experimental values at higher temperatures. Obviously the theoretical values would exceed the values of C_v, if necessary data for their calculation existed, at still lower temperatures.

The values of the heat capacity of zinc oxide agree with those of Maier, Parks and Anderson within 0.2% at their lowest temperature, 88°K., but become appreciably lower at higher temperatures. At room temperature the deviation is 2%. Although widely different methods of calculation were employed, the entropy which they give, $S°_{298} = 10.4$, differs but little from the present value of 10.28.

No significance is to be attached to the agreement of various combinations of theoretical curves for heat capacity with the experimental values of this quantity, for all such mathematical treatments rest upon hypotheses not entirely true and, furthermore, are designed to give values of C_v and not C_p. However, extrapolations by means of these curves cannot be far from correct when the last measured value of the heat capacity is not more than 4 calories per mole, and they undoubtedly approach the absolute zero correctly.

After reviewing the direct determination of the heat of formation of zinc oxide and comparing the values obtained from the temperature coefficients of the equilibrium constant of the reaction $ZnO + CO = Zn + CO_2$ and of the e.m.f. of the cell $ZnO + Zn \mid Ba(OH)_2$ soln. $\mid H_2$, Maier, Parks and Anderson[4b] give 83,000 cal. as the best value. Roth and Chall[6] have recently obtained 82,905 cal. for dense zinc oxide and 82,825 for less dense material at 50°, while Parks, Hablutzel and Webster[7] give 83,240 cal. at 20°. We shall choose for $Zn_{(s)} + \frac{1}{2} O_{2\,(g)} = ZnO_{(s)}$; $\Delta H = -83,000$.

Maier after a review (to be published soon) of the data, has chosen 62,000 as the probable value of the heat of formation of cadmium oxide.

For zinc and cadmium, Lewis, Gibson and Latimer[8] give $S°_{298} = 9.83$ and 11.80, respectively, and for O_2 we may use, as before, Millar's[3] value 49.2.

We have $Zn_{(s)} + \frac{1}{2} O_{2(g)} = ZnO_{(s)}$, $\Delta H_{298} = -83,000$, $\Delta S°_{298} = -24.15$, $\Delta F°_{298} = -75,800$; and $Cd_{(s)} + \frac{1}{2} O_{2(g)} = CdO_{(s)}$, $\Delta H_{298} = -62,000$, $\Delta S°_{298} = -23.23$, $\Delta F°_{298} = -54,200$.

Since the value of the free energy of zinc oxide which Maier, Parks and Anderson obtained from cells, −75,930, is doubtless much more nearly accurate than our knowledge of the heat of formation, it is more logical to calculate the latter from the entropy of formation. We obtain $\Delta H = -83,130$, a value probably accurate to within 100 calories.

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[6] Roth and Chall, *Z. Elektrochem.*, **34**, 185 (1928).

[7] Parks, Hablutzel and Webster, THIS JOURNAL, **49**, 2792 (1927).

[8] Lewis, Gibson and Latimer, *ibid.*, **44**, 1008 (1922).

Summary

1. The heat capacities of zinc and cadmium oxide from 70 to 300° Kelvin have been determined.

2. The entropy of zinc oxide at 298°K. is 10.28 ± 0.05 cal./mole/degree, and of cadmium oxide is 13.17 ± 0.1 cal./mole/degree.

3. For zinc oxide we find from an accurate value of the free energy and the entropy of formation $\Delta H = -83{,}130 \pm 100$, and for cadmium oxide we find from the entropy of formation and a somewhat uncertain value of the heat of formation, $\Delta F°_{298} = -54{,}200$.

[CONTRIBUTION NO. 582 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

THE EQUILIBRIUM $2K_3Fe(CN)_6 + 2KI \rightleftarrows 2K_4Fe(CN)_6 + I_2$ IN AQUEOUS POTASSIUM CHLORIDE SOLUTIONS

BY VICTOR K. LA MER AND KARL SANDVED

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I. Introduction

This paper comprises one phase of a study of the kinetics of ionic reactions which proceed to a measurable equilibrium state, the purpose of the study being to investigate the velocity of the reaction not only in its initial stages but also in the neighborhood of equilibrium.

The reaction between ferricyanide and iodide ions yielding ferrocyanide and iodine, as follows

$$2Fe(CN)_6^{---} + 2I^- \rightleftarrows 2Fe(CN)_6^{----} + I_2 \qquad (1)$$

possesses certain advantages for such a study since

1. The reaction reaches an equilibrium state after 2–13% conversion, depending upon the composition and the amount and character of added neutral salts. The equilibrium state is therefore accessible to experimental measurement and is well adapted for a study of salt effects.

2. The velocity of the reaction is also highly sensitive to neutral salt catalysis, a subject of considerable theoretical interest at the present time.[1]

3. Previous studies[2,3,4] have shown that the velocity of the reaction, unlike most reversible ionic reactions, is of a magnitude that can be followed.

In the investigations of Donnan and Le Rossignol,[2] Just[3] and Wagner,[4] the reaction was followed by adding measured amounts of thiosulfate and

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[1] For a critical discussion see J. N. Brönsted, "Acid and Basic Catalysis," Copenhagen, **1926**, translated from the Danish by the authors for *Chemical Reviews*, September, 1928, particularly Chapters 4 and 5 and appendix.

[2] Donnan and Le Rossignol, *J. Chem. Soc.*, **83**, 703 (1903).

[3] Just, *Z. phys. Chem.*, **63**, 513 (1908).

[4] Wagner, *ibid.*, **113**, 261 (1924).