[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Silver Oxide: The Heat Capacity of Large Crystals from 14 to 300°K.

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A sample of macrocrystalline, annealed Ag_2O was prepared by long heating in contact with water at 325° under 200 atm. of O_2. The heat capacity of this sample was measured from 14 to 300°K. and failed to show the thermal anomaly in the range 20 to 45°K. previously observed for finely divided (precipitated) Ag_2O.

In 1937 Pitzer and Smith[2] observed a thermal anomaly in finely divided (precipitated) Ag_2O in the temperature region 20 to 45°K. An entropy increment of 0.48 cal./degree mole was associated with the excess heat capacity of the anomaly. The present paper is the first of a series directed toward the understanding of this anomaly.

It should be noted at the outset that Kobayashi[3] discovered a second thermal anomaly which manifests itself by heat evolution (315 cal./mole) on the first heating of a precipitated sample of Ag_2O through the range 370 to 470°K. Dr. C. N. R. Rao[4] has verified this effect by differential thermal analysis. Presumably this is an annealing effect associated with the removal of crystal imperfections and possibly some crystal growth.

Since the original low temperature investigation involved an unannealed sample of very fine precipitated Ag_2O, it seemed desirable to prepare and study a sample of the largest and most perfect crystals obtainable. The present investigation comprises the preparation of such a sample and low temperature heat capacity measurements there-upon.

Sample Preparation.—An initial sample was precipitated by mixing carbonate-free sodium hydroxide solution with aqueous silver nitrate and was washed repeatedly with hot distilled water. The crystal size and perfection were then enhanced by heat treatment at 325° under 200 atm. of oxygen in contact with water for 22 days. The sample was contained in a covered platinum test tube inside the pressure bomb. The oxygen pressure employed is over 4 times the calculated equilibrium dissociation pressure of Ag_2O. The sample was then dried under one atm. of purified oxygen at 110°.

Analysis of the final material showed approximately 0.05% copper and less than 0.01% of other impurities except for 0.04% water for which a correction was made. The oxide content from acid neutralization was 100.2% of theoretical for Ag_2O and the silver content 99.5%. These results indicate a surprisingly large amount of a higher oxide of silver but an amount too small to be likely to affect our thermal measurements.

The average particle size appeared to be 0.02 mm. edge length. The cultured material was black with strong specular reflection. It poured freely and packed to an average density of 2.8 g./cc. in contrast to the ordinary precipitated Ag_2O which aggregates strongly and yet packs to only 1.5 g./cc. density. The X-ray diffraction pattern of the cultured material was distinctly sharper than that of ordinary silver oxide. Additional details of the sample preparation, the calorimeter and the measurements may be found elsewhere.[5]

Calorimeter.—The heat capacity measurements were made with a cryostat of a basic design that has become standard in this Laboratory, and with a gold calorimeter designed and built for this research.

The important features of the basic design are discussed in a series of papers by Giauque and co-workers[6] and hence need not be discussed here.

The calorimeter, while basically similar to other gold calorimeters in this Laboratory, differed from most in having an axial re-entrant well for mounting a strain-free platinum thermometer.

After the body of the calorimeter had been completed, thermally cycled between room temperature and liquid air temperature a number of times, and leak tested, it was wound (after first being coated with Bakelite lacquer and rice paper) with a gold alloy wire heater-thermometer. The heater, whose resistance at room temperature was ~ 425 ohms, was wound with terminating turns of No. 30 copper wire for leads, as is customary; in addition, at one end were wound two separate loops of No. 30 copper wire, by which connections between No. 40 copper wires coming from the copper block terminals and the (platinum) potential leads of the strain-free thermometer were made so as to minimize the contribution of the unavoidable platinum–copper junction to the observed potential. No such provision was necessary for the current leads, so No. 40 platinum leads were connected directly between the block terminals and the thermometer current leads. No. 40 copper wires were used for the leads between the appropriate block terminals and the thermometer-heater on the outer surface.

Since optimal thermal contact between the strain-free thermometer and the calorimeter was desired, the strain-free thermometer case was carefully tinned with Rose's metal, as was the well in the calorimeter. Upon assembly, sufficient additional Rose's metal was introduced into the well to fill it with the thermometer in place. The thermometer was not removed between measurements on the empty and the full calorimeter.

The weight of the calorimeter containing one

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[2] K. S. Pitzer and W. V. Smith, *J. Am. Chem. Soc.*, **59**, 2633 (1937).

[3] K. Kobayashi, *Sci. Rep. Tohoku Univ.*, **35**, 173 (1951).

[4] Reported briefly by K. S. Pitzer, R. E. Gerkin, L. V. Gregor and C. N. R. Rao, *Pure and Applied Chem.*, **2**, 211 (1961).

[5] R. E. Gerkin, Ph.D. Dissertation, University of California, 1960.

[6] See W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

atmosphere of helium, and with the thermometer in place, was 432 g.; the volume was 112 ml.

The ancillary equipment was that employed previously except as required by the replacement of a thermocouple by a strain-free resistance thermometer as the absolute thermometer. Thus the energy input circuit, the timer, the strained thermometer–heater circuit and the control thermocouple circuit were those employed also by the other workers in this laboratory.

TABLE I

HEAT CAPACITY OF MACROCRYSTALLINE Ag_2O

UNITS: CAL./DEGREE MOLE

Temp., °K.	C_p	Temp., °K.	C_p
Series I			
13.50	2.03	193.02	13.63
15.28	2.44	198.85	13.80
17.22	2.96	204.77	13.93
19.12	3.39	211.08	14.09
21.25	3.95	217.57	14.26
23.58	4.51	223.79	14.39
25.93	5.00	230.21	14.54
28.44	5.53	237.15	14.67
31.51	6.07	243.70	14.85
35.05	6.65	250.06	14.98
39.10	7.18	256.28	15.09
43.44	7.68	262.56	15.22
47.74	8.09	268.81	15.35
52.22	8.46	275.47	15.46
57.03	8.80	281.52	15.56
62.09	9.09	288.07	15.62
67.01	9.38	294.66	15.70
76.12	9.79	301.67	15.75
81.40	10.01	Series II	
87.16	10.24	24.50	4.68
92.87	10.42	26.63	5.14
98.27	10.61	29.17	5.64
103.66	10.79	32.43	6.21
109.25	10.96	36.25	6.82
114.86	11.17	40.49	7.34
120.55	11.35	45.38	7.84
126.47	11.58	50.52	8.32
132.62	11.77	55.35	8.69
138.80	12.01	60.11	9.00
144.95	12.19	64.78	9.26
150.98	12.37	69.64	9.50
157.12	12.59	74.36	9.69
163.07	12.77	78.97	9.90
168.82	12.93		
174.90	13.13		
180.95	13.29		
186.92	13.46		

Temperature Scale.—The strain-free platinum resistance thermometer used as a working standard in the calorimeter was manufactured by Leeds and Northrup and was compared in this Laboratory at five to six degree intervals with three similar thermometers which had been calibrated by the National Bureau of Standards. Comparisons were also made at various fixed points with satisfactory agreement. Unfortunately the glass seal on the working thermometer was broken after completion of the heat capacity measurements and before the final calibration. However, it was possible to seal the thermometer with the lead wires still in the glass head into a large case in a manner which could have at most a very slight effect on the calibration.

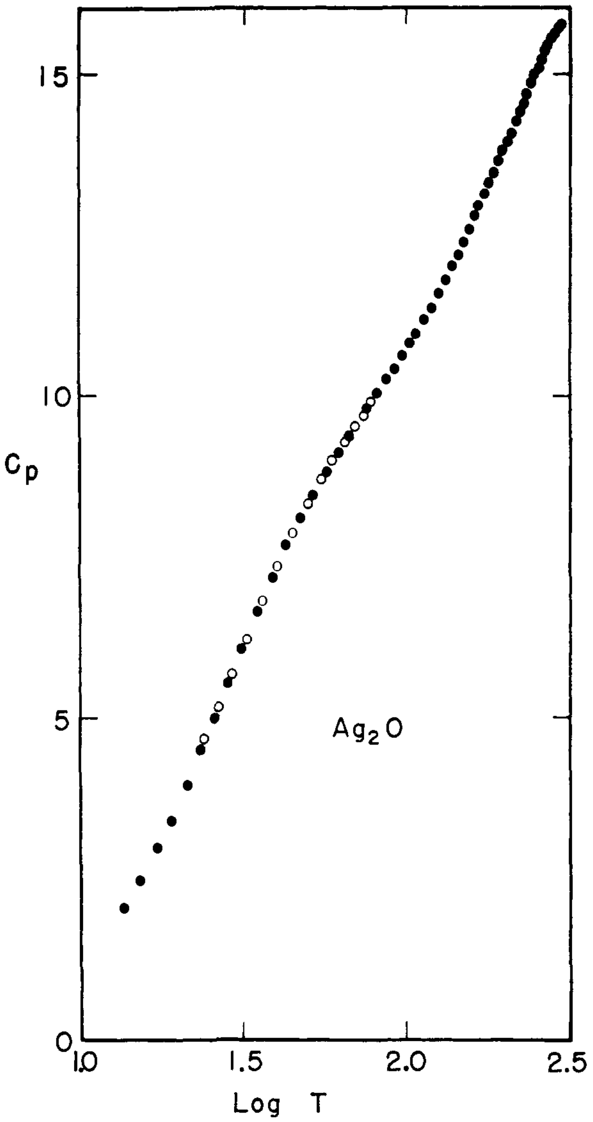

Fig. 1.—Heat capacity of macrocrystalline silver oxide.

In the region above the oxygen boiling point our temperature scale is the International Scale of 1948 and below the oxygen boiling point it is the N.B.S. low temperature scale, but in each region the temperature is reduced by 0.01°. This has the effect of correcting to the new value 273.15°K. for the ice point. While a fractional instead of a subtractive correction would appear to be more logical, the deviations of the scales mentioned above from the thermodynamic scale as now known are predominantly positive in the region of interest and consequently the subtraction of 0.01° seems preferable.

Heat Capacity Measurements.—The substitution of the strain-free resistance thermometer for the thermocouple did not significantly alter the method of heat capacity measurement and calculation previously employed in this Laboratory. Data are reported in the defined calorie equal to 4.1840 abs. Joules and based upon the molecular weight 231.760. The resulting measured heat capacities are reported in Table I and shown in Fig. 1.

Discussion and Conclusions

It is apparent at once from Fig. 1 that this macrocrystalline annealed silver oxide shows no thermal anomaly at all. This disappearance of the anomalously high heat capacity from the region 20 to 45°K. is the principal result of the present investigation. The two series of measurements agree well with one another and confirm this conclusion. Measurements below 14°K. on this sample and at various temperatures on another sample will be reported in a subsequent paper. Entropy calculations and further interpretation will be based on all of these data.

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Silver Oxide: The Heat Capacity from 2 to 80°K. and the Entropy; the Effects of Particle Size

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The heat capacity of Ag_2O has been measured from 2.2 to 80°K. for a finely divided annealed sample and from 3.3 to 24°K. for a macrocrystalline annealed sample. The anomalously high heat capacity originally observed in unannealed Ag_2O between 20 and 50°K. is also found in the finely divided sample, though the anomalous region is smaller and narrower, and its maximum occurs at a lower temperature. No anomalous peak in the heat capacity of macrocrystalline Ag_2O is observed down to 3.3°K., but the heat capacity of this material is higher below 14°K. than that of the finely divided sample. The heat capacity of the various samples of Ag_2O is discussed in terms of its unusual crystal structure, and a mechanism proposed to correlate the anomalous behavior of Ag_2O below 15°K. and between 20 and 40°K. The mechanism involves the interaction of the two independent sublattices of the structure of Ag_2O, and it is proposed that for very small particles, there is a transition from a symmetric high-temperature structure to a slightly distorted low-temperature structure in the vicinity of 20 to 30°K. Revised values of the thermodynamic properties of macrocrystalline Ag_2O at 298.15°K. are given, based on the observed heat capacity data below 15°K. The results are

$$S_{298.15}{}^0 = 28.91 \pm 0.07 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$H_{298.15}{}^0 - H_0{}^0 = 3387 \pm 5 \text{ cal. mole}^{-1}$$

$$\left(-\frac{F^0 - H_0{}^0}{T}\right)_{298.15} = 17.55 \pm 0.07 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Introduction

The preceding paper[3] together with this one describes a series of low temperature calorimetric studies undertaken with the aim of understanding the anomalously high heat capacity of Ag_2O observed by Pitzer and Smith[4] in the region 20–45°K. A second region of anomalous behavior in silver oxide was noted by Kobayashi[5] in which heat is evolved in the region 100–200° the first time that freshly precipitated and dried Ag_2O is heated through this range. Since the Pitzer and Smith measurements were made on precipitated Ag_2O which had not been annealed by heating through the 100–200° range, it seemed desirable to study more highly annealed samples.

In the first investigation, which is reported in the preceding paper, macrocrystalline Ag_2O was prepared by extended culturing of precipitated material under 200 atm. of oxygen in contact with water at 325°. It was found that the heat capacity curve was quite normal through the 15–45°K. range; in other words the anomaly had disappeared. However, the quantitative trend of heat capacity with temperature from 15 to 20°K. deviated appreciably from the Debye function. Hence it seemed wise to study this macrocrystalline material below 15°K. as well as to prepare and measure samples with characteristics intermediate between the macrocrystalline sample and the freshly precipitated and dried material.

A sample of Ag_2O was annealed without greatly changing its particle size distribution, and its heat capacity was measured from 2 to 80°K. The heat capacity of the macrocrystalline Ag_2O was also measured below 15°K. In addition, subsidiary experiments were performed to determine the surface areas of the various Ag_2O samples. Measurements of the effects of annealing on the behavior of the Ag–Ag_2O electrode are reported in another paper.[6]

Experimental Methods

Preparation of Annealed Small-particle Ag_2O.—The calorimetric sample of small-particle Ag_2O was prepared by the reaction of aqueous $AgNO_3$ with carbonate free aqueous NaOH. Only freshly boiled distilled water was used for solution preparation, washing, rinsing, etc., and all glassware and equipment were thoroughly cleaned and

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(3) R. E. Gerkin and K. S. Pitzer, *J. Am. Chem. Soc.*, **84**, 2662 (1962).

(4) K. S. Pitzer and W. V. Smith, *ibid.*, **59**, 2633 (1937); see also H. L. Johnston and J. H. Hu, *ibid.*, **73**, 4550 (1951).

(5) K. Kobayashi, *Sci. Repts. Tohoku Univ.*, First Series, **35**, 173 (1951).

(6) L. V. Gregor and K. S. Pitzer, *J. Am. Chem. Soc.*, **84**, 2671 (1962).