

TRANSITIONS AND THERMAL ANOMALIES IN SILVER OXIDE

KENNETH S. PITZER, ROGER E. GERKIN, LAWRENCE V. GREGOR and
C. N. R. RAO

University of California, Berkeley, California, U.S.A.

In 1937 Pitzer and Smith¹ measured the heat capacity of silver oxide (Ag_2O) over the range 13–300°K and found anomalously high values in the range 20–40°K. Hysteresis effects were noted with respect to the excess heat capacity. The entropy associated with the anomaly was approximately $0.5 \text{ cal } ^\circ\text{C}^{-1} \text{ mole}^{-1}$. Kobayashi² measured the heat capacity of silver oxide at higher temperatures and observed a heat evolution of approximately 315 cal/mole in the range 100–200°C the first time that a given sample was heated through this region. Repeat heating gave no further heat evolution. In each case the sample was precipitated from aqueous solution and was dried at temperatures not exceeding 115°C. The present investigation was designed to yield further information about these peculiar effects.

EXPERIMENTAL

Samples

Several silver oxide samples were prepared under a variety of conditions. The decomposition pressure of silver oxide reaches 1 atm at about 460°K, hence high temperature preparations had to be carried out in a bomb under oxygen pressure. A platinum lining was used in the bomb. In all cases the samples were initially precipitated from aqueous solution at room temperature in the absence of carbon dioxide. Care was taken to avoid contact with reducing agents. Analyses yielded the theoretical composition Ag_2O within experimental error. No reduction such as that reported by Faivre³ was observed. Spectroscopic analysis showed 0.05 per cent of Cu and less than 0.01 per cent of other impurities. The samples may be placed in three classes: (A), precipitated and dried at 95°C; (B) precipitated, dried, and annealed by heating to 180°C under 140 atm pressure of oxygen; and (C), precipitated, crystal growth promoted under 200 atm of oxygen in contact with water for 20 days at 325°C, and then dried in pure oxygen at 110°C.

Optical microscopy showed material (A) to be exceedingly fine whereas material (C) had crystals of approximately 0.02 mm edge length. X-ray diffraction showed a lattice parameter of $4.72 \pm 0.01 \text{ \AA}$ for all samples, but samples (B) and (C) showed somewhat sharper lines. Electron spin resonance measurements gave no evidence for unpaired electrons in either annealed or unannealed samples.

Thermal measurements at 20–40°K

The low temperature heat capacity measurements were made in the usual manner. Minor variations in the calorimeter will be described when the measurements are presented in detail. *Figure 1* shows as open circles and

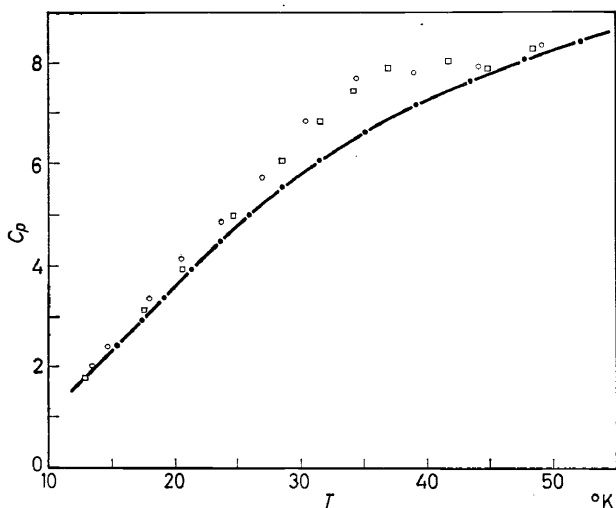


Figure 1. The heat capacity of silver oxide. \circ , \square results of Pitzer and Smith¹ on two different samples of type (A); \bullet new results on large crystals (sample C)

squares two of the series of measurements of Pitzer and Smith on a sample of type (A) and as closed circles the new measurements on sample (C), i.e. large annealed crystals. It is apparent that the anomaly has disappeared. The large crystals show slightly smaller heat capacity over the remainder of the temperature range. This effect of surface or of particle size has been observed for other substances.

Heat capacity measurements have also been made on samples (B) but calculations are not yet complete. The anomaly is still present but is substantially reduced in magnitude as compared with sample (A). The entropy value calculated for sample (C) is given in *Table 1* along with the values for sample (A) and that reported by Hamer and Craig⁴ from cell measurements. The value for the large crystals of sample (C) is in excellent agreement with that of Hamer and Craig.

Table 1. The entropy of silver oxide at 298.15°K (cal °C⁻¹ mole⁻¹)

Sample A	total	29.09
	without hump	28.61
Sample C		28.38
Hamer and Craig ⁴	(cell E.M.F.)	28.32

Thermal measurements at 370–470°K

The apparatus used in this range was of the differential thermal analysis type described by Pask and Warner⁵. We are indebted to Professor Pask

TRANSITIONS AND THERMAL ANOMALIES IN SILVER OXIDE

for the use of this equipment. The apparatus is sensitive to heat effects of 0.2 to 0.5 cal with a sample of 2 g of silver oxide. Heating curves for unannealed samples of type (A) uniformly showed exothermic peaks near 200°C in agreement with the result of Kobayashi. Neither the annealed samples (B) and (C) nor samples of type (A) which had been heated through the 200°C peak showed any exothermic peak. All samples absorbed heat in the region above 250°C; this was presumably caused by decomposition of silver oxide to metal and oxygen.

DISCUSSION

The measurements reported above show that neither of the thermal anomalies observed for freshly precipitated and dried silver oxide is observed with large perfect crystals. Both anomalies are associated in some way with the large surface or the crystal imperfection of the precipitated material. The heat evolution above room temperature could readily arise from the annealing of crystal defects and the reduction of surface by crystal growth. We have observed similar effects in magnesium oxide. Since the energies associated with defects or surface may be large and it is known that the precipitated material is extremely finely divided, there is no contradiction with the rather substantial heat of 315 cal/mole observed by Kobayashi².

It is much more difficult to explain the low temperature anomaly. Since the effects at 20–40°K are reversible, although with hysteresis, only thermal energies corresponding to these temperatures can be involved. Thus the appropriate quantity for interpretation is the entropy of approximately 0.5 cal °C⁻¹ mole⁻¹. If the surface atoms were shifting from single positions to random distributions over a modest number of positions, then roughly 10 per cent of the atoms would have to be on the surface. This seems unlikely. Another possibility is some sort of condensation or aggregation, whereby the entropy change per mole of surface atoms might be 10–20 cal °C⁻¹ mole⁻¹. Even this postulate requires 1 to 5 per cent of the atoms to participate, which seems a large percentage.

It is known from work⁶ on magnesium oxide that surface entropy of very fine material can approach 0.25 cal °C⁻¹ g-atom⁻¹, but in that case the extra heat capacity is distributed more uniformly over the entire temperature range. The values in *Table 1* for sample (A) (without hump) and for sample (C) show that this difference is present in the silver oxide in addition to the anomaly at 20–40°K.

The crystal structure of silver oxide has an unusual characteristic which might lead to abnormal behaviour. The silver oxide structure comprises two separate but interpenetrating lattices which are nowhere directly bonded to one another. Thermal energy at high temperatures would cause each lattice to occupy on the average the centre of the vacancies of the other lattice and thereby have maximum freedom for thermal motion. Conceivably, however, at low temperatures the two sub-lattices could move toward one another and find a lower potential energy in an unsymmetrical state. Since this would involve co-ordinated motion of all atoms of a given crystal, it is possible that the rate of transformation is significant only for very small crystals. If this sort of change is involved, the restraining forces for lattice vibrations should be somewhat larger in the low temperature

asymmetric form. From the points in *Figure 1* it appears that the heat capacity curves cross at about 14°K with the small crystals showing smaller heat capacity below that temperature. This result is consistent with the postulated type of change, but the accuracy of the measurements below 20°K is hardly great enough to make this conclusion completely definite. Various aspects of this problem are under further study.

This work received support from the U.S. Atomic Energy Commission.

References

- ¹ K. S. Pitzer and W. V. Smith. *J. Am. Chem. Soc.*, **59**, 2633 (1937)
- ² K. Kobayashi. *Sci. Rep. Tōhoku. Univ.* (I), **35**, 173 (1951)
- ³ R. Faivre. *Compt. rend.*, **210**, 398 (1940); *Ann. Chim.*, **19**, 58 (1944)
- ⁴ W. J. Hamer and D. N. Craig. *J. Electrochem. Soc.*, **104**, 206 (1957)
- ⁵ J. A. Pask and M. F. Warner. *Am. Ceram. Soc. Bull.*, **33**, 168 (1954)
- ⁶ G. Jura and C. W. Garland. *J. Am. Chem. Soc.*, **74**, 6033 (1952), and other references there cited