Thermochimica Acta, 30 (1979) 163–171

HEAT CAPACITIES OF THE TUNGSTEN OXIDES WO_3, $W_{20}O_{58}$, $W_{18}O_{49}$ AND WO_2

F. R. SALE
Metallurgy Department, Manchester University, Grosvenor Street, Manchester M1 7HS (Gt. Britain)
(Received 24 April 1978)

ABSTRACT

The heat capacities of the tungsten oxides WO_3, $W_{20}O_{58}$, $W_{18}O_{49}$ and WO_2 have been measured over the temperature range 340–999 K using differential scanning calorimetry. The lower oxides were prepared by controlled reduction of WO_3 in H_2/H_2O gas atmospheres. Previous calorimetric work on WO_3 is confirmed in the temperature range 340–800 K, however, significant increases in heat capacity were observed in the range 800–999 K prior to the orthorhombic–tetragonal phase transition. $W_{20}O_{58}$ is shown to behave similarly to WO_3. A high temperature phase change is evident, however, this appears to be complete by 970–990 K. The measured values of heat capacity for $W_{18}O_{49}$ are in close agreement with estimated data for $W_{18}O_{49}$. There is no evidence of any phase transitions for this oxide in the temperature range studied. The heat capacity data for WO_2 confirm previous drop calorimetry measurements and give no evidence of any phase changes for WO_2 in the temperature range 340–990 K.

INTRODUCTION

The tungsten oxygen system[1] contains the stable oxides WO_3, $W_{20}O_{58}$, $W_{18}O_{49}$ and WO_2. Recently, these oxides have been prepared and characterised by Basu and Sale[2, 3] as part of a study which has attempted to understand and control the parameters that determine the particle morphologies of tungsten powder obtained by the hydrogen reduction of WO_3. The lower oxides have been shown to play an important role in the tungsten production process. The heat capacities of WO_3 and WO_2 have been measured by King et al.[4] in the temperature range 396–1800 K by drop calorimetry and these data have been joined smoothly at 298.15 K with low temperature data, also obtained by the same authors, to yield the values given for these two oxides in the JANAF tables[5]. Comment is made in the JANAF tables that King et al.[4] were apparently unaware of the solid-state transition of WO_3 at 593 K, as reported by Perri et al.[6], and insufficient measurements had been made in the region of this phase transition. Nevertheless, the heat capacity data were adopted as a smooth curve through the region of the transition because of the insufficiency of the data and also because the heat effect appeared to be either very small or very gradual. Heat capacity data for the oxides $W_{20}O_{58}$ and $W_{18}O_{49}$ have been estimated from the data for WO_3 and WO_2 because the oxides have similar monoclinic structures (up to 593 K for WO_3)[7].

It was thus apparent that direct measurements of the heat capacities of all the oxides prepared and characterised in the previous work of the present author would help to resolve the potential problems in the data for WO_3 and also provide the first experimentally determined values for $W_{20}O_{58}$ and $W_{18}O_{49}$, and hence test the validity of the estimated data given for these oxides in the JANAF tables[5].

EXPERIMENTAL PROCEDURE

Materials

The preparations of WO_3, $W_{20}O_{58}$, $W_{18}O_{49}$ and WO_2 have been described in detail previously[2, 3]. In summary, WO_3 was prepared from "Analar" purity ammonium paratungstate crystals by thermal decomposition in air at 1000 K. The lower oxides were prepared from the WO_3 by controlled reduction at 900 K in H_2O/H_2 atmospheres in a glass-spring thermogravimetric balance. All the oxides were characterised by X-ray diffraction analysis using Cu*K* radiation with a "Siemens Kristalloflex 4" diffractometer and by scanning electron microscopy using a "Cambridge Stereoscan 180" microscope[2, 3].

Heat capacity measurements

Heat capacity measurements were made using a Perkin-Elmer DSC2 differential scanning calorimeter. The calorimeter was operated in the conventional manner for heat capacity measurements which entails an "empty–empty" scan over the required temperature range, an "empty–calibrant" scan over the same temperature range and finally an "empty–specimen" scan over the same range. The experimental data were treated in the manner discussed by Richardson[8] and Mills and Richardson[9]. The primary aim of this procedure is to construct "full minus empty" curves by subtracting the curve for the empty calorimeter from those for the calorimeter containing the calibrant and the specimen. The relative displacements of the calibrant and specimen curves are then used to give heat capacities at "point" temperatures. Experimental runs in which the baseline isothermals differed by greater than 5% of the full-scale deflection of the chart recorder were disregarded.

The temperature calibration of the calorimeter was carried out using the conventional DSC–DTA standards, namely In, Sn, Pb, Zn, K_2SO_4 and K_2CrO_4. Gold specimen pans were used in all experiments with specimen weights in the range 0.05–0.06 g. All experiments were carried out in purified argon using mainly a scanning rate of 10 K min^{-1}. The temperature ranges scanned in any given run varied from 50–200 K, although ranges of only 10 K were used in the vicinity of expected solid-state transitions. In the regions of these transitions scanning rates as low as 0.31 K min^{-1} were used, no significant effects were observed in the experimental data. A "Calorimetry conference" synthetic sapphire of weight 0.06162 g was used as the calibrant in all the heat capacity measurements. Initial studies used ignited alumina powder (DTA standard) because it was anticipated that powdered alumina would be a more appropriate physical form of calibrant for powder specimens. However, the difficulties associated with the dehydration of the alumina (see following section) made this calibrant unsuitable and so the synthetic sapphire was used for all subsequent experiments.

RESULTS AND DISCUSSION

Powdered alumina calibrant

Figure 1 shows typical heat capacity data obtained for the powdered alumina using synthetic sapphire as the calibrant. The adsorption of water vapour on the surface of such DTA calibrant powder is quite well documented, and it is recommended that the powder is fired frequently. The data shown in Fig. 1 were obtained for ignited powder that had been heated to 900 K in the calorimeter and then left to stand in the calorimeter over one weekend in a supposedly still argon atmosphere. The extent of readsorption of water vapour by back-diffusion down the gas exit is quite apparent by the excessively large heat capacity values in the range 300–500 K caused by the removal of the water, and thus indicates that dehydration of the powder is required on each occasion prior to its use. As the use of the DSC for heat capacity measurements requires three experimental runs to be made without any significant shift in baseline isothermals, it was felt that the addition of an extra heating and cooling stage for dehydration added too much to the experimental complexity for, at best, a marginal advantage in the use of the powder standard. Consequently, the synthetic sapphire disc was used for all heat capacity determinations.

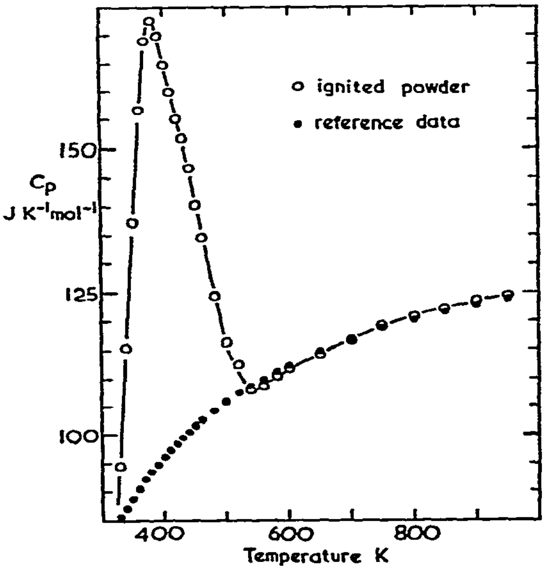


Fig. 1. Heat capacity data obtained for powdered alumina relative to synthetic sapphire.

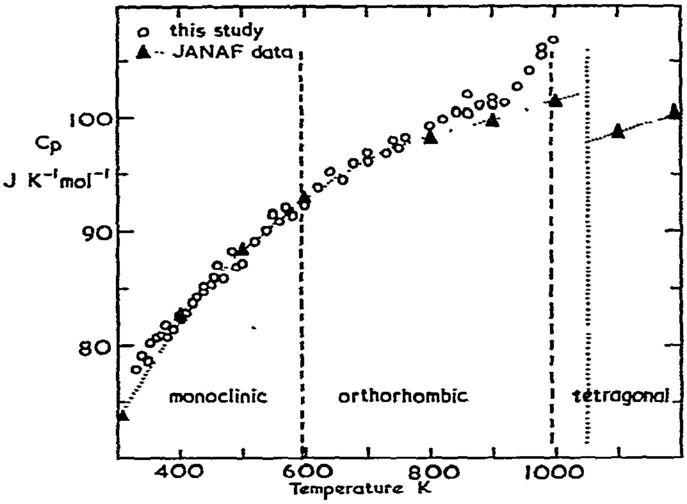


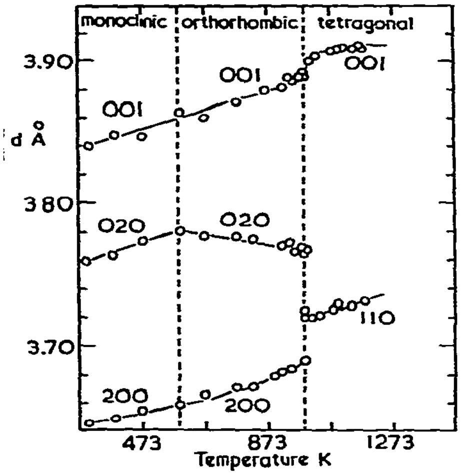
Fig. 2. Heat capacity of WO_3 as a function of temperature.

$WO_3(c)$

The heat capacity of $WO_3(c)$ determined over the temperature range 340–999 K is shown in Fig. 2. The smoothed data given in the JANAF tables[5] is presented as the dotted line. The dashed lines on Fig. 2 at 593 and 993 K show the temperatures of the monoclinic–orthorhombic and orthorhombic–tetragonal phase transitions, respectively, as determined by Perri et al.[6] in their high temperature X-ray diffraction study of WO_3. A temperature of 1050 K is given in the JANAF tables for the orthorhombic–tetragonal phase change and this is represented by the vertical dotted line on Fig. 2.

It can be seen that at temperatures up to 800 K there is good agreement between the data obtained in this study and that of the drop calorimetric study of King et al.[4] given in the JANAF tables[5]. At temperatures greater than 800 K the present experimental data depart increasingly from the JANAF data. It is known that the overall accuracy and reproducibility of data from the DSC decrease as the top temperature limit is approached, however, many separate experiments yielded the type of effect shown in Fig. 2 and it is felt that this effect is real and there is a significant increase in heat capacity as the orthorhombic–tetragonal transition is approached. Such "lattice-loosening" effects prior to major enthalpy increments, such as those which occur at phase transitions, are common and have been discussed for Cu_2Te by Mills and Richardson[9]. It is apparent that the orthorhombic–tetragonal transition did not occur at temperatures up to 999 K in the present study (even when the upper limit was scanned at 0.31 K min^{-1}) and so it may be assumed that the value of 993 K given by Perri et al.[6] for this transition is too low and a value approaching the 1050 K given in the JANAF table may be more appropriate.

Many more measurements of heat capacity were made in the present study in the region of the monoclinic–orthorhombic transition at 593 K than are actually shown in Fig. 2. (The reproducibility of all the measurements was better than ±1.5% and confirms the belief of Mills and Richardson[9] that heat capacity data may be obtained to an accuracy of ±1% with DSC measurements). Even at heating rates of



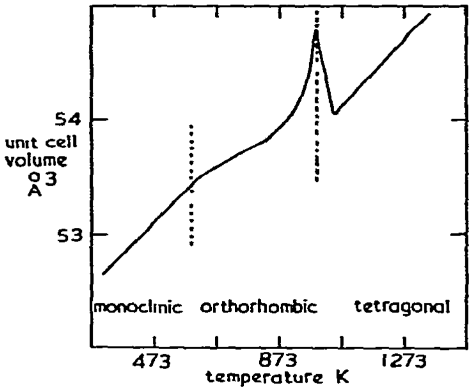


Fig. 3. X-ray diffraction data showing the lattice expansion of WO_3. (After Perri et al.[6].)

Fig. 4. Variation of unit cell volume of WO_3 with temperature. (After Perri et al.[6].)

0.31 K min^{-1} no large heat capacity variations were observed in the region of 593 K and so it can be concluded that there is no significant thermal effect associated with this transition. Consequently, the comments in the JANAF table with reference to the work of King et al.[4] are a little unjust. Nevertheless, it is interesting to speculate why no thermal effects can be detected for this transition. The X-ray diffraction data of Perri et al.[6] are replotted in Figs. 3 and 4. Figure 3 shows the variation in *d*-spacing of the (001), (020) and (200) reflections over the temperature range 300–1273 K. It can be seen that there are gradual changes in positions of these lines over the temperature range 300–993 K and this indicates a fairly smooth gradual transition from monoclinic to orthorhombic structures. At 993 K the (200) and (020) reflections of the orthorhombic phase disappear with the appearance of the (110) reflection of the tetragonal phase. This indicates a far greater structural change. Figure 4 shows the relationship between unit cell volume of WO_3 and temperature. Again it can be seen that a smooth change occurs at the monoclinic–orthorhombic transition and hence little change in heat capacity may be expected with a consequently small thermal effect. It is interesting to note the increase in cell volume as the orthorhombic–tetragonal transition is approached and this produces a curve which is apparently analogous to the heat capacity measurements reported in the present study. (Confirmatory evidence for the unit cell volume effect found by Perri et al.[6] is given by Foëx[10] in the results of a dilatometric study).

$W_{20}O_{58}$(c)

The heat capacity of $W_{20}O_{58}$(c) determined over the temperature range 340–999 K is shown in Fig. 5. The estimated data given in the JANAF table for this oxide are presented as the dotted line. The calculated data seem to implicity assume that the room temperature monoclinic phase identified by Magneli et al.[7] is stable up to the maximum temperature reported (3000 K) despite the known transitions in

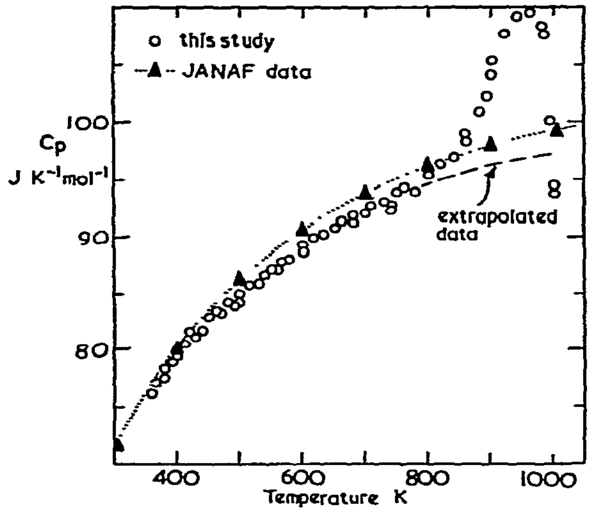


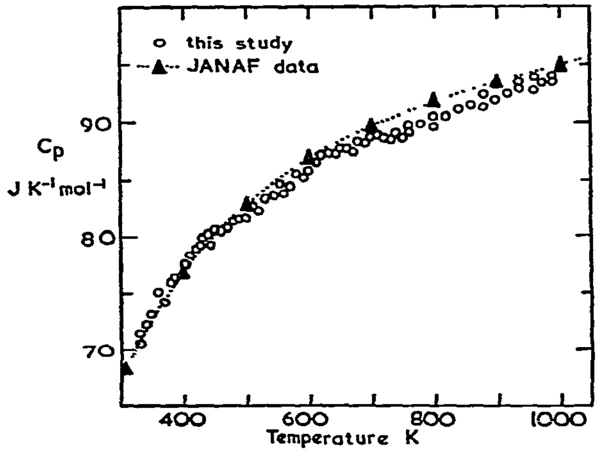
Fig. 5. Heat capacity of $W_{20}O_{58}$ as a function of temperature.

WO_3. From Fig. 5 it can be seen that the calculated data are consistently higher than the experimental values in the range 340–800 K. At 800 K the experimental heat capacity increases and crosses the line for the estimated data and seems to reach a maximum value in the region of 970 K. This behaviour is similar to that observed for WO_3. The only difference between the behaviour of the two oxides is that a decrease in the heat capacity was observed for $W_{20}O_{58}$ at temperatures greater than 970 K. As mentioned in the previous section it is fully realised that the accuracy of DSC measurements at such elevated temperatures is open to some debate, however, the decrease in heat capacity was obtained for different samples in a number of separate experiments. Consequently, it would appear that $W_{20}O_{58}$ undergoes a slow solid-state transition similar to that of WO_3 in the region of 993–1050 K, but the transition occurs at a lower temperature for $W_{20}O_{58}$. However, the form of the heat capacity curve given in Fig. 5 is not that expected for such a solid-state transition.

If the area below the experimentally determined data and above the extrapolated heat capacity data is integrated from 800 to 990 K, it is found to correspond to an enthalpy of 1330 J mole^{-1} which is quite similar to that given in the JANAF table for the enthalpy of the orthorhombic–tetragonal transition in WO_3 at 1050 K (1485 J mole^{-1}).

$W_{18}O_{49}(c)$

The experimental data determined for the heat capacity of $W_{18}O_{49}$(c) are shown in Fig. 6 along with the calculated data given in the JANAF table. It can be seen that there is extremely good agreement between the experimental and calculated values at temperatures up to 700 K, after which there is a slight departure upto the maximum temperature studied (999 K). However, the maximum departure is of the order of 2%, which falls close to the experimental accuracy at these elevated temperatures. It is interesting to note that there is no indication of the increase in heat capacity that was observed for WO_3 and $W_{20}O_{58}$ at temperatures above 800 K and was ascribed



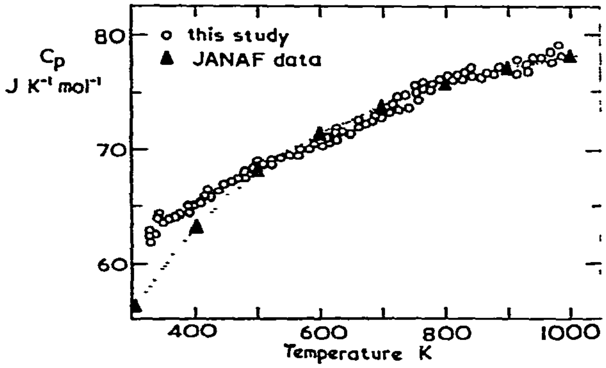


Fig. 6. Heat capacity of $W_{18}O_{49}$ as a function of temperature.

Fig. 7. Heat capacity of WO_2 as a function of temperature.

to some form of "lattice loosening" effect prior to the orthorhombic–tetragonal transition in the WO_3. It is apparent that $W_{18}O_{49}$ does not undergo this type of thermal transition in this temperature range and indicates that the crystal structure of $W_{18}O_{49}$ is thermally more stable than the two higher oxides. Microscopic studies of the oxides[2, 3] certainly show that $W_{18}O_{49}$ is produced from WO_3 during the controlled reduction studies in a newly crystallised state with a characteristic whisker-like form, whereas $W_{20}O_{58}$ cannot be distinguished from WO_3 by microscopy alone.

$WO_2(c)$

Figure 7 shows the experimentally determined data obtained for the heat capacity of WO_2(c) along with the JANAF data which are based on the drop calorimetric studies of King et al.[4]. Experimentally it was found that the reproducibility of the measurements made for WO_2 was poor (in the region of ±15%) unless great care was taken to ensure that the scanning calorimeter was flushed with argon for many hours prior to measurement and the WO_2 was sealed into the gold specimen pan using the standard press. The other oxides were studied in pans in which the lid was simply laid upon the oxide powder. When due care and attention was paid to the experimental technique, data were obtained with a reproducibility of the order of ±2.5%. The reason for the lack of reproducibility in the "open" pans was that the WO_2 seemed to oxidise slightly at temperatures above 600 K.

From Fig. 7 it can be seen that at temperatures above 500 K the scanning calorimeter data is clustered around the JANAF data, which is based upon the drop calorimetric work of King et al.[4], and thus confirms this latter work. Again, as for $W_{18}O_{49}$, there is no evidence of abnormal heat capacity increases at temperatures close to the temperature of the orthorhombic–tetragonal transition in WO_3, and indicates an absence of this type of transition for WO_2 in the temperature range studied, although X-ray diffraction data for a tetragonal form of WO_2 have been reported[11]. At temperatures below 500 K the present data give higher heat capacity values than the drop calorimetric data. At 350 K the DSC data is some 5 J mole^{-1} greater than the drop calorimetric value of 59.75 J mole^{-1}. This is equivalent to a maximum difference in the two sets of data of some 8%.

CONCLUSIONS

(1) The heat capacity of WO_3 shows a smooth change through the monclinic–orthorhombic transition and no detectable thermal effect is associated with this gradual transition. The present DSC data confirm the earlier drop calorimetric data upto 800 K. However, the heat capacity of WO_3 increases above the smoothed data given in the JANAF table as the orthorhombic–tetragonal transition is approached. This is taken to indicate significant "lattice loosening" prior to transformation. The temperature of 993 K determined by Perri et al.[6] for this transition is too low and a value approaching the 1050 K given in the JANAF table may be more appropriate.

(2) The experimental heat capacity of $W_{20}O_{58}$ is lower (by some 2–2.5%) than the estimated JANAF data over the temperature range 500–800 K. At temperatures greater than 800 K there is a marked increase in heat capacity which is followed, at temperatures greater than 970 K, by a marked decrease. (It is realised that these measurements are in the least accurate range of DSC operation, however, they appear to be consistent). If the experimental data are extrapolated from 770 to 990 K (Fig. 5) then the area above this line and beneath the experimental line corresponds to an enthalpy of transition of 1330 J mole^{-1} which is similar to the value of 1485 J mole^{-1} given in the JANAF table for the orthorhombic–tetragonal transition for WO_3 at 1050 K. It is thus postulated that $W_{20}O_{58}$ behaves similarly to WO_3. However, the high temperature solid-state transition occurs at a lower temperature for $W_{20}O_{58}$ than for WO_3.

(3) Reasonable agreement exists between the measured and estimated heat capacity data for $W_{18}O_{49}$. There is no evidence of any solid state transitions for this oxide in the temperature range 350–999 K.

(4) The DSC data for the heat capacity of WO_2 confirms the earlier drop calorimetric data for this oxide in the temperature range 500–900 K. Higher values (upto 5 J mole^{-1}) were obtained in the present study at temperatures in the range 340–500 K. Again no solid-state transition was detected for this oxide in the temperature range studied.

ACKNOWLEDGEMENTS

The author would like to thank Professor E. Smith and Dr. F. H. Hayes for the provision of funding for the DSC used in this work, and Dr. A. K. Basu who prepared the samples of oxide as part of his Ph. D. studies on the control of particle morphology of tungsten powder.

REFERENCES

1 G. R. St Pierre, W. T. Ebihara, M. J. Pool and R. Speiser, *Trans. Metall. Soc. AIME*, 224 (1962) 259.

2 A. K. Basu and F. R. Sale, *Trans. Inst. Min. Metall., Sect. C*, 86 (1977) C134.

3 A. K. Basu and F. R. Sale, *Trans. Inst. Min. Metall., Sect. C*, 86 (1977) C169.

4 E. G. King, W. W. Weller and A. U. Christensen, *U.S., Bur. Mines, Rep. Invest.*, (1960) 5664.

5 *JANAF Thermochemical Tables*, Vol. 37, U.S. National Bureau of Standards, Washington, D.C., 1971, 2nd edn.

6 J. A. Perri, E. Banks and B. Post, *J. Appl. Phys.*, 28 (1957) 1272.

7 A. Magneli, G. Anderson, B. Blomberg and L. Kihlborg, *Anal. Chem.*, 24 (1952) 1998.

8 M. J. Richardson, *J. Polym. Sci., Part C*, 38 (1972) 251.

9 K. C. Mills and M. J. Richardson, *Thermochim. Acta*, 6 (1973) 427.

10 M. Foëx, *C.R.*, 220 (1945) 917.

11 J. D. H. Donnay and H. M. Ondik (Eds.), *Crystal Data, Determinative Tables*, Vol. 2, *Inorganic Compounds*, U.S. National Bureau of Standards and Joint Committee on Powder Diffraction Standards, 1973.