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Thermophysical measurements on transition-metal tungstates

I. Heat capacity of zinc tungstate from 5 to 550 K [a]

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Redetermination of the heat capacity of $ZnWO_4$ after chemical removal of the ZnO phase from a previous sample has provided better values for chemical thermodynamic properties. At 298.15 K C_p, $S°$, and $-\{G°(T) - H°(0)\}/T$ are found to be 27.44, 28.51, and 12.991 $cal_{th}\ K^{-1}\ mol^{-1}$.

1. Introduction

Zinc tungstate is isostructural with the $NiWO_4$-type tungstates (*e.g.* $MnWO_4$ (hübnerite), $FeWO_4$ (ferberite), $CoWO_4$, and $NiWO_4$) and, hence, its heat capacity is important as an estimate of the lattice heat-capacity contribution in resolving the magnetic transitions of the other substances. Previously reported heat capacities of zinc tungstates[1,2] are deficient in that a separate zinc oxide phase was ascertained as present by X-ray analysis and subsequent chemical analysis indicated (3.51 ± 0.7) per cent by mass or 12.3 moles per cent of the oxide. Although adjustment for the presence of the ZnO was made on the basis of additivity, development of chemical methods for the successful removal of oxide phases from other transition metal tungstates[3] has permitted us to remove the zinc oxide from the sample and measure directly the heat capacity of the now pure zinc tungstate sample. The direct determination of the heat capacity has led to values differing by approximately 1 per cent from those previously reported; the chemical analysis is apparently at fault.

2. Experimental

The sample described in the previous work[1] was crushed to a fine powder in an agate mortar, washed in dilute (0.2 mol dm^{-3}) hydrochloric acid, rinsed in distilled water, and dried in an oven. All X-ray lines found were indexed as pertinent to the

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zinc tungstate lattice; no ZnO lines were detected. The lattice parameters derived for this sample: $a = (0.4692 \pm 0.0001)$ nm, $b = (0.5719 \pm 0.0002)$ nm, $c = (0.4927 \pm 0.0001)$ nm, and $\beta = (90.61 \pm 0.02)°$, are in good accord with those of other investigators.[1] Details of the X-ray powder pattern are given elsewhere.[3] Duplicate analyses for zinc and tungsten[4] indicate 20.42 and 20.67 mass per cent zinc (theor. 20.87) and 57.80 and 57.64 mass per cent of tungsten (theor. 58.70). The mean values correspond to a mole ratio $n(W)/n(Zn)$ of (1.000 ± 0.004) and, hence, unity within the reliability of the determinations. Earlier tests on this sample reveal the difficulty of obtaining complete dissolution of the sample; systematic deviation from the theoretical values is therefore not considered important.

As was done originally,[1] values were determined in calorimeter W-30 in the Mark-II adiabatic cryostat and in W-22-0 in the Mark-IV adiabatic thermostat. All conditions parallel closely those described earlier except that the sample masses were somewhat reduced to about 57.8 g.

3. Results and discussion

The experimental heat capacities corrected for curvature have been listed in chronological sequence in table 1 so that the temperature increments can be deduced approximately from the mean temperatures. These results have been taken against the IPTS-48 temperature scale. The molar mass of $ZnWO_4$ was taken as 313.2276 g mol^{-1}. The precision of these results parallels that in the original presentation.[1]

The heat capacity and derived thermodynamic properties presented in table 2 at selected temperatures are similarly defined and were smoothed and/or integrated by digital computer and compared with large-scale graphical plots.

The original heat capacity adjusted for impurity is consistently 1 per cent lower from 100 K to 350 K than the results reported here. Below 100 K the curves of the heat capacities approach and cross so that the original values are higher than the present values below 40 K. The discrepancy indicates the inadequacy of the original adjustment made for the contribution of the zinc oxide impurity. To explain the lack of accord, we have ascertained the amount of zinc oxide originally present both by leaching it from the original sample and by comparison of the heat capacities involved. For the former, a portion of the original sample was crushed, dried to constant mass, leached with 0.2 mol dm^{-3} aqueous HCl, dried to constant mass, and reweighed. After correcting for the solubility of pure $ZnWO_4$ in the acid (determined for these conditions), the mass loss was found to be (2.1 ± 0.3) per cent. Moreover, the mass per cent of ZnO which best reproduced the originally observed heat capacity of impure $ZnWO_4$[1] from the new heat-capacity value for this substance over the range 100 to 300 K—the only range of reliable heat capacities of ZnO[5]—was found to require the presence of (2.00 ± 0.03) mass per cent of ZnO in the original sample. These values are in good accord with each other but are substantially lower than the (3.5 ± 0.7) mass per cent obtained by interpretation of ultimate commercial analyses in the previous study.[1]

TABLE 1. Heat capacity of zinc tungstate
(cal_{th} = 4.184 J)

T/K	C_p/cal_{th} K^{-1} mol^{-1}	T/K	C_p/cal_{th} K^{-1} mol^{-1}	T/K	C_p/cal_{th} K^{-1} mol^{-1}	T/K	C_p/cal_{th} K^{-1} mol^{-1}
			In Mark II cryostat				
	Series I	300.50	27.56	147.95	17.21	15.08	0.186
140.68	16.45	310.18	27.94	158.05	18.20	16.71	0.262
147.72	17.17	319.75	28.36			18.63	0.369
158.64	18.25	329.22	28.74			20.86	0.523
168.00	19.13	338.62	29.06		Series III	23.24	0.724
178.12	20.01	346.07	29.32	5.11	0.006	25.56	0.952
188.98	20.91			5.70	0.008	27.90	1.203
199.53	21.71			6.17	0.011	30.59	1.521
209.79	22.45			6.64	0.024	33.72	1.923
219.80	23.17		Series II	7.27	0.019	37.42	2.434
229.60	23.80	82.24	9.181	7.97	0.025	42.32	3.132
239.76	24.43	89.63	10.25	8.69	0.032	47.62	3.926
250.29	25.05	97.67	11.31	9.40	0.043	52.95	4.758
260.64	25.63	107.39	12.56	10.25	0.064	59.00	5.638
270.81	26.15	117.72	13.84	11.29	0.072	65.46	6.685
280.83	26.69	127.64	15.02	12.33	0.094	73.05	7.805
290.73	27.08	137.70	16.12	13.58	0.123	81.08	9.004
			In Mark IV thermostat				
	Series I	331.45	28.73	378.53	30.22		Series V
332.82	28.82	341.45	29.09	388.53	30.56	460.63	32.49
342.97	29.11					470.74	32.72
353.04	29.47					480.80	32.90
363.03	29.81		Series III		Series IV	490.80	33.17
372.95	30.22	298.83	27.41	392.24	30.69	500.75	33.38
382.80	30.37	308.82	27.84	402.15	30.96		
		318.70	28.22	411.99	31.27		Series VI
		328.69	28.56	421.92	31.63	502.46	33.28
	Series II	338.79	28.90	431.95	31.89	515.64	33.47
330.87	27.56	348.81	29.26	441.92	32.18	525.68	33.72
311.17	27.94	358.74	29.56	451.97	32.43	535.86	33.75
321.35	28.39	368.60	29.94	462.11	32.62	546.00	33.79

TABLE 2. Thermodynamic properties of $ZnWO_4$
($cal_{th} = 4.184$ J)

T / K	C_p / $cal_{th}\ K^{-1}\ mol^{-1}$	$\{S°(T) - S°(0)\}$ / $cal_{th}\ K^{-1}\ mol^{-1}$	$\{H°(T) - H°(0)\}$ / $cal_{th}\ mol^{-1}$	$-\{G°(T) - H°(0)\}/T$ / $cal_{th}\ K^{-1}\ mol^{-1}$
5	0.006	0.002	0.008	0.001
10	0.049	0.017	0.125	0.004
25	0.893	0.290	5.511	0.070
50	4.294	1.880	67.73	0.525
100	11.619	7.169	470.52	2.464
150	17.41	13.026	1202.5	5.009
200	21.75	18.66	2187.1	7.725
250	25.03	23.88	3360.1	10.442
300	27.52	28.68	4676.9	13.087
350	29.36	33.06	6101	15.63
400	30.94	37.09	7609	18.07
450	32.32	40.82	9192	20.39
500	33.29	44.27	10834	22.61
550	33.85	47.48	12514	24.72
273.15	26.28	26.15	3954.2	11.678
298.15	27.44	28.51	4626.1	12.991

We consider that the possibility that 1.5 per cent by mass of ZnO could still remain in the pure sample is excluded by the following facts. (1) The present mole ratio $n(Zn)/n(W)$ is (1.00 ± 0.004); whereas a 1.5 mass per cent of ZnO contamination would yield a mole ratio of 1.059. (2) The Guinier X-ray technique is capable of detecting impurity phases of less than 0.5 mass per cent, one third of the level required to account for the discrepancy, but no zinc oxide lines are observed from the pure sample.

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