

Low-temperature heat capacity and thermodynamic functions of IrO_2 ^a

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The heat capacity from 5 to 350 K of IrO_2 has been measured by quasi-adiabatic equilibrium calorimetry. The values for the thermodynamic properties at 298.15 K have been calculated as $C_{p,m}(T)/R = 6.687$, $\Delta_0^{\circ}S_m^{\circ}/R = 6.133$, $\Delta_0^{\circ}H_m^{\circ}/(R \cdot K) = 1039.5$, and $\Phi_m^{\circ}(T, 0)/R = 2.647$. The low-temperature heat capacity shows typical metallic behavior with an electronic coefficient $\gamma/R = 0.00067 \text{ K}^{-1}$. The entropy at 298.15 K is shown to be consistent with the volumetric dependence of this quantity.

1. Introduction

Transition-metal dioxides with rutile and related structures display an interesting range of physical properties which correlate with the number of free d-electrons of the metal ions, ranging from insulators (TiO_2 , d^0) through semi-metallic and on to metallic conductors (MoO_2 , TcO_2 , RuO_2 , RhO_2 , WO_2 , ReO_2 , OsO_2 , IrO_2 , PtO_2) as well as providing the interesting metal-to-insulator transitions as for VO_2 , NbO_2 and magnetic ordering (MnO_2 , CrO_2). Their stability and electrical properties make them important materials for technical applications as electrodes, film resistors, heating elements, crucibles, and catalysts.

The thermochemical properties of IrO_2 have been extensively studied by means of electromotive force, oxygen dissociation pressure, high-temperature enthalpy increment, thermogravimetric, and d.t.a. measurements.

Calorimetric heat-capacity measurements available were only those below 10 K (by Passenheim and McCollum)⁽¹⁾ and above 290 K (by Wöhler and Jochum).⁽²⁾ These latter values have been often criticized as being unreliable. Only recently Cordfunke⁽³⁾ has re-measured the high-temperature enthalpy increments and

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re-evaluated experimental results in the literature with the new values calculated here, obtaining consistent results for third-law evaluations.

2. Experimental

The IrO_2 was prepared by oxidation (in oxygen) of IrCl_3 at 1273 K overnight. The IrCl_3 was obtained as a green microcrystalline powder by chlorination of iridium powder at about 873 K. The analysis of the iridium content of the IrO_2 sample was 86.04 per cent by mass (calculated 85.73).

A 36.80 g sample was loaded into the gold-plated copper calorimeter (laboratory designation W-50) provided with a screw-type closure with a stainless-steel knife edge and an annealed gold gasket. The loaded calorimeter was evacuated and 2.7 kPa of helium gas was added at 300 K to facilitate thermal contact between sample and calorimeter.

Heat-capacity measurements were made in the range 5 to 350 K in the Mark II adiabatic cryostat.⁽⁴⁾ The calorimeter was surrounded by a shield system provided with automatic temperature control. A Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-5) was used for temperature determinations. The thermometer was calibrated at the U.S. National Bureau of Standards (N.B.S.) against IPTS-48 (as textually revised in 1960)⁽⁵⁾ for temperatures above 90.2 K, against the N.B.S. provisional scale from 10 to 90 K, and by the calibration technique of McCrackin and Chang⁽⁶⁾ below 10 K. These calibrations are judged to reproduce thermodynamic temperatures to within 0.03 K from 10 to 90 K and to within 0.04 K above 90 K. Determinations of mass, current, potential difference, and time are referred to standardizations and calibrations performed at the N.B.S. The accuracy of a single heat-capacity measurement is considered to be about 0.5 per cent from 10 to 15 K increasing to about 0.1 per cent between 30 and 350 K.

3. Results

The heat-capacity of IrO_2 is represented by a simple sigmate curve with contributions only from the free-electron gas and the lattice vibrations. The measured heat capacity of IrO_2 is listed in chronological order in table 1 and represented graphically in figure 1. The experimental heat capacities were processed by subtraction of the heat capacity of the empty calorimeter and corrected for the small differences in the amounts of helium gas and gold gasket relative to the calorimeter when measured empty. The calorimeter and (thermometer + heater) assembly represent 20 to 30 per cent of the total measured heat capacity except in the region of high C_p , where they decreased to 5 per cent. Curvature corrections were applied to obtain the heat capacity $\{C_p = (\partial H / \partial T)_p\}$ from the measured $\Delta H / \Delta T$ values. The approximate temperature increments employed usually can be estimated from the adjacent mean temperature in table 1. The results were fitted to a power series in orthogonal polynomials as described by Justice.⁽⁹⁾ Below 5 K, heat-capacity values were extrapolated by fitting the measured values below 65 K to a polynomial with only odd powers in T .

TABLE 1. Measured molar heat capacity of IrO_2 ($R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Series I		77.39	1.645	179.52	4.490	287.40	6.531	11.30	0.0223	31.09	0.2317
62.48	1.1387	84.63	1.901	187.75	4.680	298.10	6.685	12.67	0.0283	33.63	0.2849
66.68	1.2766	91.67	2.128	197.20	4.885	308.62	6.839	14.06	0.0345	36.57	0.3514
72.20	1.4630	98.80	2.341	206.72	5.078	319.06	6.982	15.37	0.0422	39.93	0.4324
80.02	1.733	107.21	2.592	216.01	5.278	327.33	7.084	16.45	0.0492	43.62	0.5301
89.56	2.059	116.59	2.866	225.10	5.455	334.43	7.164	17.74	0.0568	48.07	0.6661
98.65	2.331	125.80	3.128	234.01	5.629	340.86	7.219	19.02	0.0674	52.76	0.8141
106.96	2.572	134.67	3.375	242.23	5.789	345.71	7.275	20.53	0.0806	57.73	0.9726
Series II		143.89	3.621	251.14	5.953	Series III		22.29	0.0989	63.09	1.1545
60.06	1.0572	153.32	3.866	260.78	6.116	6.13	0.0057	24.25	0.1209	68.57	1.3418
65.25	1.2341	162.39	4.092	268.59	6.246	8.13	0.0107	26.42	0.1515		
70.62	1.4165	171.13	4.300	277.56	6.387	9.67	0.0150	28.77	0.1890		

The thermodynamic functions in table 2 were calculated through integration of the fitted polynomial, excluding nuclear-spin and isotope-mixing contributions, and are thus practicable for use in thermochemical calculations.

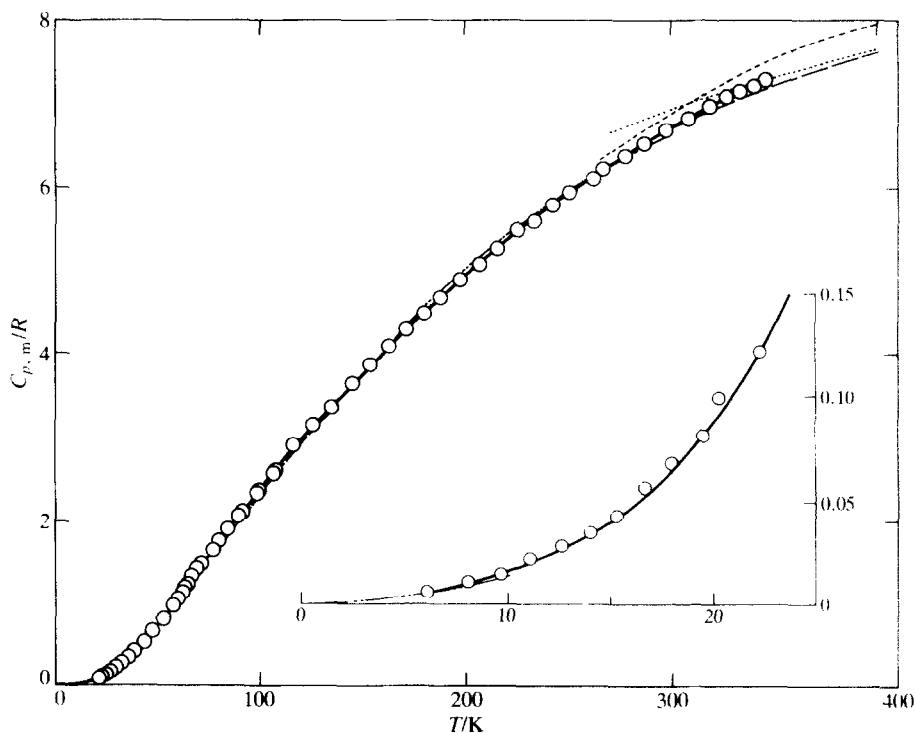


FIGURE 1. The molar heat capacity of IrO_2 over the range 0 to 400 K: —○—, this research; ·····, Passenheim and McCollum,⁽¹⁾ ·-·-·, Wöhler and Jochum,⁽²⁾ - - - -, Cordfunke,⁽³⁾ - - - -, the estimates of Bell *et al.*⁽⁷⁾ The molar heat capacity of isostructural TiO_2 (rutile) of Shomate⁽⁸⁾ (50 to 300 K) is also shown: - - - -.

TABLE 2. Thermodynamic properties of IrO_2 ($R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T K	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^f S_m}{R}$	$\frac{\Delta_0^f H_m}{R \cdot K}$	$\frac{\Phi_m(T, 0)}{R}$	T K	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^f S_m}{R}$	$\frac{\Delta_0^f H_m}{R \cdot K}$	$\frac{\Phi_m(T, 0)}{R}$
5	0.005	0.004	0.010	0.0018	140	3.516	2.30	207.0	0.8266
10	0.016	0.010	0.058	0.0041	160	4.034	2.809	282.6	1.0429
15	0.039	0.021	0.197	0.0077	180	4.506	3.312	368.1	1.2672
20	0.076	0.039	0.479	0.0126	200	4.941	3.810	462.6	1.4966
25	0.133	0.061	0.992	0.0195	220	5.354	4.300	565.6	1.729
30	0.212	0.090	1.843	0.0285	240	5.746	4.785	676.6	1.964
40	0.435	0.179	5.005	0.0538	260	6.105	5.257	795.2	2.199
50	0.725	0.307	10.758	0.0914	280	6.423	5.721	920.5	2.434
60	1.052	0.467	19.62	0.1403	300	6.713	6.175	1051.9	2.668
70	1.392	0.655	31.84	0.2001	320	6.992	6.210	1188.8	2.901
80	1.738	0.864	47.50	0.2698	350	7.278	7.256	1403.2	3.247
90	2.067	1.087	66.54	0.3481					
100	2.378	1.321	88.77	0.4336	273.15	6.318	5.564	876.9	2.353
120	2.961	1.80	142.22	0.6218	298.15	6.687	6.133	1039.5	2.647

4. Discussion

Electric-resistivity measurements made on this compound indicated that electron-phonon and electron-electron interband scattering mechanisms account for the observed temperature dependence.^(10,11) The results are consistent with a single d-type band. The product χV_m of the paramagnetic susceptibility and the molar volume, and the electronic heat-capacity coefficient γ , are believed to be due mainly to this narrow band. The most important term in χV_m is the Pauli contribution which for a non-interacting electron gas is related to the coefficient γ by the relation:

$$\chi V_m = 3\gamma\mu_B^2\mu_0/\pi^2k^2,$$

where μ_B is the Bohr magneton, k is the Boltzmann constant, and μ_0 is the permeability of vacuum. The value given by Ryden and Lawson⁽¹²⁾ for χV_m is $(2.95 \pm 0.06) \times 10^{-9} \text{ m}^3 \cdot \text{mol}^{-1}$ which is about three times higher than our calorimetric estimation ($\chi V_m = 0.97 \times 10^{-9} \text{ m}^3 \cdot \text{mol}^{-1}$). This discrepancy has been interpreted as an enhancement factor in χV_m due to the exchange interaction of the electrons in the gas.⁽¹²⁾

Our value $\{\gamma/(R \cdot \text{K}^{-1}) = 6.7 \times 10^{-4}\}$ agrees with the calorimetric value reported by Passenheim and McCollum⁽¹⁾ $\{\gamma/(R \cdot \text{K}^{-1}) = 6.6 \times 10^{-4}\}$, although our Debye temperature ($\Theta_D = 430 \text{ K}$) estimated below 15 K from the T^3 term in our fitting equated to $3(12R\pi^4/5)(T/\Theta_D)^3$ is lower than theirs. Θ_D increases steadily up to 200 K and then remains practically constant up to the highest temperature: $\Theta_D = 770 \text{ K}$ or 790 K if we correct the electronic contribution to the heat capacity assuming a constant γ value over the whole range of temperatures and neglect the adjustment from C_p to C_v . These values are in considerably better agreement with the values obtained from resistivity ρ measurements at high temperatures $\{\Theta_D = (700 \pm 100) \text{ K}\}$ than the previous comparisons made over different temperature regions for C_p and ρ .

The values estimated by enthalpy differences from the old measurements from Wöhler and Jochum⁽²⁾ (adjusted to the correct atomic number) fit with our results only over the limited overlap with our highest temperatures (330 to 350 K) and do so somewhat better than the estimates of Bell *et al.*⁽⁷⁾ based on seven other MO₂-type solids (M = metal). (Cordfunke⁽³⁾ reports the contrary to be true at higher temperatures.) Moreover, the linear dependence of $C_{p,m}$ against T that they reported has been found to be excessive by Cordfunke with new high-temperature enthalpy increments measured over the range 400 to 900 K with respect to 300 K. Cordfunke's values measured on a portion of the same sample agree well with the present values. The determinations of Passenheim and McCollum⁽¹⁾ below 10 K yield a similar value of γ (as already noted) but are about 15 per cent below our values at 10 K. This discrepancy (compare figure 1) is outside their estimated 5 per cent uncertainty limit. They observed the tail of a nuclear-spin ordering transition below 1 K.

Although the cationic mass of titanium is about 0.25 that of Ir, the molecular volumes are 0.03200 nm³ for IrO₂ and 0.03122 nm³ for isostructural TiO₂ (rutile); the 298.15 K molar entropies of IrO₂ and TiO₂ (6.133R and 6.004R) are nearly identical. This is consistent with volumetric dependence advanced by Chirico and Westrum,⁽¹³⁾ and by Westrum,⁽¹⁴⁻¹⁶⁾ over the entropy-producing temperature region, and is in contrast with that of Latimer's scheme⁽¹⁷⁾ based on cationic masses.

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