

THE HEAT CAPACITY AND DERIVED THERMOPHYSICAL PROPERTIES OF In_2O_3 FROM 0 TO 1000 K

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(Received 6 February 1991; accepted 28 August 1991)

Abstract—The heat capacity from 5 to 350 K of In_2O_3 has been measured by adiabatic calorimetry. For the thermophysical properties at room temperature $C_p^\circ(298.15 \text{ K}) = (99.08 \pm 0.09) \text{ J mol}^{-1} \text{ K}^{-1}$ and $S^\circ(298.15 \text{ K}) = (101.80 \pm 0.06) \text{ J mol}^{-1} \text{ K}^{-1}$ have been derived. Enthalpy increments relative to 298.15 K have been measured by drop calorimetry from 502 to 959.2 K:

$$[H^\circ(T) - H^\circ(298.15 \text{ K})] / \text{J mol}^{-1} = 109.1383(T/\text{K}) + 13.73786 \times 10^{-3}(T/\text{K})^2 \\ + 16.22947 \times 10^5(T/\text{K})^{-1} - 39,204.2.$$

The thermodynamic functions, including the formation properties $\Delta_f H^\circ(T)$ and $\Delta_f G^\circ(T)$, have been derived for temperatures up to 1000 K.

Keywords: Indium sesquioxide, heat capacity, entropy, enthalpy increment, thermodynamic functions.

1. INTRODUCTION

Indium oxide has interesting physicochemical properties. It is an *n*-type semiconductor with a relatively high electrical conductivity over a wide range of temperature. The electrical conductivity of In_2O_3 depends strongly on the number of lattice defects present, and the compound is, therefore, of considerable technological interest because of its application in the form of highly conductive thin films transparent to wavelengths in the visible and near infrared spectra [1]. Remarkably enough little is known about the fundamental thermophysical properties of this material. For instance, the low-temperature heat capacity has been measured only from 2 to 40 K [2], whereas in the high-temperature region enthalpy increments have been measured only once from 388 to 1605 K [3]. As a result, it is hardly possible to evaluate the thermodynamic properties of the formation of In_2O_3 with sufficient accuracy. These properties are needed, for instance, to model the chemical processes occurring in nuclear accidents since indium alloys are present as control rods in certain types of nuclear reactors. We, therefore, measured the low-temperature heat capacity of In_2O_3 by adiabatic calorimetry to obtain accurate values for the standard entropies. In addition, we measured high-temperature enthalpy increments by drop calorimetry to cover the temperature range of interest for this compound.

2. EXPERIMENTAL

The In_2O_3 sample was prepared from indium metal (Highways 5N5). The indium granules were dissolved in 4 N HCl at about 370 K, after which an ammonia solution was added dropwise until all the indium was precipitated as $\text{In}(\text{OH})_3$. After filtration and washing, the precipitate was dried in the air. After homogenization it was then heated in dry oxygen at 975 K to obtain a pure sample of In_2O_3 . The In content of it was determined complexometrically to be $82.57 \pm 0.04\%$ (calc. 82.71%).

Calorimetric techniques

The low-temperature heat capacity of In_2O_3 was measured in an adiabatic calorimetric cryostat [4] (laboratory designated Mark XIII) over the temperature range 5–350 K (Table 1). A gold-plated, high conductivity, oxygen free, copper calorimeter (laboratory designation W-139) was used. The calorimeter has a mass of 13.21 g and an internal volume of 23 cm³. The temperature of the calorimeter was measured with a Leeds & Northrup platinum encapsulated platinum resistance thermometer in an entrant well. The thermometer was calibrated by the U.S. National Bureau of Standards against IPTS-48 [5] and is considered to reproduce the thermodynamic temperature scale within 0.03 K from 5 to 300 K.

About 20.4267 g sample were put in the calorimeter. This represents about 0.07357 moles when

Table 1. Molar heat capacities of In_2O_3

T (K)	C_p° ($\text{J mol}^{-1} \text{K}^{-1}$)	T (K)	C_p° ($\text{J mol}^{-1} \text{K}^{-1}$)	T (K)	C_p° ($\text{J mol}^{-1} \text{K}^{-1}$)	T (K)	C_p° ($\text{J mol}^{-1} \text{K}^{-1}$)
6.94	0.0690	41.35	10.609	120.52	50.805	238.03	88.298
8.51	0.1305	43.30	11.530	125.56	52.333	243.21	89.304
9.58	0.1829	45.35	12.729	130.62	54.633	248.40	90.177
10.79	0.2311	47.50	13.794	135.70	56.680	253.56	91.200
11.89	0.3426	49.76	15.022	140.78	58.952	258.72	92.588
13.05	0.4432	52.14	16.374	145.87	60.872	263.90	93.578
14.25	0.6053	54.66	17.728	150.96	63.131	269.07	94.168
15.52	0.8190	57.30	19.728	156.09	65.035	274.24	95.033
16.90	1.0509	60.07	20.042	161.20	66.862	279.39	96.496
18.31	1.2920	62.98	22.094	166.34	68.538	284.53	97.344
19.77	1.5847	66.05	23.715	171.46	69.763	289.70	97.943
21.29	1.9489	69.27	25.413	176.58	71.289	294.85	98.425
22.81	2.3804	72.44	26.962	181.68	72.578	299.99	99.040
24.36	2.8676	75.77	28.591	186.84	74.181	305.12	99.897
25.92	3.4288	78.92	30.235	191.93	75.661	310.26	100.720
27.55	4.0283	82.85	32.024	197.05	77.132	315.40	101.634
29.23	4.7267	86.93	34.253	202.23	75.225	320.55	101.975
30.92	5.4268	91.23	36.291	207.25	79.297	325.73	102.765
32.63	6.1967	95.74	38.735	212.30	81.464	330.91	103.721
34.37	7.0023	100.49	40.912	217.38	82.960	336.11	104.345
36.05	7.8171	105.45	43.236	222.53	84.449	341.31	104.927
37.73	8.7051	110.46	45.456	227.70	85.812	346.51	105.592
39.49	9.6031	115.50	47.593	232.86	87.276		

277.638 g mol^{-1} is selected as the molar mass. To facilitate rapid thermal equilibration 2.67 kPa at 300 K of helium gas were introduced into the calorimeter after evacuation. The calorimeter containing the sample was sealed in the inert atmosphere and then reopened on the vacuum line for the introduction of helium. The calorimeter was then sealed, placed in the cryostat, and cooled. The heat capacity of the empty calorimeter represented 70–80% of the total heat capacity at temperatures below 50 K and about 50–65% at higher temperatures.

The enthalpy increments above 298.15 K were measured in an isothermal diphenyl-ether calorimeter which has been described previously [6]. Briefly, the

sample is enclosed in a spherical vitreous silica ampoule with a 0.6 mm wall thickness, a 20 mm diameter and a volume of 4.2 cm^3 . The ampoule is heated in a furnace, the temperature of which is measured with calibrated Pt/(Pt + 10 mass per cent Rh) thermocouples, to 0.1 K. After a reasonable equilibration time, the ampoule is dropped into the calorimeter. The energy of the ampoule plus the sample now melts solid diphenyl-ether in equilibrium with its liquid in a closed system. The resulting volume increase of the ether is determined by weighing the displaced mercury. The ratio of the heat input to mass of mercury making up the volume change is a constant for the apparatus (79.977 ± 0.063) J g^{-1} and is obtained by calibration with $\alpha\text{-SiO}_2$ and compared with the NBS standard reference material (No. 720), synthetic sapphire, Al_2O_3 . Our results with sapphire all agree within 0.2% with the data given by the NBS. The enthalpy contributions of the vitreous silica were determined separately.

For the present measurements 4.03438 g of In_2O_3 were enclosed in an ampoule of 1.35081 g, all masses being corrected for weighing in argon. The results of the 18 measurements are listed in Table 2. A correction was made for the difference in enthalpy between the final calorimeter temperature (300.06 K) and the standard reference temperature, 298.15 K, using $C_p^\circ(298.15 \text{ K})$.

3. RESULTS

The low-temperature heat capacity data are listed in Table 1 and plotted in Fig. 1. No special

Table 2. Enthalpy increments of In_2O_3

T (K)	$\{H^\circ(T) - H^\circ(298.15 \text{ K})\}$ (J mol^{-1})		
	Exp.	Calc.	$\delta\%$
502.3	22,205	22,313	-0.48
511.4	23,397	23,376	0.09
527.9	25,345	25,313	0.13
522.6	28,336	28,238	0.35
578.9	31,222	31,383	-0.51
604.8	34,595	34,511	0.24
630.5	37,493	37,643	-0.40
656.0	40,857	40,776	0.20
681.7	43,922	43,960	-0.09
707.2	47,207	47,144	0.13
732.1	50,213	50,276	-0.13
757.3	53,644	53,468	0.33
782.3	56,584	56,657	-0.13
834.0	63,298	63,319	-0.03
860.1	66,733	66,716	0.03
885.5	70,105	70,043	0.09
935.8	76,635	76,692	-0.07
959.2	79,803	79,813	-0.01

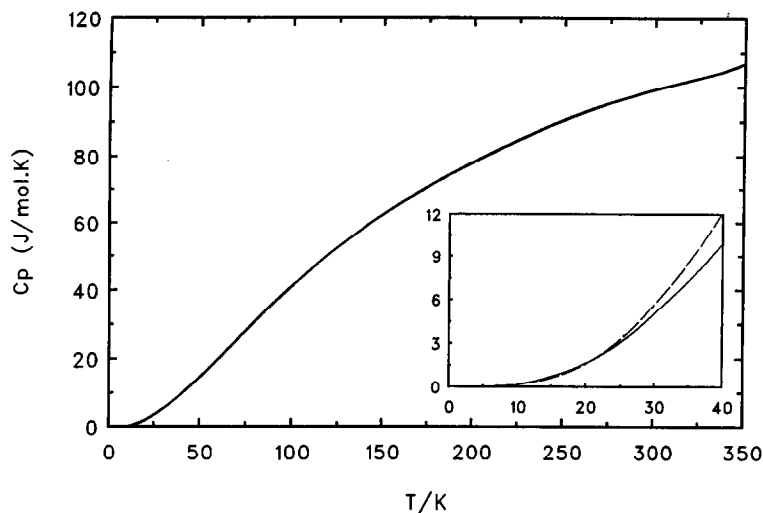


Fig. 1. The molar heat capacity of In_2O_3 . (—) this work; -- Bachmann *et al.* [2].

contributions other than that of the lattice and electronic contributions are observed in the entire temperature range of the experiment. Smoothed thermodynamic functions at selected temperatures listed in Table 3 were evaluated by extrapolating the experimental heat capacity curve to 0 K and by integrating. The computer program FITAB2 was used for all integrations and evaluations of thermodynamic functions [7], yielding at room temperature:

$$C_p^\circ(298.15 \text{ K}) = (99.08 \pm 0.09) \text{ J mol}^{-1} \text{ K}^{-1},$$

and

$$S^\circ(298.15 \text{ K}) = (101.80 \pm 0.06) \text{ J mol}^{-1} \text{ K}^{-1}.$$

The high-temperature enthalpy increments can be represented by the polynomial equation (502–959 K):

$$\begin{aligned} \{H^\circ(T) - H^\circ(298.15 \text{ K})\} / \text{J mol}^{-1} \\ = 109.1383(T/\text{K}) + 13.73786 \times 10^{-3}(T/\text{K})^2 \\ + 16.22947 \times 10^5(T/\text{K})^{-1} - 39,204.2. \end{aligned}$$

As boundary conditions $\{H^\circ(T) - H^\circ(298.15 \text{ K})\} = 0$ at 298.15 K, and $C_p^\circ(298.15 \text{ K}) = 99.07 \text{ J mol}^{-1} \text{ K}^{-1}$ were applied. The standard deviation is 93 J mol^{-1} or 0.26%. The smoothed higher temperature thermodynamic quantities of In_2O_3 are also listed in Table 3.

4. DISCUSSION

The low-temperature heat capacity and the high-temperature enthalpy increment measurements, obtained from the same sample, agree perfectly. This is demonstrated in Fig. 2 in a $\{H^\circ(T) - H^\circ(298.15 \text{ K})\} / (T - 298.15 \text{ K})$ vs T plot, where

the two data sets join smoothly at 298.15 K. Only the highest cryogenic values seem to deviate slightly from a perfect join, but this trend is within the experimental error of the induction bridge temperature measurements at the time of the determination.

Three previous heat-capacity measurements on In_2O_3 overlap in the lower and upper temperature range of the present measurements. Bachmann *et al.* [2] measured the heat capacity of In_2O_3 between 2 and 40 K. The agreement with their measurements is poor; below 20 K their values are much lower (Fig. 1); above that temperature they are higher and deviate considerably.

Shchukarev *et al.* [8] report an equation to represent the heat capacity of In_2O_3 between 361 and 982 K, however, without reference to the source of the data. These measurements do not agree with ours (Fig. 2).

Tsagareishvili and Gvelesiani [3] measured the enthalpy increment of In_2O_3 from 388 to 1605 K; their results also deviate from ours, especially below 800 K where the deviation is about 2%, and do not join the low-temperature heat capacity. At temperatures above 1000 K their measurements lie on a curve that crosses ours, and lies lower than a reasonable extension of our curve.

In view of the fact that our sample was carefully prepared under an atmosphere (*ca* 0.1 MPa) of pure oxygen to have the stoichiometric composition we would not expect lattice defects to be present and its handling at low temperatures would not have been expected to generate them so that our cryogenic data represent that of defect-free In_2O_3 . Without knowing the details of the thermal history (e.g. the nature of the ambient atmospheres) on the literature samples

Table 3. Smoothed thermodynamic properties at selected temperatures for In_2O_3

T (K)	C_p° ($\text{J mol}^{-1} \text{K}^{-1}$)	$S^\circ(T) - S^\circ(0)$ ($\text{J mol}^{-1} \text{K}^{-1}$)	$H^\circ(T) - H^\circ(0)$ (J mol^{-1})	$-\{(G^\circ(T) - H^\circ(0))/T\}$ ($\text{J mol}^{-1} \text{K}^{-1}$)
0	0.000	0.000	0.000	0.000
5	0.075	0.075	0.191	0.042
10	0.158	0.141	0.665	0.075
15	0.732	0.299	2.686	0.116
20	1.646	0.624	8.481	0.200
25	3.076	1.131	20.021	0.333
30	5.047	1.862	40.192	0.524
35	7.300	2.810	70.931	0.782
40	9.886	3.949	113.817	1.106
45	12.497	5.263	169.824	1.488
50	15.207	6.718	239.009	1.937
60	20.520	9.969	418.053	3.002
70	25.584	13.511	648.532	4.249
80	30.772	17.269	930.311	5.637
90	35.835	21.185	1263.56	7.150
100	40.591	25.210	1645.94	8.755
110	45.139	29.292	2074.64	10.435
120	49.688	33.416	2548.73	12.181
130	54.269	37.573	3068.64	13.968
140	58.709	41.764	3633.77	15.806
150	62.775	45.954	4241.23	17.677
160	66.325	50.120	4887.30	19.572
170	69.434	54.235	5566.56	21.493
180	72.295	58.285	6274.96	23.422
190	75.122	62.267	7012.46	25.368
200	78.015	66.200	7778.22	27.305
210	80.933	70.075	8573.09	29.250
220	83.744	73.908	9396.23	31.196
230	86.338	77.682	10,246.8	33.133
240	88.649	81.407	11,122.3	35.071
250	90.728	85.074	12,019.5	36.991
260	92.674	88.666	12,936.5	38.912
270	94.528	92.199	13,871.9	40.824
273.15	95.085	93.297	14,171.3	41.423
280	96.274	95.667	14,826.4	42.720
290	97.887	99.076	15,797.6	44.607
298.15	99.076	101.803	15,599.9	46.129
300	99.342	102.418	16,783.7	46.478
325	102.659	110.508	19,308.8	51.093
350	107.024	118.249	21,921.2	55.616

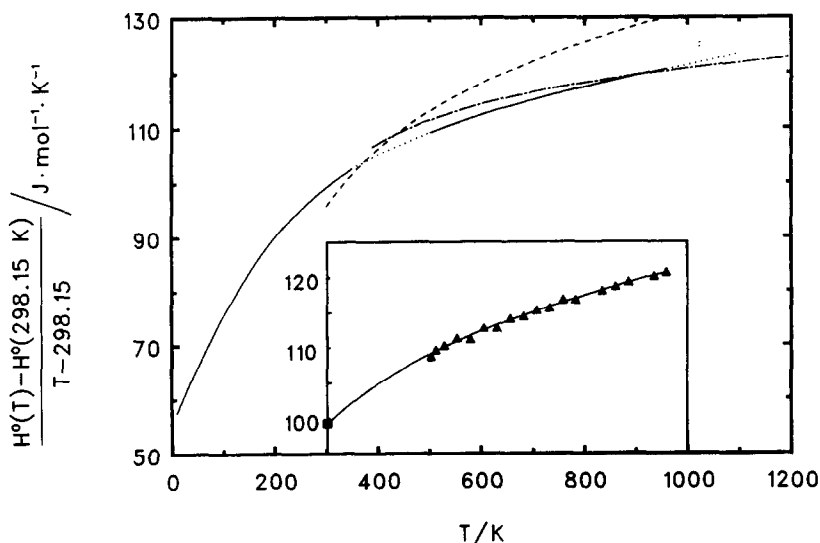


Fig. 2. The reduced enthalpy increment functions: (—) smoothed fit from the low-temperature and high-temperature enthalpy measurements; (---) Shchukarev *et al.* [8]; (-·-) Tsagareishvili and Gvelesiani [3]. Insert: experimental enthalpy increment values.

Table 4. Thermodynamic functions on In_2O_3

T (K)	C_p° ($\text{J mol}^{-1} \text{K}^{-1}$)	$S^\circ(T)$ ($\text{J mol}^{-1} \text{K}^{-1}$)	$-[G^\circ - H^\circ(298)]/T$ ($\text{J mol}^{-1} \text{K}^{-1}$)	$H^\circ - H^\circ(298)$ (J mol^{-1})	$\Delta_f H^\circ(T)$ (J mol^{-1})	$\Delta_f G^\circ(T)$ (J mol^{-1})
298	99.076	101.800	101.801	0	-923,500	-827,775
300	99.349	102.414	101.802	183	-923,498	-827,181
400	109.986	132.614	105.848	10,706	-922,989	-795,136
500	116.385	157.889	113.799	22,945	-928,611	-762,197
600	121.116	179.543	122.995	33,929	-927,151	-729,045
700	125.059	198.517	132.456	46,243	-925,315	-696,170
800	128.583	215.450	141.790	58,927	-923,172	-663,578
900	131.863	230.786	150.840	71,951	-920,753	-631,271
1000	134.991	244.842	159.547	85,295	-918,072	-599,247

it is difficult to deduce what—if any—heat-capacity contributions are occasioned by the presence and/or the generation of vacancies.

Acknowledgements—The authors wish to thank Mr A. Sembiring (visiting scientist from Bandung, Indonesia) for preparing the sample, Mr R. van der Laan for measuring the enthalpy increments, and Dr Roey Shaviv for assisting in the computer calculation of the low-temperature heat capacity data.

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