HEAT CAPACITY OF INDIUM FROM 300 TO 1000 K

ENTHALPY OF FUSION

F. GROnVOLD

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

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The heat capacity of high-purity indium has been determined by adiabatic-shield calorimetry in the range 300 to 1000 K. Values of thermodynamic functions have been calculated and $C_p(1000\, \text{K})$, $[H^\circ(1000\, \text{K}) - H^\circ(298.15\, \text{K})]$, and $[S^\circ(1000\, \text{K}) - S^\circ(298.15\, \text{K})]$ are $(27.11 \pm 0.15)\, \text{J K}^{-1}\, \text{mole}^{-1}$, $(22873 \pm 70)\, \text{J mole}^{-1}$, and $(41.567 \pm 0.125)\, \text{J K}^{-1}\, \text{mole}^{-1}$, respectively. The enthalpy of fusion is $(3283 \pm 7)\, \text{J mole}^{-1}$ and the melting temperature $(429.77 \pm 0.01)\, \text{K}$. The premelting heat capacity is compatible with the presence of a mole fraction $x \approx 1 \cdot 10^{-6}$ of a liquid-soluble/solid-insoluble impurity in the sample.

The heat capacity of indium has been studied at very low temperatures in normal and superconducting states by many investigators [1], and in the range 12 to 273 K by Clusius and Schachinger [2]. Enthalpy increments over the range 273 to 373 K were determined a century ago by Bunsen [3] and Mendeleyev [4]. More extensive measurements have since been carried out by Roth et al. [5] over the range 322 to 457 K, and by Kaznoff et al. [6] between 354 and 801 K. The heat capacity of indium has been studied by Kramer and Nöting [7] from 180 K to the melting temperature (429.8 K), and their data appear to agree rather well with the results by Clusius and Schachinger [2] and the evaluation by Hultgren et al. [1].

The generally-accepted value for the enthalpy of fusion, $3.27\, \text{kJ mole}^{-1}$ stems from the studies by Roth et al. [5] and Oelsen [8]. These concordant results were discredited by Richardson and Savill [9] on the basis of differential scanning calorimetry (DSC) work with alumina as a calibrating substance. They found support for the proposed 2 to 3 per cent higher value also in the literature data obtained by DSC, DTA and Calvet microcalorimetric techniques. The high value has so far not been confirmed by adiabatic calorimetry, and the present work was partly undertaken for that purpose.

In the absence of experimental data for the heat capacity of liquid metals, constant heat capacities have been assumed, but in the relatively few cases where constant pressure heat capacities have been measured, they decrease with increasing temperature in the beginning. The rate of decrease usually becomes smaller as the temperature is increased, and in some instances where the measurements have been extended far above the melting temperature a renewed increase is observed. This rise is understandable in terms of augmenting dilational and electronic heat capacit...
ity contributions. Quantitative data are scarce, and in the case of liquid indium only the preliminary report by Kaznoff et al. [6] seems to exist, which indicates that the heat capacity decreases very slightly from 29.5 K\(^{-1}\) mole\(^{-1}\) at the melting temperature to a constant value of 29.3 J K\(^{-1}\) mole\(^{-1}\) at 800 K.

Finally, the heat capacity of solid indium as it approaches melting deserves interest. One point is the evaluation of the excess heat capacity due to defect formation, as has been studied by Kramer and Nölting [7]. This effect is usually overshadowed closer to the melting point by that from changes in impurity distribution between solid and liquid phases. Close to the melting point intrinsic premelting might eventually also be observed.

Experimental

Sample

The 99.999 mass per cent pure indium was obtained from Kawecki-Billiton, Arnhem, The Netherlands. About 250 g of this material was melted into the calorimetric container of silica glass, together with about 1 m of 3 mm diameter silica cord. The silica cord was coiled spirally in the sample space, its purpose being to prevent breakage of the container on solidification and thermal cycling of the sample.

Calorimetric technique

The calorimetric apparatus and measurement technique have been described in detail [10], along with results obtained for the heat capacity of a standard sample of \(\alpha\)-Al\(_2\)O\(_3\). The calorimeter is operated with adiabatic shields and intermittent energy inputs with temperature equilibration between each input. The 50 cm\(^3\) sample container of fused silica has a well for the heater and platinum resistance thermometer, axially located in the cylindrical silver calorimeter. The calorimeter plus sample assembly is suspended inside a double-walled silver shield system with enclosed heaters. Outside the shields is a heated guard system, also of silver. The whole assembly is placed in a vertical tube furnace.

The temperature differences between corresponding parts of calorimeter and shield are measured by means of Pt/Pt10\%Rh thermopiles. The amplified signals are recorded and also used for automatic control of the shield heaters to maintain quasi-adiabatic conditions during input and drift periods. The temperature of the guard body is kept automatically 0.4 K below that of the shield, while the temperature of the furnace core is kept 10 K lower to secure satisfactory operation of the control units.

Heat capacity measurements of the empty calorimeter were carried out in separate series of experiments. They represented from 51 to 61 per cent of the total outside the fusion region. Small corrections were applied for differences in mass of the empty and full calorimetric containers, and for "zero" drift of the calorimeter.