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The high-temperature enthalpy increment of solid antimony

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Abstract

The enthalpy increment of solid antimony has been measured by drop calorimetry from 486 to 858 K. The results can be represented by:

$$\{H^0(T) - H^0(298.15\,\mathrm{K}\}/\mathrm{J\,mol^{-1}} = 19.5569(T/\mathrm{K}) + 6.14137 \times 10^{-3}(T/\mathrm{K})^2 - 1.83207 \times 10^{5}(T/\mathrm{K})^{-1} - 5762.3$$

In addition, an assessment of the low-temperature heat capacity data has been made, yielding $S^0(298.15\,\mathrm{K})=(45.42\pm 0.45)\,\mathrm{J\,K^{-1}\,mol^{-1}}$. From the combined results, the thermodynamic properties of solid antimony have been calculated. © 1998 Elsevier Science B.V.

Keywords: Antimony; Calorimetry; Entropy; Heat capacity; Thermodynamic properties

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1. Introduction

Hultgren et al. [1] have evaluated the heat capacity of antimony in 1968. The high-temperature values selected in this work closely agreed with the enthalpy increment measurements by Poppema and Jaeger [7], which is one of the many enthalpy-increment studies made between 1914 and 1963, as summarized in Table 1. Except for a study of the low-temperature heat capacity [10], no new experimental data have been presented since then.

Poppema and Jaeger [7] have performed measurements by drop calorimetry on two different samples, antimony powder in vacuum and antimony bar in air. The results of the two measurements differ considerably and neither of the two fits the low-temperature heat capacity measurements by Anderson [9] and the more recent ones by Vecher et al. [10] smoothly. In order to establish the high-temperature heat capacity of antimony more accurately we have measured the enthalpy increment of the solid phase.

2. Experimental

The antimony metal was purchased from Highways (Netherlands) and was specified to be 99.9999% pure. Before use it was washed in hexane and heated at 423 K in purified argon.

The enthalpy increments were measured in an isothermal diphenyl ether drop calorimeter. Details of the apparatus and the measurement procedures are described in Ref. [11]. The sample had a mass of 13.3358(2) g and was enclosed in a quartz capsule of

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Table 1
Previous enthalpy increment measurements of Sb(s)

Authors	Year	T/K
Schübel [2]	1914	373–866
Wüst et al. [3]	1918	373–1273
Awberry and Griffiths [4]	1926	449–1028
Umino [5]	1926	373–1273
Bottema and Jaeger [6]	1932	507–713
Poppema and Jaeger [7]	1935	373–850
Kochetkova and Rezukhina [8]	1963	587–885

1.15975(2) g. The molar mass of Sb was taken as 121.760 g mol^{-1} [12].

3. Results and discussion

Before presenting the results of our measurements, we will briefly discuss the low-temperature heat capacity data. Three studies of the low-temperature heat capacity were made, by DeSorbo [13] from 13 to 70 K, Anderson [9] from 66 to 293 K and Vecher et al. [10] from 46 to 352 K. Up to about 100 K the three studies are in excellent agreement, above that temperature the results of Anderson tend to be somewhat higher than those of Vecher et al. [10] (Fig. 1). Since the differences are small and there are no arguments to favour either of the two data sets, the combined results of DeSorbo, Anderson and Vecher et al. have been fitted to give for the heat capacity at room temperature:

$$C_p^0(298.15\,\mathrm{K}) = (25.28 \pm 0.25)\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

For the standard entropy we obtain

$$S^0(298.15\,\mathrm{K}) = (45.42 \pm 0.45)\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

taking S^0(13.2 K)=0.481 J K mol^{-1} as suggested by DeSorbo. The uncertainties of the values have been estimated to be 1%, taking into account the sample purity and calorimetric accuracy.

The results of our enthalpy increment measurements are listed in Table 2. The results have been fitted to the polynomial:

$$\begin{aligned}\{H^0(T) - H^0(298.15\,\mathrm{K})\}/\mathrm{J\,mol^{-1}} &= 19.5569(T/\mathrm{K}) + 6.14137 \\ &\quad\times 10^{-3}(T/\mathrm{K})^2 - 1.83207 \\ &\quad\times 10^{5}(T/\mathrm{K})^{-1} - 5762.3\end{aligned}$$

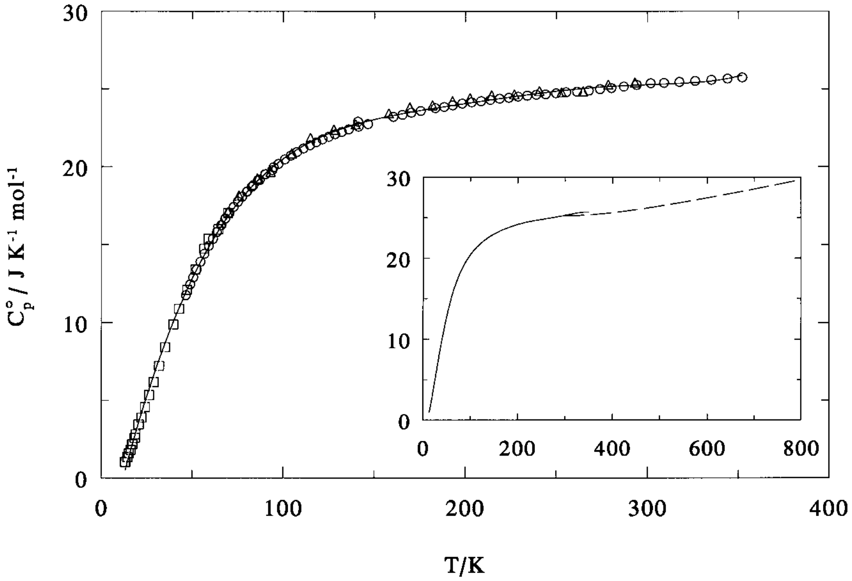

Fig. 1. The low-temperature heat capacity of antimony metal; □, DeSorbo [13]; △, Anderson [9]; ○, Vecher et al. [10]. The insert shows the extension into the high-temperature region derived by differentiation of the enthalpy increment function obtained in this work.

Table 2
The experimental enthalpy increments of Sb(s)

T/K	$\{H^0(T)-H^0(298.15\ \mathrm{K})\}$/J mol^{-1}		δ/%
	measured	calculated	
486.1	4817	4819	−0.03
526.5	5937	5889	0.81
527.8	5906	5924	−0.30
567.5	7010	6991	0.27
609.6	8120	8141	−0.26
609.7	8102	8144	−0.52
649.8	9284	9257	0.29
691.1	10422	10422	0.00
731.3	11572	11574	−0.01
773.3	12794	12797	−0.02
813.1	13965	13974	−0.07
857.5	15320	15310	0.07

applying $C_p^0(298.15\ \mathrm{K}) = 25.28$ J K mol^{-1} and $\{H^0(T)-H^0(298.15\ \mathrm{K})\}=0$ at 298.15 K as boundary conditions. The standard deviation is 25 J mol^{-1}.

The enthalpy increment function reasonably fits the low-temperature data as shown in Fig. 2, though the fit is not smooth. We consider this a mathematical artifact which is caused by limitations of the polynomial fitting approach of our software to model the following effects simultaneously: (i) the slight change in the slope of the heat capacity curve ca. 275 K which occurs in both low-temperature measurements; (ii) the excess enthalpy in the high-temperature region, which is probably due to a pre-melting process. However, for practical purposes the above fit is considered adequate because it does describe the heat capacity smoothly (see insert in Fig. 1).

The high-temperature enthalpy increment of solid Sb has been measured by Schübel [2], Wüst et al. [3], Awberry and Griffiths [4], Umino [5], Bottema and Jaeger [6], Poppema and Jaeger [7], Kochetkova and Rezukhina [8]. The results from these studies are appreciably different and in most cases do not fit the low-temperature data acceptably. As mentioned in the discussion, Hultgren et al. [1] based their critical evaluation mainly on the results of Poppema and Jaeger [7]. The differences with the results of Poppema and Jaeger are ca. 1–4%. This significant discrepancy between our data and those presented by Jaeger et al. has also been observed for Ru and Pd [14] but not for Ag [15]. This suggests that the purity and treatment of the material are the most likely reasons for the above mentioned discrepancy. This is supported by the fact that the two different treatments by Poppema and Jaeger (heating in vacuum or air) result in significant different results. The present

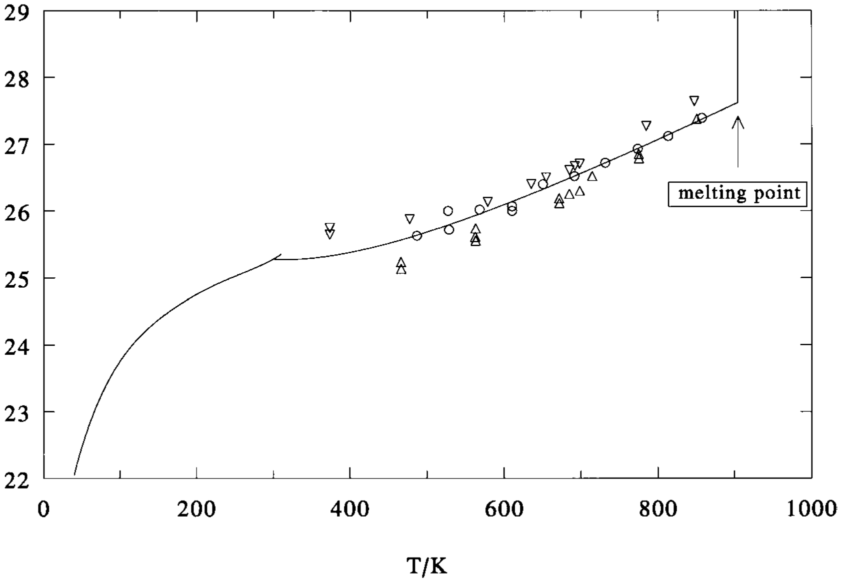

Fig. 2. The reduced enthalpy increment of antimony metal; ○, present results; △, Poppema and Jaeger, vacuum; ▽, Poppema and Jaeger, air.

Table 3
The thermodynamic functions of Sb(s)

T (K)	$C_p^0(T)$ (J K^{-1} mol^{-1})	$S^0(T)$ (J K^{-1} mol^{-1})	$-\{G^0(T)-H^0$ (298.15 K)$\}/T$ (J K^{-1} mol^{-1})	$\{H^0(T)-H^0$ (298.15 K)$\}$ (J mol^{-1})
298.15	25.28	45.42	45.42	0
300	25.28	45.58	45.42	47
400	25.62	52.88	46.41	2585
500	26.43	58.67	48.30	5185
600	27.44	63.58	50.45	7877
700	28.53	67.89	52.64	10675
800	29.67	71.77	54.79	13585
900	30.84	75.34	56.88	16610
903.9	30.88	75.47	56.96	16730

results for high purity Sb encapsulated in a closed container of quartz glass, should therefore be considered to be of better quality.

The thermodynamic functions of solid antimony as derived from the present data are listed in Table 3.

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