

HEAT CAPACITY OF INDIUM FROM 300 TO 1000 K

ENTHALPY OF FUSION

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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 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 Mendelejev [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 Nölting [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 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 capac-

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 $29.5 \text{ K}^{-1} \text{ mole}^{-1}$ at the melting temperature to a constant value of $29.3 \text{ J K}^{-1} \text{ mole}^{-1}$ 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 99.9999 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 $\alpha\text{-Al}_2\text{O}_3$. 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.

The temperature excursions of the shields from the calorimeter were of negligible importance. The thermometer resistance was measured with a Mueller bridge (Leeds and Northrup Model 8072), modified locally with stepping motors and a gated null detector, and run by a computer (Hewlett-Packard Model 2114B). The derived temperatures are judged to correspond with IPTS-68 within 0.01 K at 400 K and within 0.3 K at 1000 K. Precision is considerably better, and the temperature increments are measured to 0.0003 K. The energy inputs from a constant current supply were measured with an integrating voltmeter (Hewlett-Packard Model 2401C). The accuracy of the energy inputs is about 0.025 per cent. Both Mueller bridge and potential \times time readings are transferred automatically to punch cards (IBM 545), together with time and other relevant information, and then processed by a digital computer.

Results and discussion

Thermodynamic properties

Results of the heat capacity determinations are presented in Table I in chronological order. The approximate temperature increments used in the determinations can usually be inferred from the adjacent mean temperature values in the Table. Measurements were carried out in two different calorimeters (Mark 4 for series IV, V and VI, and Mark 5 for series I, II, III and VII). No differences of importance were observed, and the results have therefore been combined in the evaluation of the thermodynamic properties.

The curve of heat capacity against temperature is shown in Fig. 1, together with the results by Kaznoff et al. [6]. The latter agree well with ours around 350 K and become slightly higher for solid indium above 380 K. The results by Kramer and

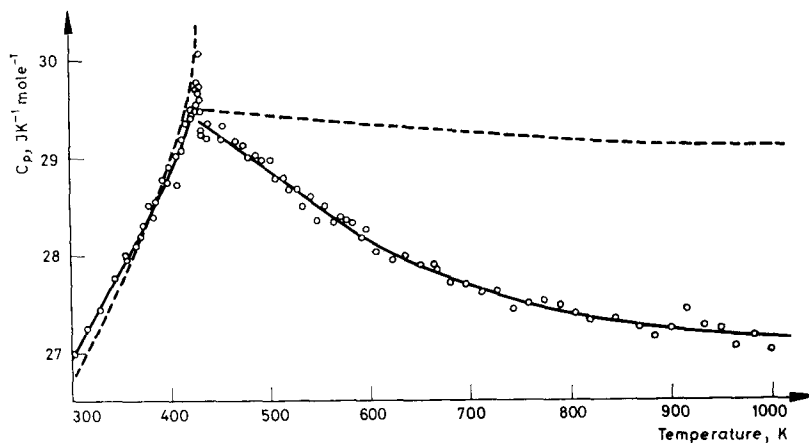


Fig. 1. Heat capacity of indium, \circ represents present results, — — — results by Kaznoff et al. [6].

Table 1. (cont.)
Heat capacity of indium

T, K	C_p J, K ⁻¹ mole ⁻¹	T, K	C_p J, K ⁻¹ mole ⁻¹
$M(\text{In}) = 114.82 \text{ g mole}^{-1}$			
Series V (Cal. 4))		Series VI (Cal. 4)	
663.70	27.89	998.20	27.01
679.06	27.70	562.05	28.33
694.77	27.69	576.60	28.35
710.30	27.60	591.24	28.16
725.71	27.61	605.98	28.01
741.55	27.43	620.83	27.93
757.32	27.49	635.73	27.98
772.62	27.51	650.76	27.88
788.01	27.46	665.91	27.84
803.28	27.38		
818.15	27.32		
844.43	27.33	Series VII (Cal. 5)	
867.35	27.25		
883.18	27.15		
899.52	27.24	429.05	30.06
915.86	27.43	429.57	69.66
932.20	27.26	429.76	10 540
948.50	27.22	430.00	6 866
964.48	27.05	430.58	29.48
981.01	27.16		

Nörling [7] are about 0.7 per cent higher than the present ones at 300 K and are practically equal to the present results at 400 K. The extrapolated heat capacity at 298 K by Clusius and Schachinger [2] is 0.6 per cent lower than found here. For liquid indium the results by Kaznoff et al. [6] agree rather closely just above the melting temperature. The considerable decrease observed here for liquid indium with increasing temperature is absent in the results by Kaznoff et al. [6], and their results are about 6 per cent higher than ours at 800 K. No obvious reason for this discrepancy is apparent, but a discrepancy in the same direction was also present in the case of liquid tin, where the values by Orr et al. [11] were about 3 per cent higher than ours [12] at 750 K.

Results of the fractional enthalpy of fusion determinations are found in Table 2. Slight pre- and post-melting contributions above the linearly extrapolated heat capacities for the solid and liquid phases (29.69 and 29.36 J K⁻¹ mole⁻¹, respectively at 429.77 K) are included in the derived enthalpy and entropy of fusion values: $\Delta H_m = 3283 \pm 7 \text{ J mole}^{-1}$ and $\Delta S_m = 7.639 \pm 0.015 \text{ J K}^{-1} \text{ mole}^{-1}$. The observed temperature of fusion, $T_m = 429.77 \pm 0.01 \text{ K}$ at zero pressure agrees within the error limit with the IPTS-68 reference value (429.784 K at 1 atm pressure [13]).

Table 2
Fractional enthalpy of fusion determinations for indium

$\langle T \rangle$, K	C_p , J, K ⁻¹ mole ⁻¹	ΔT , K	Δt , min	ΔH_m , J, mole ⁻¹	T_{fin} , K
$M(\text{In}) = 114.82 \text{ g mole}^{-1}$					
Series I, run 22–27					
429.465	110.7	0.5983	31	48.5	429.765
429.767	15 780	0.0056	27	88.2	429.770
429.771	730 900	0.0012	45	887.1	429.771
429.772	2 924 000	0.0006	80	1 754.6	429.772
429.773	370 100	0.0012	298	444.1	429.773
429.941	225.5	0.3351	37	65.7	430.108
				3 278.8	
Series III, run 2–9					
429.388	32.19	0.6552	21	1.6	429.717
429.742	813.9	0.0509	22	39.9	429.768
429.770	444 400	0.0056	77	2 488.2	429.773
429.773	702 600	0.0006	29	435.5	429.774
429.774	180 800	0.0012	60	216.9	429.775
429.778	6 963	0.0062	75	43.0	429.781
429.786	5 796	0.0074	69	42.7	429.788
429.987	73.84	0.3995	27	17.8	430.188
				3 285.6	
Series IV, run 14–16					
429.600	95.84	0.3329	23	21.7	429.767
429.768	22 350	0.0020	30	44.6	429.769
430.402	2 585	1.2611	108	3 222.0	431.030
				3 288.3	
Series VII, run 2–4					
429.567	69.66	0.3883	48	15.5	429.762
429.764	10 540	0.0037	74	38.9	429.766
430.001	6 866	0.4720	105	3 226.6	430.238
				3 281.0	

$$\begin{aligned} \Delta H_m, \text{ J mole}^{-1} &= 3\,283 \pm 7 \\ \Delta S_m, \text{ J K}^{-1} \text{ mole}^{-1} &= 7.639 \pm 0.015 \\ T_m, \text{ K} &= 429.77 \pm 0.01 \end{aligned}$$

A collection of earlier enthalpy of fusion determinations is found in Table 3. The values by Roth et al. [5] and Oelsen [8] agree with the present one within the limit of error. Nearly the same value was obtained by David [15] and Brennan and Gray [24]. The result by Malaspina et al. [23] also agrees within its error limit of 1.8 per cent. Several other determinations have led to higher results, and this was seen by Richardson and Savill [9] as support for the enthalpy of fusion value $\Delta H_m = 3350 \pm 30 \text{ J mole}^{-1}$ which they obtained by differential scanning calorimetry with $\alpha\text{-Al}_2\text{O}_3$ as calibrant. Systematic errors seem to have caused the high value, and the inference about impurity premelting in the determinations by Roth et al. [5] is questionable.

Table 3
Enthalpy of fusion determinations on indium

Authors	Year	$\Delta H_m, \text{ J mol}^{-1}$
Roth et al. [5]	1933	3272 ± 13
Oelsen et al. [8]	1955	3270 ± 17
Oelsen [14]	1957	3180
David [15]	1964	3268
Predel [16]	1964	3370
Tarwater [17]	1965	3810
Alpaut and Heumann [18]	1965	3340
Bros [19]	1966	3314
Gwinup [20]	1967	3452 ± 25
Mochovskii and Večer [21]	1969	3364 ± 100
Reznitskii et al. [22]	1970	3350 ± 345
Malaspina et al. [23]	1971	3318 ± 59
Brennan and Gray [24]	1973	3260
Flynn [25]	1974	3130
Richardson and Savill [9]	1975	3350 ± 30
Present	1977	3283 ± 7

Values of C_p , $[H^\circ(T) - H^\circ(298.15 \text{ K})]$ and $S^\circ(T) - S^\circ(298.15 \text{ K})$ are given in Table 4 for selected temperatures. Results in the region from room temperature to 429.09 K have been least squares fitted by a polynomial expression with a standard deviation of 0.31 per cent for a single measurement. For liquid indium a similarly fitted expression resulted in a standard deviation of 0.25 per cent over the range 430.52 to 998.20 K. The accuracy of the integrated thermodynamic function values is estimated to be 0.3 per cent.

A comparison of the enthalpy increments over the range 273 to 373 K obtained by us with recourse to the lower temperature results by Clusius and Schachinger [2] (2738 J mole^{-1}) shows good agreement with the result by Bunsen [3] ($2740 \pm \pm 220 \text{ J mole}^{-1}$), while that by Mendelejev [4] (2660 J mole^{-1}) was about 3.5 per cent lower. The enthalpy increments for solid indium above 291 K by Roth et al. [5] are on the average 0.78 per cent higher than found here, while the three results for liquid indium up to 457.38 K average 0.11 per cent higher.

Table 4
Thermodynamic properties of indium

T, K	$C_p,$ $\text{J, K}^{-1} \text{mole}^{-1}$	$H^\circ(T) - H^\circ(298.15 \text{ K}),$ J, mole^{-1}	$S^\circ(T) - S^\circ(298.15 \text{ K}),$ $\text{J, K}^{-1} \text{mole}^{-1}$
		$M(\text{In}) = 118.42 \text{ g mole}^{-1}$	
298.15	26.90	0	0
300	26.93	49.8	0.167
350	27.87	1420.3	4.390
400	28.85	2837.1	8.172
429.77 (s)	(29.69)	3707.9	10.272
429.77 (l)	(29.36)	6691	17.911
450	29.29	7583	19.258
500	28.85	9035	22.318
600	28.14	11884	27.513
700	27.66	14672	31.811
800	27.40	17423	35.485
900	27.25	20155	38.704
1000	27.11	22873	41.567

Premelting behavior

The constant pressure heat capacity of solid indium shows a moderate upwards trend above 300 K due to dilational conduction electron and structural disorder contributions. The latter was evaluated by Kramer and Nölting [7] on the basis of linear behavior of the sum of the other components. Thereby a disorder energy of $41 \pm 2 \text{ kJ mole}^{-1}$ was obtained and the corresponding disorder at the melting point was 0.053 per cent. When the present heat capacity results are combined with those by Clusius and Schachinger [2], an inflection, or minimum rise in heat capacity with temperature, occurs around 250 K, and the heat capacity is about $0.20 \text{ J K}^{-1} \text{ mole}^{-1}$ lower than observed by Kramer and Nölting [7] at 300 K. A re-analysis based on estimates of the different contributions to the heat capacity would therefore probably lead to a lower value for the disorder energy, but in the absence of precise expansivity and compressibility data for indium above 300 K such an analysis would be rather uncertain and has therefore not been performed.

A more substantial rise in heat capacity occurs as the melting temperature is approached. This is apparent from run 22 of series I (see Table 2) with an average heat capacity of $110.7 \text{ J K}^{-1} \text{ mole}^{-1}$. The energy input of this determination was so large that the final temperature was only about 0.01 K below the fusion temperature. Thus, the average heat capacity is considerably higher than the real heat capacity at the mean temperature.

The results of this and further experiments for the determination of heat capacities in the premelting region — uncorrected for curvature — are shown in Fig. 2 on a semi-logarithmic scale. They accord well with the excess heat capacity which arises from the presence of the mole fraction $1 \cdot 10^{-6}$ of a liquid-soluble/solid-

insoluble impurity. It causes the following premelting heat capacity under ideal conditions (26, 27):

$$C_i(\text{premelting}) \approx x^*RT_m^2/(T_m - T_i)^2 - (\Delta T/2)^2$$

Here x^* is the total mole fraction of impurity, T_m the melting temperature of the pure sample, and T_i and ΔT the temperature and the temperature interval to which the premelting heat capacity refers. The premelting behavior is thus com-

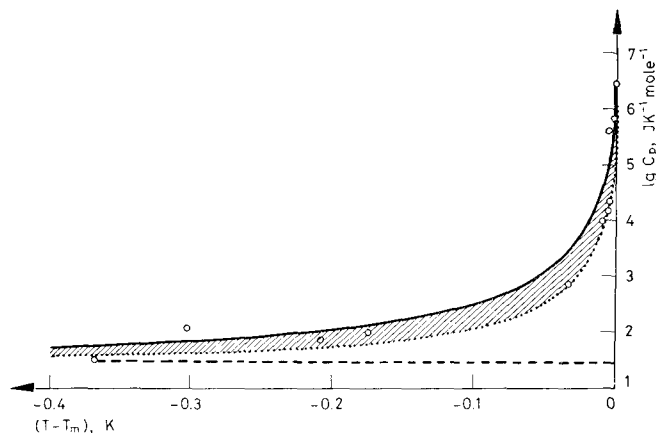


Fig. 2. Premelting heat capacity of indium. \circ represents present results, $- - -$ extrapolated lattice heat capacity, $—$ and \dots calculated values for the mole fractions 2×10^{-6} and 5×10^{-7} of a liquid-soluble/solid-insoluble impurity.

patible with the purity of the sample and resembles that observed earlier by the author for tin [12] and bismuth [28]. Again, an even higher purity metal has to be investigated in order that the intrinsic premelting heat capacity might be unambiguously distinguished from impurity premelting.

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References

1. R. HULTGREN, P. D. DESAI, D. T. HAWKINS, M. GLEISER, K. K. KELLEY and D. WAGMAN, Selected Values of the Thermodynamic Properties of the Elements, Amer. Soc. Metals, Ohio, 1973.
2. K. CLUSIUS and L. SCHACHINGER, Z. Angew. Physik, 4 (1952) 442.
3. R. W. BUNSEN, Poggend. Ann. Phys., 141 (1870) 1.
4. D. MENDELEYEV, Bull. Acad. Sci. St. Pétersbourg, 16 (1871) 45.
5. W. A. ROTH, I. MEYER and H. ZEUMER, Z. Anorg. Allgem. Chem., 214 (1933) 309.
6. A. I. KAZNOFF, R. L. ORR and R. HULTGREN, Unpublished results according to ref. 1.

7. W. KRAMER and J. NÖLTING, *Acta Met.*, 20 (1972) 1353.
8. W. OELSEN, O. OELSEN and D. THIEL, *Z. Metallk.*, 46 (1955) 555.
9. M. J. RICHARDSON and N. G. SAVILL, *Thermochim. Acta*, 12 (1975) 221.
10. F. GRØNVOLD, *Acta Chem. Scand.*, 21 (1967) 1695.
11. R. L. ORR, H. HEFFAN and R. HULTGREN, Unpublished results according to ref. 1.
12. F. GRØNVOLD, *Rev. Chim. Minérale*, 11 (1974) 568.
13. The International Practical Temperature Scale of 1968, *Metrologia*, 5 (1969) 35.
14. W. OELSEN, *Arch. Eisenhuettenw.*, 28 (1957) 1.
15. D. J. DAVID, *Anal. Chem.*, 36 (1964) 2162.
16. B. PREDEL, *Z. Metallk.*, 55 (1964) 97.
17. J. P. TARWATER, Ph. D. Thesis, Case Inst. of Technology, 1965, according to ref. 1.
18. O. ALPAUT and T. HEUMANN, *Acta Met.*, 13 (1965) 543.
19. J. P. BROS, *Bull. Soc. Chim. France*, 8 (1966) 2582; see also *Colloq. CNRS*, 156 (1967) 275.
20. P. D. GWINUP, Thesis (Oklahoma State University, 1967.) according to *Diss. Abstr.*, 28B (1968) 4965B.
21. L. A. MECHKOVSKII and A. A. VECHER, *Russ. J. Phys. Chem.*, 43 (1969) 751.
22. L. A. REZNITSKII, V. A. KHOLLER and S. E. FILIPPOVA, *Russ. J. Phys. Chem.*, 44 (1970) 299.
23. L. MALASPINA, R. GIGLI and V. PIACENTE, *Rev. Int. Htes Temp. et Réfract.*, 8 (1971) 211.
24. W. P. BRENNAN and A. P. GRAY, *Thermal Analysis Applications Study No. 9*, Perkin-Elmer Corp. Corp. U.S.A., 1973.
25. J. H. FLYNN, *Thermochim. Acta*, 8 (1974) 69.
26. H. L. JOHNSTON and W. F. GIAUQUE, *J. Amer. Chem. Soc.*, 51 (1929) 3194.
27. E. F. WESTRUM, JR., G. T. FURUKAWA and J. P. McCULLOUGH, *Experimental Thermodynamics*, Butterworths, London Vol. 1., 1968, p. 189.
28. F. GRØNVOLD, *Acta Chem. Scand.*, A29 (1975) 945.

RÉSUMÉ — La chaleur spécifique de l'indium de haute pureté a été déterminée entre 300 et 1000 K par calorimétrie adiabatique. Les valeurs des fonctions thermodynamiques suivantes ont été calculées: $C_p(1000\text{ K}) = (27.11 \pm 0.15) \text{ J K}^{-1} \text{ mol}^{-1}$, $[H^\circ(1000\text{ K}) - H^\circ(298.15\text{ K})] = (22\,875 \pm 70) \text{ J mol}^{-1}$ et $[S^\circ(1000\text{ K}) - S^\circ(298.15\text{ K})] = (41.567 \pm 0.125) \text{ J K}^{-1} \text{ mol}^{-1}$. L'enthalpie de fusion est $(3283 \pm 7) \text{ J mol}^{-1}$ et la température de fusion $(429.77 \pm 0.01) \text{ K}$. La chaleur spécifique de pré-fusion est compatible avec la présence d'une fraction molaire $x \approx 1 \times 10^{-6}$ d'une impureté dans l'échantillon, soluble dans le liquide, insoluble dans le solide.

ZUSAMMENFASSUNG — Die Wärmekapazität von hochreinem Indium wurde im Bereich von 300 bis 1000 K durch adiabatische Schildkalorimetrie bestimmt. Die Berechnungen der thermodynamischen Funktionen: $C_p(1000\text{ K})$, $[H^\circ(1000\text{ K}) - H^\circ(298.15\text{ K})]$ und $[S^\circ(1000\text{ K}) - S^\circ(298.15\text{ K})]$ ergab $27.11 \pm 0.15 \text{ J K}^{-1} \text{ Mol}^{-1}$, $(22\,875 \pm 70) \text{ J Mol}^{-1}$, bzw. $(41.567 \pm 0.125) \text{ J K}^{-1} \text{ Mol}^{-1}$. Die Schmelzenthalpie beträgt $(3283 \pm 7) \text{ J Mol}^{-1}$ und die Schmelztemperatur $(429.77 \pm 0.01) \text{ K}$. Die Vorschmelz-Wärmekapazität ist mit der Gegenwart einer Molfraktion $x \approx 1 \times 10^{-6}$ einer flüssig-löslich/fest-unlöslichen Verunreinigung in der Probe vereinbar.

Резюме — С помощью адиабатически-экранированной calorиметрии была определена теплоемкость высоко чистого индия в области температур от 300 до 1000 К. Были вычислены термодинамические функции: $C_p(1000\text{ K})$, $[H^\circ(1000\text{ K}) - H^\circ(298.15\text{ K})]$ и $[S^\circ(1000\text{ K}) - S^\circ(298.15\text{ K})]$, которые соответственно равны: $27.11 \pm 0.15 \text{ Дж} \cdot \text{К}^{-1} \cdot \text{моль}^{-1}$, $22875 \pm 70 \text{ Дж} \cdot \text{моль}^{-1}$ и $41.567 \pm 0.125 \text{ Дж} \cdot \text{К}^{-1} \cdot \text{моль}^{-1}$. Энтальпия плавления составляла $3283 \pm 7 \text{ Дж} \cdot \text{моль}^{-1}$, а температура плавления — $429.77 \pm 0,01 \text{ К}$. Теплоемкость предварительного плавления совместима с присутствием жидкостно-растворимой/твердотельно-нерастворимой примеси в образце с мольной фракцией $x \approx 1.10^{-6}$.