Thermodynamic properties of tin: Part I

Experimental investigation, ab-initio modelling of alpha-, beta-phase and a thermodynamic description for pure metal in solid and liquid state from 0 K

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Thermodynamic properties of tin:

Part I Experimental investigation, ab-initio modelling of α -, β -phase and a thermodynamic description for pure metal in solid and liquid state from 0K

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Abstract

Thermodynamic data for crystalline white and grey tin were assessed using an extended Einstein model from 0 K. Ab-initio simulations in the framework of density functional theory (DFT) with the quasiharmonic approximation (QHA) were carried out to define the heat capacities for both phases of tin from 0 K up to room temperatures. Good agreement was observed between theoretical and experimental heat capacities, which makes it possible to combine theoretical and experimental data to determine the standard entropies. Data for the liquid phase were described using a two state model. During the assessment, careful analysis of the experimental data was carried out. In order to fulfil the need for a precise evaluation of S°_{298} we needed to use an additional technique using multiple Einstein functions, which allows the experimental heat capacity and enthalpy data for the solid phase to be approximated accurately from 0 K up to the melting point and to estimate solid phase transition entropy and enthalpy which are difficult to measure due to a high activation barrier. Additional measurements of heat capacity were carried out where existing data were scarce.

Key Words: tin, two state liquid model, expanded Einstein model, ab-initio calculation, adiabatic calorimetry

1. Introduction

The basis underlying the thermodynamic models used in the present work originates from the developments carried out at the Ringberg workshop in 1995 which were later published in the proceedings [1]. The models were then modified as a result of the SGTE collaboration. The aim of these models is to adopt a universal approach which incorporates multiple physical contributions to the thermodynamic properties [2] for the solid phases and uses a two state model to describe the thermodynamic properties of the liquid phase.

As was discussed earlier in our assessment of data for Pb [3], the decision to use the Einstein model rather than the Debye model was taken because of the complexities in the derivation of the thermodynamic functions such as the enthalpy, entropy and Gibbs energy using the Debye model. Furthermore, in practice, calculations are generally useful for temperatures only above 100 K.

Additional parameters are introduced into the Einstein model in order to take into account anharmonicity, electronic effects and the correction from constant volume to constant pressure. There is also a requirement for an accurate re-evaluation of the value of $S^{\circ}_{298.15}$, which requires a careful evaluation of the C_p data from 0 K to the melting point. In order to do this we used a technique and software developed at MSU [4-5], which allows an detailed analysis of the experimental heat capacity and enthalpy data for the solid phase to be carried out and an accurate approximation from 0 K up to the melting point to be derived.

The extrapolation of data for the solid phase above the melting point was carried out in a similar way to previous work towards the definition of data for the elements in the SGTE database [6] by merging the heat capacity function of the solid phase to that of the liquid phase at high temperatures above the melting point.

The two state model for the liquid phase was developed by Ågren [7] and later accepted during the Ringberg workshop [8]. This approach has also been successfully applied in the recent work for other elements [9-12].

2. Literature analysis

Reviews

At ambient pressures Sn is stable in two crystalline forms in addition to the liquid phase. At temperatures below 286.35 K Sn is stable in a diamond structure similar to Ge and Si [13] and is commonly referred to as grey tin. Above this temperature and up to the melting point, Sn is stable in a body centred tetragonal phase (white tin). The melting point 505.078 K [14] is fixed on the ITS-90 temperature scale. The transformation between grey tin and white tin is notoriously sluggish especially on cooling and this makes it possible to study the properties of white tin even down to 0 K.

The data for the grey tin have been reviewed by Hultgren [15] (Figure 1a). There are several reviews on the thermodynamic data for white tin. One of the earliest corresponds to Stull and Sinke [16]. Later two more reviews were carried out by Corruccini and Gniewek [17] and Kelley [18]. The first of these covered the experimental data from 0 K to 300 K and the latter from 350 K up to the melting point (Figure 1b,c). The recommended data from Kelley [18] overlap with those from Stull and Sinke [16]. The later review of Hultgren [15] covers the interval from 0 K to the melting point. It should be noted that the resulting data in the temperature interval where white tin is stable phase are lower than those obtained by Kelley [18], while the low temperature interval is in agreement with the review of Corruccini and Gniewek [17]. More recent reviews were carried out by Cox et al. [19] and Gurvich et al. [20], which are in a good agreement with the data from Hultgren [15] up to room temperature. At the high temperatures, especially close to the melting point, the data from Cox et al. [19] and Gurvich et al. [20] are higher than those recommended by Hultgren [15] but still lower than those from Kelley [18].

There are a large number of reviews of data for the liquid phase (Figure 1d). The earlier reviews suggested a constant C_p for the liquid phase, while the more recent evaluations report the C_p values decreasing immediately above the melting point and then either remaining constant [15] or increasing again [19-20]. It should be also noted that the more recent reviews suggest that the C_p of the solid white tin is higher than that of the liquid phase in the region of the melting point.

b

c

d
Figure 1 – Comparison of heat capacity calculated from assessed datasets: a) grey tin; b,c) white tin; d) Liquid tin. Please note that the curves are drawn from the values tabulated by the assessors and are therefore smooth.

Heat capacity of α -tin (Grey tin)

The information about heat capacity measurements on solid tin are summarized on Figures 2 and 3 and Table 1.

The heat capacity of the grey tin was measured in the temperature range 79.8-288.9 K by Brönsted [21]. They are rather lower than the extrapolated values for room temperature obtained in later work. Rodebush [22] explained this by noting Brönsted [21] worked with finely divided metal in the container, which made it difficult to obtain thermal equilibrium at low temperatures. The later measurements of Lange [23] are higher than those of Brönsted [21] and were later confirmed by the results obtained by Hill [24] by adiabatic calorimetry. These data were given more weight in the present work in the temperature range 7-102 K. Lange [23] made an extrapolation of the data to the room temperature (283.7 K) giving a result for the heat capacity at 288 K of 25.65 J/(mol·K), which is appreciably higher than the value measured by Brönsted [21] of 24.73 J/(mol·K). Because these values were extrapolated in the temperature interval between 102 and 288 K more weight was given to the data from Brönsted [21] keeping in mind that it may be slightly too low. It should be noted that the data of Brönsted [21] suggest an almost constant behavior of the C_p at high temperatures with a very slight increase. In contrast, in the review of Hultgren the heat capacity increases with the temperature.

The heat capacity over the low temperature interval was measured by Webb and Wilks in 1955 [25] and their data are in reasonable agreement with the data from Lange [23].

From the preceding discussion, it may be concluded that the measurement of the heat capacity of grey tin should be an object of special investigation. According to IUPAC recommendation, thermodynamic properties which have been obtained by only one scientific group should be seen as preliminary. As can be seen from Figure 2, the range of temperatures which overlap in the data in the scientific literature is too small (75 – 100 K).

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Figure 2 – Experimental heat capacity data for α -tin: a) 0-300 K; b) 0-50 K

Heat capacity of β -tin (White tin)

The low temperature heat capacity of the white tin (Figures 3 a-b) was measured by Keesom and van den Ende (2-20 K) [26], Lange (9.1-101.1 K) [23], Corak and Satterthwaite (1.122- 4.341 K) [27], Ramanathan and Satterthwaite (3.77-4.08 K) [28], Zavaritskii (3.16-4.33 K) [29], Bryant (0.4-4.389 K) [30], O'Neal (0.009-1.126 K) [31], Cetas (4-30 K) [32], Naumov et al. (3.97-311 K) [33], Keesom and Van Laar (1.067-3.768 K) [34] and Yaqub (0.604-1.653 K) [35]. The superconducting point was determined to be at 3.71 K by Keesom [26,34] and later confirmed by Ramanathan and Srinivasan [28]. It was observed that when no magnetic field is applied the discontinuity is detected at the normal transition point. Later Keesom and van Laar reported that

their early measurements [26] were not accurate enough due to the insensitivity of the constantan (copper-nickel alloy based) thermometer [34]. In their later work [34] they carried out new investigations of the low temperature heat capacity in the normal state by applying a magnetic field of 23794 A/m (299 gauss). The obtained values are lower than those in previous measurements and are in a good agreement with more recent work of Zavaritskii [29] and higher temperature values from Corak and Satterthwaite [27] and Ramanathan and Srinivasan [28]. No discontinuity was observed in this case (Figure 3a). Corak and Satterthwaite [27] applied the magnetic field of 63816 A/m (800 oersted (oe)) in order to obtain the data for the normal state, however the transition is still observed and the values are in agreement with early work of Keesom and van den Ende [26] where no magnetic field was applied. O'Neal [31] applied magnetic field of 79770 A/m (1000 oe). The data from O'Neal [31] are higher than the earlier measurements of Keesom and van den Ende [26], Bryant [30] and Corak and Satterthwaite [27], but in agreement with Keesom and van Laar [34] and Yaqub [35]. The data from Bryant [30] are seriously lower than the results from the other work both at temperatures below and higher than 3.7 K. These data were excluded from consideration in our work. Above the 3.7 K there is good agreement between the experimental data from Keesom and van den Ende [26], Corak and Satterthwaite [27], Lange [23], Zavaritskii [29], Cetas [32] and the most recent measurements from Naumov et al. [33] (Figure 3b).

In the temperature interval between 50 and 300 K (Figures 3 c-d) there are experimental data from Brönsted [21], Lange [23], Rodebush [22], Cetas [32], Kramer and Nölting [36] and Naumov et al. [33] (Figure 3c). The early measurements from Brönsted [21] and Lange [23] have larger uncertainty. For this reason these data were given a lower weight. There is almost ideal agreement between the measurements from Rodebush [22], Cetas [32], Kramer and Nölting [36] and Naumov et al. [33].

The heat capacity in the higher temperature interval from 311 K up to the melting point was measured only by Klinghardt [37], Kramer and Nölting [36] and Bartenev [38] (Figure 3d). The data from Klinghardt are very scattered [37]. The results from Bartenev [38] are higher than the other results [36,37].

Finishing a review of literature data about tin heat capacity, it can be concluded that white tin has been investigated more thoroughly than grey tin. In case of white tin, measurements of C_p in the temperature interval 110-190 K only, are not available. For this reason it was decided to carry out an additional experimental investigation of the heat capacity of white tin in this temperature interval.

a

b

Table 1. Experimental determinations of the heat capacity

Temperature interval, K	Relative uncertainty, %	Method	Purity as reported in the original publications, %	Weight	Reference
α -Tin (Grey tin)					
1.5-4	1%	Adiabatic calorimetry	n/a	1 (due to the absence of other data)	Webb and Wilks [25]
7-100	1% above 10K, below 10K the accuracy decreases down to 20%	Adiabatic calorimetry	99.95%	1 in the temperature interval above 10K, 0.1 below 10K	Hill and Parkinson [24]
15.5-102.6	3%	Adiabatic calorimetry	n/a	1	Lange [23]

79.8-288.1	1%, up to 5% lower than data from Lange [21] and Hill and Parkinson [22]	Adiabatic calorimetry	n/a	0.1 in the temperature interval 79.8- 100K; 0.8 in the temperature interval 100- 288.1 (due to the absence of other data)	Brönsted [21]
β -Tin (White tin)					
0.1-1 superconduc tive state/ 0.08-4.2K normal state (79770A/m (1000Oe)) magnetic field)	1%	Vacuum adiabatic calorimetry	99.9999%	1	O’Neal [31]
0.4374- 4.389K superconduc tive state/ 0.4026- 3.874K normal state (39885A/m (500Oe) magnetic field)	1-3%	Vacuum adiabatic calorimetry	99.999%	1	Bryant [30]
0.604- 1.653K normal state (39789A/m (500gauss))	1-2%	Adiabatic calorimetry	99.9%	1	Yaqub [35]
1.13-3.982 superconduc tive state/ 1.122-4.341 normal state (63816 A/m (800 Oe) magnetic field)	0.6% normal state 0.9%superconducti ve state	Adiabatic calorimetry	99.999%	1	Corak and Satterthwaite [27]
1.373- 20.170	n/a	Vacuum adiabatic calorimetry	n/a	0.5	Keesom and van den Ende [26]
1.143- 3.794K	n/a	Vacuum adiabatic calorimetry	99.992%	1	Keesom and van Laar [34]

superconductive state/ 1.537-3.768 normal state(23794 A/m (299 gauss))					
1.72-3.5 superconductive state/ 3.97-311.43 normal state	0.5% for the 1.7- 3.7K; 0.36% for the 3.8-17K; 0.03% for the 17- 250K, 0.08% above 250K	Adiabatic calorimetry	Monocrystalline sample, 99.9999%	1	Naumov et al. [33]
3.16-4.33	n/a	Adiabatic calorimetry	99.998%	1	Zavaritskii [29]
3.7675- 4.0835	3%	Vacuum adiabatic calorimetry	n/a	1	Ramanathan and Srinivasan [28]
4-30	0.5%	Tray calorimeter using heat-pulse method	99.999	0 (no raw data only smoothed values)	Cetas [32]
15.5-102.6	3%	Adiabatic calorimetry	n/a	0.8	Lange [23]
69.63-101	1%	Adiabatic calorimetry	n/a	0.8	Rodebush [22]
79.8-288.1	1%(as published) Up to 5% lower than data from Lange[21] and Hill[22]	Adiabatic calorimetry	n/a	0.1 in the temperature interval 79.8- 100K;	Brönsted [21]
182.875- 505.76	1%	Adiabatic calorimetry	99.999%	1	Kramer and Nölting [36]
317.51- 518.45	1%	Method of heating with glowing electrons	n/a	0	Klinghardt [37]
323.15- 473.15	1%	Heating/cooling method	99.84% (0.1%Cu+0.06 other impurities)	0	Bartenev [38]
Liquid					
480-620	2%	DSC	99.999%	1	Chen and Turnbull [50]
506.2-804.1	5%		99.99%	1	Heffan [48]
523.15- 623.15	1%	Heating/cooling method	99.84% (0.1%Cu+0.06 other impurities)	0	Bartenev [38]

531-834.5	1%	Method of heating with glowing electrons	n/a	0	Klinghardt [37]
867-1227.6	2.4%	Method of radial temperature waves	n/a	0	Yurchak and Philippov [49]

Enthalpy increments measurements of solid tin

A large fraction of the enthalpy increment measurements and latent heat measurements, especially very early ones, were made using water or ice calorimeters. In the very early studies, the actual measurements were frequently concerned with the change in temperature of the water rather than determination of the heat as we may understand it now. These early experiments [actually depended](#) critically on the definition of the calorie as the heat needed to increase the temperature of 1g of water by 1 degree. However the temperatures of the water at which the measurements were carried out were different [39] and the heat needed to raise the temperature from 0 to 1⁰C and from 15 to 16 ⁰C are different. Different calories were used even after 1935 when thermochemical calorie was determined to be 4.184 J, and even after the international calorie was accepted to be 4.1868 J in 1956 [40]. The 15 C calorie was frequently used in experimental measurements. The value was determined as the amount of energy required to warm 1 gram of water from 14.5 to 15.5 C and was accepted to be equal to 4.1855J. The 20 C calorie was mostly used in the works of USSR scientists in 1934-1957. It was determined as energy needed to warm 1 gram of water from 19.5 to 20.5 C and was equal to 4.182J. This gives an additional, although small, deviation of several Joules when we interpret the original values. One should also keep in mind that the temperatures of the calorimeter were different. For example in the earliest measurements of Wüst et al. [41] the actual measurement was for $H^{\circ}(T)-H^{\circ}(273)$. Similar measurements were carried out later by Jaeger and Bottema [42], Figure 4a, and they provide more reliable data, although both set of measurements are in reasonable agreement. Iitaka [43], Awbery and Griffiths [44] and Umino [45] carried out measurements of $H^{\circ}(T)-H^{\circ}(293)$. From this set of measurements the data from Awbery and Griffiths [44] and Umino [45] are in a good agreement with each other, while data from Iitaka differ significantly [43], Figure 4b. The most recent measurements were carried by Genot [46], however the actual temperature of the calorimeter was specified in the paper as 471K (198 ⁰C), which makes it impossible to compare with experimental measurements from other authors.

Table 2 – experimental values of the enthalpy increments for solid white tin

Temperature interval, K	Relative uncertainty, %	Method	Purity as reported in the original	Units to be used for	Measured value	Reference
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			publications %	transfer into J		
373.15- 493.15	5%	Oberhoffer vacuum calorimeter, which is Bunsen calorimeter combined with electric vacuum furnace	n/a	15 °C calorie	$H^{\circ}(T)-H^{\circ}(273)$	Wüst et al. 1918 [41]
357-474	n/a	Drop water calorimeter Tc=293.15	99.79% purity 0.084%Pb, 0.054%Cu, 0.035%Fe, 0.021Zn, 0.019%As	15 °C calorie	$H^{\circ}(T)-H^{\circ}(293)$	Iitaka 1919 [43]
291.15- 560.15	n/a	Drop water calorimeter Tc=291.15	99.98%	20 °C calorie	$H^{\circ}(T)-H^{\circ}(293)$	Awber y and Griffit hs 1926 [44]
323-873	1%	Drop water calorimeter	99.989% purity with 0.003% Pb and 0.008% Cu	15 °C calorie	$H^{\circ}(T)-H^{\circ}(293)$	Umino 1926 [45]
273.15- 473.15	0.2%	Drop calorimetry	n/a	Not obvious taken as thermoch emical calorie	$H^{\circ}(T)-H^{\circ}(293)$	Jaeger and Bottem a 1932 [42]
471-723	1%	Drop water calorimeter	n/a	Thermoc hemical calorie	$H^{\circ}(T)-H^{\circ}(471)$	Genot 1960 [46]

Figure 4 Enthalpy increments measurements for β-tin a) $H^\circ(T)-H^\circ(273)$; b) $H^\circ(T)-H^\circ(293)$

Enthalpy of $\alpha \rightarrow \beta$ transition

There is a lack of data for the enthalpy of $\alpha\text{Sn} \rightarrow \beta\text{Sn}$ transformation. Cohen and van Eijk [47] determined the heat of transformation as 3.05 kJ/mol using an electrochemical cell consisting of the grey and white tin connected by an aqueous tin hexachloride solution. However, in more recent calorimetric work of Brönstedt [21], the enthalpy of transformation was determined to be 2.23 kJ/mol. Hultgren [15] estimated the heat of transformation to be 1.97 kJ/mol and temperature of transformation as 286.35 K from a third law analysis. Even today the accuracy of the values both for enthalpy of transformation and the temperature of transformation are not well determined.

Heat capacity of Liquid tin.

Heat capacity measurements of liquid tin have been carried out by Klinghardt [37], Bartenev [38], Heffan [48], Yurchak and Philippov [49] and Chen and Turnbull [50] (Figure 5, Table 1). Klinghardt [37] carried out measurements from the melting point up to 835 K, Yurchak and Philippov [49] carried out measurements using a radial temperature waves method from 867 K to 1227 K. Both authors suggest an almost constant behavior of the heat capacity. The data from Yurchak and Philippov [49] suggest a slow increase in the heat capacity from 1100 K. In contrast to these results, the measurements of Chen and Turnbull [50], Heffan [48] and Bartenev [38] suggest a decrease of the heat capacity in the temperature interval from the melting point to 804 K. The results from these three studies are in a good agreement with each other (Figure 5).

Enthalpy increments measurements of the liquid tin

The other source of thermodynamic data for liquid tin is from enthalpy drop measurements. Similar peculiarities were taken into account as in the analysis of data as for solid tin enthalpy drop data. A comparison of the data from Iitaka [43], Awbery and Griffiths [44] and Umino [45] showed that these results are in reasonable agreement (Figure 6). The only high temperature measurements were carried out by Feber et al. [51] These results seem to be in agreement with lower temperature data.

Table 3 – experimental values of the enthalpy increments for liquid tin

Temperature interval, K	Relative uncertainty, %	Method	Purity as reported in the original publications, %	Units to be used for transfer into J	Measured value	Reference

513.15-1273.15	5%	Oberhoffer vacuum calorimeter, which is Bunsen calorimeter combined with electric vacuum furnace	n/a	15°C calorie	$H^\circ(T)-H^\circ(273)$	Wüst et al. 1918 [41]
536-785		Drop water calorimeter Tc=293.15	99.79% purity 0.084%Pb, 0.054%Cu, 0.035%Fe, 0.021Zn, 0.019%As	15°C calorie	$H^\circ(T)-H^\circ(293)$	Iitaka 1919 [43]
506.15-560.15	n/a	Drop water calorimeter Tc=291.15	99.98%	20°C calorie	$H^\circ(T)-H^\circ(293)$	Awbery and Griffiths 1926 [44]
523-873		Drop water calorimeter	99.989% purity with 0.003% Pb and 0.008% Cu	15°C calorie	$H^\circ(T)-H^\circ(293)$	Umino 1926 [45]
471-723	1%	Drop water calorimeter	n/a	Thermochemical calorie	Temperature of calorimeter is not known	Genot 1960 [46]
1222-1745	$\pm 120\text{J/mol}$	An adiabatically shielded drop calorimeter Tc=298.15	99.9999%	Thermochemical calorie	$H^\circ(T)-H^\circ(298)$	Feber et al. 1969 [51]

Figure 6 - Enthalpy increments measurements for liquid tin $H^{\circ}(T)-H^{\circ}(293)$ (Data from Feber et al. [51] are for $H^{\circ}(T)-H^{\circ}(298)$)

Fusion

The melting temperature of tin is a fixed point of the ITS-90 and is defined to be 505.078 K [14]. This value is accepted in the present work. The earliest attempts to measure the enthalpy and temperature of fusion was made by Irvine and Black approximately in 1780 and were later cited and reproduced by Irvine Junior in 1804 [52]. This works refer to the time when the actual measurement was done relative to the temperature change of the water where the sample was placed. The work [52] provides detailed information for the investigations of the measurements for Bi, but almost no details for the investigations on Sn. For this reason the recalculated value from Stølen and Grønvold of 9110 J/mol [40] seems to be rather speculative. There also could be a misunderstanding concerning the original units as the original investigation temperature was measured in Fahrenheit and the weight of samples in grains not calories per grams as indicated in [40].

Richards determined the value for the latent heat using a method and apparatus [39] similar to the one used by Pionchon [53], with the difference that sample was introduced from the temperature close to the melting point [54]. Despite the fact that for the early measurements the purity of the samples and sensitiveness of the equipment was not as good as in the later measurements still the obtained values for enthalpies of fusion are within experimental range of values we have for the more recent papers.

The analysis of data obtained from 1947 shows that the lowest values were obtained by Bartnev [55], Olsen [56] and Chiotti et al. [57]. It should be noted that in 1955 Olsen published 3 papers [56,58-59] where the measurement of enthalpy of fusion of tin was carried out. The average value between 3 sets of measurements is 7046 ± 170 (J/mol). The highest values were obtained by Nagasaki and Fujita [60], Pascard [61] and Reznitskiy et al. [62]. The lowest and highest values were excluded from further analysis. In 1993 Grønvold [63] carried out additional investigations and updated the value for enthalpy of fusion of indium which had been used as a reference material for calibration of instruments (e.g. in the works of Alpaut and Heumann [64], Breuer and Eysel [65], Höhne et al. [66]). The average value between the remaining measurements is 7169 J/mol with a deviation within 2% and is very close to the value 7179 J/mol reported by Grønvold. Among the most recent measurements the most accurate seems to be the one reported by Grønvold, which was actually focused on determination of the enthalpy of fusion values, while for the other two, Wolf et al. [67] and Zahra and Zahra [68] were actually aiming to evaluate the precision of their

instruments using the data from Grønvold as a reference point for comparison. Zahra and Zahra [68] also reported some instability of the baseline and several other shortcomings of the instrument which they used, which decreased the precision of their measurements in comparison with other works.

Table 4 – Experimental measurements of the enthalpies of fusion

T, K	H fusion J/mol	Relative uncertainty, %	Method	Purity as reported in the original publications, %	Units to be used for transfer into J	Reference/ date
501			Temperature change measurement of the water in the water calorimeter.			Irvine [52] 1804
	6617.258	3% (± 99 J/mol)	Early thermal analysis measurement using ice calorimeter, where time to decrease the temperature by 10K across the melting temperature was used as a measure of the latent heat.	n/a	0°C calorie	Rudberg [69] 1830
508.15	7105	n/a	Drop water calorimeter	n/a	15°C calorie	Person [70] 1846
n/a	7086	n/a	Drop water calorimeter	n/a	15°C calorie	Person [71] 1848
500.45	7280	n/a	Water calorimeter, temperature measurement	n/a	15°C calorie	Spring [72] 1886
	7254	n/a	Water calorimeter, double method of mixtures	L'etain de Banca	15°C calorie	Pionchon [53] 1887
N/a	7234.3	n/a	Water calorimeter, double method of mixtures	n/a	15°C calorie	Richards [39,54] 1893
503.15	6983	10%	Drop-Water	n/a	15°C calorie	Robertson [73] 1902
	7105	7%	Electric calorimeter, cooling curve	n/a	15°C calorie	Guinchant [74] 1907
505.15	6981	10%	Oberhoffer vacuum calorimeter, which	n/a	15°C calorie	Wüst et al. [41]

			is Bunsen calorimeter combined with electric vacuum furnace.			1918
n/a	6648	n/a	Drop water calorimeter T _c =293.15	99.79% purity 0.084%Pb, 0.054%Cu, 0.035%Fe, 0.021Zn, 0.019%As	15°C calorie	Iitaka [43] 1919
505.15	7254	n/a	Drop water calorimeter	99.98%	15°C calorie	Awbery and Griffiths [44] 1926
n/a	7055	2%	Drop water calorimeter	99.989% purity with 0.003% Pb and 0.008% Cu	15°C calorie	Umino [45] 1926
n/a	6934	n/a	Cooling and heating curves	n/a	Thermochemical calorie	Bartnev [55] 1947
505	7615	n/a	DSC	n/a	Thermochemical calorie	Nagasaki and Fujita [60] 1952
n/a	7074	3%	Tammann thermal analysis	n/a	15°C calorie	Oelsen et al. [58] 1955
	7199	1.2% (±42J/mol)	Drop-water-scanning	n/a	15°C calorie	Oelsen et al. [59] 1955
	6864	n/a	Drop-water-scanning	n/a	15°C calorie	Oelsen [56] 1955
505.05	7306	n/a	DTA	n/a	Thermochemical calorie	Pascard [61] 1959
505.15	7071	n/a	Water calorimeter	n/a	Thermochemical calorie	Schürmann and Träger [75] 1961
	7075	1% (±32J/mol)	DTA	99.999%	Thermochemical calorie	Speros and Woodhouse [76] 1963
	7053	±745J/mol	DTA, 10C/min	Chemically pure (C.p.), flattened sample	15°C calorie	David [77] 1964
505.15	7241	2%(±79.5)	DTA	99.96%	Thermochemical calorie	Alpaut and Heumann [64]

						1965
	6886	2%	DTA- Adiabatic calorimeter	99.999%	Thermochemical calorie	Chiotti et al. [57] 1966
	7279	2.4% (± 87)	DSC	n/a	Thermochemical calorie	Gwinup [78] 1967
n/a	7406	6%	DSC Tian-Calvet	n/a	Thermochemical calorie	Reznitskiy et al. [62] 1970
505.15	7190	14%	DSC DuPont thermal analyser	99.999%	n/a	Breuer and Eysel [65] 1982
504.9	7140	1.2% ($\pm 40\text{J/mol}$)	Power compensated DSC (Perkin-Elmer)	n/a	n/a	Höhne et al. [66] 1983
	7190	1% ($\pm 30\text{J/mol}$)	Heat Flux DSC (DuPont)	n/a	n/a	
505.1	7200	n/a	Adiabatic calorimeter	99.999%	n/a	Kano [79] 1991
505.1 ± 0.01	7148.716	11%	Drop calorimetry	n/a	n/a	[80] 1992
505.11	7140.407	8%	DSC	n/a	n/a	Callanan [81] 1992
505.07 ± 0.02	7179	0.4% ($\pm 15\text{J/mol}$)	DSC	99.9999% 0.07 $\cdot 10^{-6}\%$ Al 0.2 $\cdot 10^{-6}\%$ Cr 0.16 $\cdot 10^{-6}\%$ Cu 0.2 $\cdot 10^{-6}\%$ Fe 0.02 $\cdot 10^{-6}\%$ Na	n/a	Grønvold [63] 1993
505.05	7162	2%	Linseis DSC-L63	99.999%	n/a	Wolf et al. [67] 1994
505.08	7291.168	1%	DTA Perkin Elmer 1020 series	99.99%	n/a	Zahra and Zahra [68] 1996

3. Methodology of current work

3.1. Experimental investigations

Adiabatic calorimetry

The heat capacity of tin was measured in an automated vacuum adiabatic calorimeter combined with a computer-measuring system. The detailed device configuration and calorimetric technique are described in [82,83]. The temperature of the calorimeter was measured by a rhodium/iron resistance thermometer ($R_0 \sim 50 \Omega$), which was calibrated to ITS-90 [84] over the temperature range 5-373 K. The temperature difference between the container and adiabatic shell was measured by

an eleven-junction (copper + 0.1 wt% iron)-Chromel differential thermocouple. The adiabatic performance of the calorimeter was maintained by digital control using the computer-measuring system with an accuracy of $\pm 3 \cdot 10^{-3}$ K. The error of measurements of the temperature of the container was estimated to be $\pm 2 \cdot 10^{-2}$ K. The high vacuum inside the calorimetric cell was maintained by means of cryosorption provided with an efficient charcoal getter. The heat capacity of the substance was measured in the process of heating the sample. The mass of the sample was determined with a precision of $\pm 5 \cdot 10^{-2}$ mg on a Mettler balance. The method of calorimetric determinations was checked by the measurement of the heat capacity of pure copper having the mass fraction 0.9995. The relative standard uncertainty of the heat capacity measurements, $u_r(C_{p,m})$, was 0.02 within temperature range 7-20 K, 0.007 within temperature range 20-40 K, 0.004 within temperature range 40-80 K and 0.002 above 80 K.

Enthalpy increment measurements

Enthalpy increment measurements were carried out using an AlexSys 1000 isoperibol calorimeter. Samples of Sn (of 99.999% purity) were dropped from room temperature into the hot calorimeter at a temperature where Sn is liquid, under a purified argon atmosphere (99.998%). The heat effect is then equal to the sum of heat content of the sample and the heat of fusion.

$$\int_{298}^T C_p dT + \Delta H_{fus} \quad (1)$$

Experiments were carried out at 600, 650, 700, 750 and 800 K. At each temperature the calorimeter was stabilized in order to get a stable baseline, and calibrated. The calibration was carried out using both Al₂O₃ sapphire supplied by NIST, and 99.999% Pt. From 3 to 7 drops were made to obtain the values for the calibration factors at each temperature. The typical mass of the samples of alumina (for calibration) and tin was 10-20 mg. The Calisto software was used for recording the signals from calorimeter and assessment of the results.

3.2 Methodology of ab-initio calculations of C_p

Thermodynamic calculations for grey and white tin were performed within the framework of density functional theory using the Vienna *ab-initio* simulation package VASP code [85-88]. The interaction between ions and electrons were described using the projector augmented-wave (PAW) method [89, 90] with fourteen highest electrons (4d¹⁰5s²5p²) as valence electrons and a plane wave energy cut-off of 400 eV for both phases. For calculation of exchange–correlation energy we used the Local Density approximation (LDA) with the scheme of Ceperley-Alder [91].

Two basis atoms with coordinates (0, 0, 0) and ($a/4, a/4, a/4$) were chosen as the unit cell for the cubic diamond structure of α -Sn (Fd-3m space group). The crystal structure of β -Sn with body-centered tetragonal Bravais lattice (I4₁/amd space group) also was set with two atoms

in the basis at $(a/8, 7a/8, a/4)$ and $(7a/8, a/8, 3a/4)$. The integration over the Brillouin zone was performed with an equivalent unit cell k-point grid or better than $16 \times 16 \times 16$ for α -phase and $20 \times 20 \times 20$ for β -phase. All the calculations were carried out using the Methfessel–Paxton smearing (first order) [92] with a broadening of $\sigma = 0.2$ eV. The convergence criterion for electronic subsystem was chosen to be equal to 1 meV/atom.

We calculated the heat capacity as a sum of the lattice contribution and the electronic one. The lattice heat capacity and enthalpy $S^{\circ}_{298.15}$ were calculated in a quasi-harmonic approximation, which is required the calculation of phonon spectra with several volumes. Seven volumes were chosen in the range $-6 \dots +6$ % of equilibrium volume with a 2 % step. A small displacement method with a single atomic displacement value of 0.01 Å was used to calculate the vibration frequencies in both phases for all the chosen volumes. The phonon spectra and the thermodynamic properties were calculated using the PHONOPY code [93]. The electron contribution was calculated in the Sommerfeld approximation, for which we calculated the electron density of states for both phases and found the number of states at the Fermi level. Note that the alpha phase is a semi-metal and the number of states at the Fermi level is negligible; therefore, the electron contribution for this phase was not calculated.

We carried out the convergence of the results depending on the size of the supercells and found that in the alpha phase convergence is achieved for a value of $4 \times 4 \times 4$. In the beta phase, we found a strong dependence on the size of the supercell and, in addition dynamic instability for all supercells, up to the size $5 \times 5 \times 5$. The greatest stability is observed on the supercell $4 \times 4 \times 4$, that is the reason of choosing it for calculating the thermodynamic properties. We will discuss the issue of dynamic stability and the choice of approximations in more detail in a forthcoming publication [94].

3.3 Thermodynamic Models

The modelling part was carried out in a similar way to that published earlier for Pb [3] following the recommendation of the Ringberg seminar [1] and using an evaluation procedure for S°_{298} using the approach of Voronin and Kutsenok for the obtaining a precise description of $C_p(T)$ [4].

The heat capacity at constant pressure representing a combination of the Einstein model and a polynomial correction term is described as:

$$C_p = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} + aT + bT^2 + cT^3 + dT^4 \quad (2)$$

Here the polynomial takes into account the anharmonic and electronic effects and the conversion from C_V to C_p , etc.

Integration of this equation allows us to obtain equations for other thermodynamic functions (with the inclusion of a term $3/2R\theta_E$ to H and G [2]):

$$S = 3R \left[\frac{\theta_E/T}{(e^{\theta_E/T} - 1)} + \ln \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)} \right] + aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4 \quad (3)$$

$$H = E_0 + \frac{3}{2}R\theta_E \frac{(e^{\theta_E/T} + 1)}{(e^{\theta_E/T} - 1)} + \frac{a}{2}T^2 + \frac{b}{3}T^3 + \frac{c}{4}T^4 + \frac{d}{5}T^5 \quad (4)$$

$$G = E_0 + \frac{3}{2}R\theta_E - 3RT \ln \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)} - \frac{a}{2}T^2 - \frac{b}{6}T^3 - \frac{c}{12}T^4 - \frac{d}{20}T^5 \quad (5)$$

In order to ensure that the crystalline phase does not become stable at very high temperatures the following equation is used to describe the thermodynamic properties of the crystalline phases above the melting point.

$$Cp = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} + a' + b'T^{-6} + c'T^{-12} \quad (6)$$

with the coefficients a' , b' and c' selected so that the heat capacity and its derivative are continuous at the melting point and merge with those of the liquid phase at some high temperature.

The thermodynamic properties of the liquid phase were represented using the two state model [7-8]. According to this model it is assumed that the liquid phase consists of the two types of atoms mixing ideally: atoms with vibrational motion with no translational degrees of freedom and atoms with translational motion. The atoms with vibrational motion can be thought of as representing a pure amorphous phase. This could also be expressed in terms of different energy states, an increase in space or degrees of translational and vibrational freedom available to the atoms.

For a given temperature the two types of atoms are in equilibrium so as to give a minimum in the total Gibbs energy. The relative amounts of these “translational” and “vibrational” atoms depend on the difference in Gibbs energy between them.

At each temperature a transition of atoms takes place from one state to another in order to achieve equilibrium with χ of translational atoms and $1-\chi$ fraction of vibrational atoms. The equilibrium value of χ is determined by the equation:

$$\chi = \frac{e^{-\Delta G_{dif}/RT}}{1 + e^{-\Delta G_{dif}/RT}} \quad (7)$$

where ΔG_{dif} is the difference in Gibbs energy between the translational and vibrational atoms. The Gibbs energy of the vibrational atoms can be approximated by the Einstein equation, which includes additional parameters which may be optimized in order to obtain agreement with experimental data.

$$G^{vib} = E_0 + \frac{3}{2}R\theta_E + 3RT \ln \frac{(e^{\theta_E/T} - 1)}{e^{\theta_E/T}} + A + aT^2 + bT^3 \quad (8)$$

The value for the Einstein temperature was taken initially to be the same as that of the crystalline phase. The parameters A , a and b were optimized. These parameters here refer only to the liquid phase. The Gibbs energy difference between the **vibrational atoms** and the **translational atoms** can be described as:

$$\Delta G_{dif} = G^{trans} - G^{vib} = B + CT + D T \ln T \dots \quad (9)$$

Thus the total Gibbs energy G^L will then be given by:

$$G^L = G^{vib} - RT \ln \left[1 + e^{(-\Delta G_{dif}/RT)} \right]. \quad (10)$$

The optimization of data for the liquid phase (A , a , b , B , C and D) was carried out using experimental data for the liquid phase.

Voronin and Kutsenok method

In order to evaluate S°_{298} the heat capacity data were fitted using multiple Einstein functions as described in the work of Voronin and Kutsenok [4]. The method allows standard thermodynamic functions to be approximated with an accuracy corresponding to experimental measurements from 0 K up to the melting point.

Using this approach the experimental $C_p(T)$ data can be approximated using following equation

$$C_p(T) = 3R \sum_i \alpha_i \frac{(\Theta_i/T)^2 e^{\Theta_i/T}}{(e^{\Theta_i/T} - 1)^2} \quad (11)$$

Then an integration of the equation (11) with addition of $3/2R\theta_E$ (which corresponds to zero-point lattice vibration) leads to the following expressions for thermodynamic functions [6]:

$$S^\circ(T) = 3R \sum_i \alpha_i \left(\frac{\Theta_i/T}{e^{\Theta_i/T} - 1} - \ln(1 - e^{-\Theta_i/T}) \right) \quad (12)$$

$$H^\circ_T(T) - H^\circ_0 = \frac{3}{2} \theta_E + 3R \sum_i \alpha_i \Theta_i (e^{\Theta_i/T} - 1)^{-1} \quad (13)$$

$$G^\circ_T(T) - H^\circ_0 = \frac{3}{2} \theta_E + 3R \sum_i \alpha_i \Theta_i (e^{\Theta_i/T} - 1)^{-1} - 3RT \sum_i \alpha_i \left(\frac{\Theta_i/T}{e^{\Theta_i/T} - 1} - \ln(1 - e^{-\Theta_i/T}) \right) \quad (14)$$

where α_i , Θ_i ($i = 1, 2, \dots$) are parameters determined by fitting the experimental heat capacity data to equation (11). θ_E is the true Einstein temperature of Sn.

4. Results and Discussion

4.1. Experimental results

Adiabatic measurements of C_p

According to the Figure 3 the temperature dependence of the heat capacity of β -Sn in the temperature range 100–170 K could be defined only from the results of Naumov et al. [33], so these data required validation. Using adiabatic calorimetry, we obtained the values for the heat capacity of white tin in the temperature range 70–370 K. Figure 7 shows a comparison of the results obtained in this work with the works of Brönsted [21], Naumov et al. [33] (error 0.3%), Kramer and Nölting [36] (error 1%), the errors of our work correspond to 0.3%. The raw data are listed in Appendix 1.

The obtained values of the heat capacity agree with the data from Naumov et al. [33] within the measurement error over the whole of the investigated temperature interval. Our experimental values and those of Naumov et al. [33] were given the same mathematical weight over the whole temperature range. Moreover, it should be noted that the data from Naumov et al. [33] are in good agreement with the data from Kramer and Nölting [36] up to 300 K.

Enthalpy drop results

The experimental results of the enthalpy drop measurements for liquid tin obtained in this work are provided in Table 5 and Figure 8. These results are in a good agreement with the previous measurements.

Table 5. Values of enthalpy increment $H_T - H_{298}$ (J/mol) calculated from the drops of pure tin from room temperature to temperature of calorimeter T at 0.1 MPa under Ar-atmosphere

T , K	Number of drops	$H^\circ(T) - H^\circ(298)$, J/mol	Error of measurement, %
---------	-----------------	-------------------------------------	-------------------------

873.15	4	22104	1.38
923.15	7	24115	1.54
973.15	5	26351	1.06
1023.15	5	27340	1.29
1073.15	6	28013	1.84

Figure 8- Experimental results of the enthalpy drop measurements of the liquid tin in comparison with existing experimental literature values. Experimental uncertainties of $H(T)-H(298)$ values in our experiments are comparable with the size of symbols.

4.2 Ab-initio calculations of C_p

Heat capacity of grey and white tin at a constant pressure were calculated in the temperature range from 0 to 300 K. These calculations, therefore, fill a gap in the experimental heat capacity values for both phases. Theoretical calculations of the heat capacity of α -tin (C_p) in comparison with experimental measurements from Ref. [21, 23-25] are shown in Fig.9. We observe very good agreement between theory and experiment, especially in the low temperature range where the anharmonic effects are small. There is a small deviation in the range of high temperature due to increasing contribution from anharmonic effects. The values for standard entropy were also calculated from ab-initio methods and appeared to be for α -tin $S^\circ_{298.15} = 43.89$ J/K/mole, for β -tin $S^\circ_{298.15} = 51.56$ J/K/mole.

Figure 9 - Experimental and ab-initio data of the heat capacity for α -tin for the temperature range: 0-300 K.

Figure 10 represent full and partial contributions to heat capacity at a constant pressure (C_p) for β -tin phase. Our calculations accurately reproduce experimental results in the whole temperature range (see the insert picture in Figure 10).

Figure 10 – Experimental and *ab-initio* data of the heat capacity for β -tin for the temperature range 0-300 K.

4.3 Evaluation of $S_{298.15}^\circ$

Grey (α) tin

An experimental investigation of the temperature dependence of C_p for α -tin is presented only in four works: Brönsted [21], Lange [23], Hill [24], Webb and Wilks [25]. So, all of these experimental points were included in our calculation, but with different mathematical weights. We attempted to extrapolate data from Lange [23] with an Einstein function (Fig. 11, orange line) and to compare this with his own extrapolation. Our extrapolation curve is in good agreement at temperatures above 200 K with the Brönsted [21] experimental points taking into account the likely error of the experimental results assumed to be about 1%. Therefore, in this temperature range, the data of Brönsted [21] were assigned the maximum mathematical weight. The heat capacity values obtained by extrapolation of the data of Lange [23] were not taken into account in the calculation. In the low temperature range the data from Lange [23], Hill [24], Webb and Wilks [25] were given the maximum mathematical weight, but the data from Brönsted [21] were given lower weight ($w = 0.5$)

Figure 11 – Comparison of experimental and calculated data for α -tin

The parameters obtained as a result of the joint approximation of the low temperature data are listed in Table 6 and the calculated thermodynamic functions are listed in Table 7. The unknown parameters α_i and Θ_i of Eq. (11) were determined by the solution of a system of nonlinear equations using a least squares method embodied in the software package “Cpfit” available from the site [5]. All the parameters are given with an excess number of significant digits as the use of rounded values of α_i and Θ_i may lead to greater uncertainty in the calculated heat capacity values in comparison with the experimental uncertainties. A detailed description of the calculation

procedure and uncertainty estimation is given in the Manual which is available from the same address [5].

As can be seen from Table 7, there is an excellent agreement between the *ab-initio* calculated standard entropy and the assessed value derived with two Einstein function.

Table 6 Parameters for the joint approximation $C_p(T)$ data for α -tin (*)

i	α_i	Θ_i	Standard deviation		Max deviation	
			absolute	relative %	absolute, J/(mol·K)	relative %
1	0.664046±0.01	238.552±5	0.112	16.12	0.1924 at	67.83% at
2	0.369633±0.02	67.1438±2			22.35 K	7 K
<i>(*) In the temperature range up to 190 K data from Lange [23], Hill [24] are given a weight 1 (w=1), in the temperature range above 190 data from Brönsted [21] are given a weight 1 (w=1)</i>						

Table 7 Approximated value of standard thermodynamic functions of α -Sn at 298.15K.

Calculated value			Standard deviation (absolute)		
$C_{p,298.15}$	$S^\circ_{298.15}$	$H^\circ_{298.15}-H^\circ_0$	$C_{p,298.15}$	$S^\circ_{298.15}$	$H^\circ_{298.15}-H^\circ_0$
J/(mol·K)		J/mol	J/(mol·K)		J/mol
24.89	43.68	5674.4	0.05	0.07	7.7

White (β) tin

4.3.1. Analysis of the low temperature data

The data from the publications of Naumov et al. [33], Lange [23], Rodebush [22], Zavaritskii [29], Yaqub [35], O'Neal [31], Keesom [34] and our adiabatic calorimetry data were taken into consideration during the analysis of the low temperature data. In the temperature range up to 298.15K, the results of our work and those of Naumov et al. [33] overlap in terms of the temperature range studied, and are sufficient for the calculation: from the point of transition to the normal state up to 370 K. Moreover, these data are the only ones in the temperature range 100-200 K. So, our data together with those of Naumov et al. [33] should be taken as the most reliable and in the case of any discrepancies with the other works, assigned the maximum mathematical weight.

Table 8 Parameters for the joint approximation $C_p(T)$ data for β -tin (*).

I	α_i	Θ_i	Standard deviation		Max deviation	
			Absolute	relative %	absolute, J/(mol·K)	relative %
1	0.175386±0.01	1264.02±44	0.06603	18.31	0.4911 at 32.7 K	99.91% at 3.076 K
2	0.227599±0.06	251.216±22				
3	0.604408±0.04	123.98±8				
4	0.224656±0.03	50.4622±3				
(*) Data from Naumov [33], Kramer [36] (180-320K), Zavaritskii [29] and our adiabatic experiment are given a weight 1 ($w=1$), data from Lange [23], Rodebush [22], Keesom [34] are given a weight 0.5 ($w=0.5$), data from Yaqub [35], O'Neal [31] and Kramer [36] (above 320K) are given a weight 0.01 ($w=0.01$).						

Table 9. Approximated value of standard thermodynamic functions of β -Sn at 298.15K.

	Calculated value			Standard deviation (absolute)		
	$C_{p,298.15}$	$S^{\circ}_{298.15}$	$H^{\circ}_{298.15}-H^{\circ}_0$	$C_{p,298.15}$	$S^{\circ}_{298.15}$	$H^{\circ}_{298.15}-H^{\circ}_0$
	J/(mol·K)		J/mol	J/(mol·K)		J/mol
1	26.96	51.12	6316.5	0.01	0.02	1.0
2	26.97	51.13	6317.6	0.006	0.03	1.1
Comments: 1. Low temperature data: Naumov et al. [33], Lange [23], Rodebush [22], Zavaritskii [29], Yaqub [35], O'Neal [31], Keesom [34], our adiabatic calorimetry data (70-300K) 2. Joint analysis of low and high temperature data: Naumov et al. [33], Lange [23], Rodebush [22], Zavaritskii [29], Yaqub [35], O'Neal [31], Keesom [34], our adiabatic calorimetry data (70-370K), Kramer [36]						

One useful possibility emerging from the approximation of $C_p(T)$ using the combination of Einstein functions is that it provides an estimate of the entropy and enthalpy of the α - β transition. By using Eq.12 and the parameters from Tables 6 and 8, the temperature dependence $S^{\circ}(T)$ for both solid phase can be calculated and the difference of entropy at the temperature of reversible phase transition is determined. According to our calculation, it's equal to 7.603 J/(mol·K) at 286.35 K and $\Delta_{tr}H = 2177$ J/mol.

4.4. SGTE modelling

α-tin

It is known that it is not possible to describe the heat capacity of crystalline Ge and Si using one Einstein temperature. This suggests that the diamond phase (in our case *α*-tin) should be described using two Einstein temperatures for consistency [95]. For this reason equation (2) was modified as follows:

$$C_p = \frac{3}{2}R\left(\alpha'\left(\frac{\theta'_E}{T}\right)^2 \frac{e^{(\theta'_E/T)}}{(e^{(\theta'_E/T)}-1)^2} + \alpha''\left(\frac{\theta''_E}{T}\right)^2 \frac{e^{(\theta''_E/T)}}{(e^{(\theta''_E/T)}-1)^2}\right) + aT + bT^2 + cT^3 + dT^4 \quad (15),$$

Where $\alpha' + \alpha'' = 1$

Due to the fact that there are no experimental data from 100 K up to the temperature of the transformation for the present assessment we used low temperature experimental data and heat capacity data obtained from *ab-initio* calculations. We had to take into account that C_p obtained from *ab-initio* calculations always have lower values than the experimental values. In order to take this into account we considered the values estimated by Lange [23] as the upper limit and also results from the approximations we obtained in the present work, when analyzing the values of S°_{298} . The stability of grey tin and conditions of the transformation remain an open question and the problem will be discussed in more detail in the Part II of this paper. At the moment we made a decision to model the E_0 parameter of the Gibbs energy in the way that grey tin is stable at low temperature and white tin is stable at higher temperature. We used differences in energies which were obtained from *ab-initio* calculations in order to estimate the E_0 parameter for the Gibbs energy function. The calculated heat capacity is presented on Figure 12. The calculated temperature and heat of transformation from *α*-tin to *β*-tin are 286.35 K (13.2 C) and 2101 J/mol respectively. The calculated value of S°_{298} is 43.68 J/(mol·K), which is in agreement with the estimated value obtained by *ab-initio* and by fitting $C_p(T)$ data with sum of two Einstein functions without strict requirement $\alpha' + \alpha'' = 1$ (according to Table 6, $a_1 + a_2 = 1.03 \pm 0.02$).

β -tin

In order to determine parameters of the model for β -tin in the high temperature interval (200-500 K), higher weight were given to the data from Kramer and Nölting [36] and Naumov [33]. Zero weight was given to the data from Brönsted [21], Klinghardt [37] and Bartenev [38]. In the intermediate interval high weight was given to our experimental data and the data from Naumov [33]. Smaller weight was given to the data from Lange [23] and Rodebush [22]. The evaluated value for S°_{298} was used as a fixed point. The first round of optimization of the parameters a , b and c and the Einstein temperature (in the equation 2) showed that we couldn't obtain reasonable fit down to 100 K. For this reason a similar approach using 2 Einstein temperatures was used. The model we obtained allowed us to have a reasonable description for C_p down to 20 K (Figure13a-c). A comparison of the calculated values and results of enthalpy drop measurements showed reasonable agreement with the existing data of Awbery and Griffiths [44], Umino [45] and Genot [46] (Figure 14a-c).

In order to avoid stabilization of the solid phase above melting point the parameters a' , b' , c' of the equation 6 were optimized. This required the selection of some constant heat capacity for very high temperatures, which was selected within the range of values of the heat capacity of liquid phase above the melting point. The parameter a' is equal as the difference between $3R$ and selected heat capacity. The parameters b' and c' were obtained knowing values for the heat capacity and its derivative at the melting point.

Figure 14 – Calculated $H^{\circ}(T)-H^{\circ}(298)$ (a), $H^{\circ}(T)-H^{\circ}(273)$ (b), $H^{\circ}(T)-H^{\circ}(471)$ (c) and in comparison with experimental values

The calculated value for $S^{\circ}_{298} = 51.12 \text{ J/(mol K)}$, which is equal to the evaluated value derived with a combination of four Einstein functions (Table 8).

Liquid phase

There is no reason to use two Einstein temperatures for the description of data for the liquid phase. For this reason we evaluated a single value of 107.02 K for the Einstein temperature using the data for the β -tin. Using this value the parameters for the liquid phase were optimized putting more weight on the temperature of fusion and enthalpy of fusion data. Of the C_p data, more weight was given to the data from Bartenev [55], Heffan [48] and Chen and Turnbull [50]. At the first step of the optimization the parameters B and C in the equation (9) were taken to be equal to the enthalpy and entropy of fusion as a starting point. The parameter A was taken as a free parameter for optimization. Then all three parameters A , B and C were optimized together. It appeared that for the description of the liquid phase no other parameters were needed to fit the existing experimental data. The calculated value for the enthalpy of fusion is 7187 J/mol which is identical to the value derived from the measurements carried by Grønvold [63]. The entropy of fusion is calculated to be equal to 14.224 J/(mol·K) and temperature of fusion is equal to 505.08 K in comparison to 505.078 K according to ITS-90. The comparison of calculated values with the experimental C_p and enthalpy drop measurements are presented in Figure 15 (a,b,c). Values of χ from the two-state model were calculated over the entire temperature range and presented on figure 16. The complete heat capacity curve is presented in figure 17.

c

Figure 15 – a) Calculated heat capacity in comparison with the experimental data from the literature [48,50,55]; b) calculated enthalpy increments for the liquid phase in comparison with literature data [43-45,51] and experiments undertaken in the present work; c) calculated enthalpy increments for the liquid phase in comparison with data from Genot [46]

Figure 16 – χ fraction of translational atoms and $1-\chi$ fraction of vibrational atoms

Figure 17– Calculated heat capacity curve for pure tin.

Table 10. Assessed parameters for pure tin

Phase	
α -tin	$\theta'_E = 218.4858 \text{ K}$ $\alpha' = 0.67374$ $\theta''_E = 61.9652 \text{ K}$ $\alpha'' = 0.32626$ $0 < T < 505.08 \text{ K}$ $G = -9849.7499 + \frac{3}{2}R \cdot (\alpha'\theta'_E + \alpha''\theta''_E) - 3RT(\alpha'\ln\frac{e^{\theta'_E/T}}{e^{\theta'_E/T} - 1})$ $+ \alpha''\ln\frac{e^{\theta''_E/T}}{e^{\theta''_E/T} - 1} - \frac{+1.1454E - 03}{2}T^2$ $T > 505.08^\circ\text{K}$ $G = -9849.7499 + 241.721315 + \frac{3}{2}R \cdot (\alpha'\theta''_E + \alpha''\theta''_E)$ $- 3RT(\alpha'\ln\frac{e^{\theta'_E/T}}{e^{\theta'_E/T} - 1} + \alpha''\ln\frac{e^{\theta''_E/T}}{e^{\theta''_E/T} - 1}) - 0.731164278T$ $+ \frac{-6.93646E + 14}{30}T^{-5} + \frac{1.40929E + 30}{132}T^{-11}$
β -tin	$\theta'_E = 159.07493 \text{ K}$ $\alpha' = 0.64684$ $\theta''_E = 61.12222 \text{ K}$ $\alpha'' = 0.35316$ $0 < T < 505.08 \text{ K}$ $G = -7873.56153 + \frac{3}{2}R \cdot (\alpha'\theta'_E + \alpha''\theta''_E) - 3RT(\alpha'\ln\frac{e^{\theta'_E/T}}{e^{\theta'_E/T} - 1})$ $+ \alpha''\ln\frac{e^{\theta''_E/T}}{e^{\theta''_E/T} - 1} - \frac{+3.9694 - 03}{2}T^2 - \frac{+1.5563E - 05}{6}T^3$ $T > 505.08 \text{ K}$ $G = -7873.56153 + 144.6411036 + \frac{3}{2}R \cdot (\alpha'\theta'_E + \alpha''\theta''_E)$ $- 3RT(\alpha'\ln\frac{e^{\theta'_E/T}}{e^{\theta'_E/T} - 1} + \alpha''\ln\frac{e^{\theta''_E/T}}{e^{\theta''_E/T} - 1}) + 16.88719177T$ $- 2.9962T\ln(T) + \frac{-3.48163E + 15}{30}T^{-5} + \frac{+6.91728E + 30}{132}T^{-11}$
Liquid	$\theta_E = 107.0238 \text{ K}$ $G = -3974.00518 + \frac{3}{2}R\theta_E + 3RT\ln\frac{(e^{\theta_E/T} - 1)}{e^{\theta_E/T}}$ $\Delta G_{dif} = G_m^{trans} - G_m^{vib} = 7317.41566 - 18.3219791T$

Summary

A description of the thermodynamic data for pure tin was obtained using an extended Einstein model for the crystalline phases and a two state model for the liquid phase. During the assessment was concluded that more then one Einstein temperatures were needed to describe both the solid phases. So two possible variants were proposed, (a) with two Einstein temperature (sum of amplitude is equal to 1) and additional polynomial part, (b) with a variable number of Einstein functions (two or four) and arbitrary sum of parameters a .

During critical evaluation of the thermodynamic data it was concluded that there is lack of experimental values for the heat capacity of the solid phases. For this reason experimental investigations of the heat capacity for the β -tin were carried out in the temperature interval between 100 and 170 K. Because the transformation from the white tin to grey tin is very difficult, particularly if the samples are pure, we used results from the *ab-initio* calculation in order to evaluate the model for the grey and white tin. The values of the entropy and enthalpy of transition at temperature of reversible phase transformation that we obtained are in good agreement with an estimation carried out based on the Voronin and Kutsenok method.

The question about the stability of the grey tin still remains open. This will be discussed in more detail in the Part II of the present work.

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Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical issues concerned with the web page. They will be later available to download from www.tmsrc.misis.ru

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Figure Captures

Figure 1 – Comparison of heat capacity calculated from assessed datasets: a) grey tin; b,c) white tin; d) Liquid tin. Please note that the curves are drawn from the values tabulated by the assessors and are therefore smooth.

Figure 2 – Experimental heat capacity data for α -tin: a) 0-300 K; b) 0-50 K

Figure 3 – Experimental heat capacity data for β -tin: a) 0-5 K; b) 0-50 K; c) 50-300 K; d) 200-500 K.

Figure 4 Enthalpy increments measurements for β -tin a) $H^{\circ}(T)-H^{\circ}(273)$; b) $H^{\circ}(T)-H^{\circ}(293)$

Figure 5 – Experimental heat capacity data for liquid tin

Figure 6 - Enthalpy increments measurements for liquid tin $H^{\circ}(T)-H^{\circ}(293)$ (Data from Feber et al. [51] are for $H^{\circ}(T)-H^{\circ}(298)$)

Figure 7 - Comparison of adiabatic calorimetry results with measurements from various scientific groups

Figure 8- Experimental results of the enthalpy drop measurements of the liquid tin in comparison with existing experimental literature values. Experimental uncertainties of $H(T)-H(298)$ values in our experiments are comparable with the size of symbols

Figure 9 - Experimental and ab-initio data of the heat capacity for α -tin for the temperature range: 0-300 K.

Figure 10 – Experimental and *ab-initio* data of the heat capacity for β -tin for the temperature range 0-300 K.

Figure 11 – Comparison of experimental and calculated data for α -tin

Figure 12 - Calculated heat capacity for the solid α -tin

Figure 13. Calculated heat capacity for the solid β -tin a) whole temperature interval; b) 0-100 K; c) 100-500 K.

Figure 14 – Calculated $H^{\circ}(T)-H^{\circ}(293)$ (a), $H^{\circ}(T)-H^{\circ}(273)$ (b), $H^{\circ}(T)-H^{\circ}(471)$ (c) and in comparison with experimental values

Figure 15 – a) Calculated heat capacity in comparison with the experimental data from the literature [48,50,55]; b) calculated enthalpy increments for the liquid phase in comparison with literature data [43-45,51] and experiments undertaken in the present work; c) calculated enthalpy increments for the liquid phase in comparison with data from Genot [46]

Figure 16 – χ fraction of translational atoms and $1-\chi$ fraction of vibrational atoms

Figure 17 – Calculated heat capacity curve for pure tin.