

A thermodynamic description of data for pure Pb from 0 K using the expanded Einstein model for the solid and the two state model for the liquid phase

A.V. Khvan^{a,*}, A.T. Dinsdale^{b,d}, I.A. Uspenskaya^c, M. Zhilin^{a,c}, T. Babkina^c, A.M. Phiri^a

^a Thermochemistry of Materials SRC, NUST MISIS, Leninskiy prosp, 4, 199049 Moscow, Russia

^b Hampton Thermodynamics, Hampton, Middlesex, UK

^c Laboratory of Chemical Thermodynamics, Lomonosov Moscow State University, 1-3 Leninskiye Gory, 119991 Moscow, Russia

^d BCAST, Brunel University London, Uxbridge UB8 3PH, UK

ARTICLE INFO

Keywords:

Lead
Two state model for liquid phase
Thermodynamic assessment
Extended Einstein model

ABSTRACT

Thermodynamic data for the crystalline and liquid phases of pure lead were critically assessed. A thermodynamic description was obtained using an extended Einstein model for the crystalline phase and a two state model for the liquid phase. The assessment was carried out through careful analysis of the experimental data published in the scientific literature. Additional measurements using enthalpy drop were also carried out in the present work to remove ambiguities in published experimental data.

1. Introduction

The theoretical basis for models to be used in future thermodynamic databases, was developed during the Ringberg workshop in 1995 and later published in its proceedings [1]. This is being further developed as a result of collaboration within SGTE (Scientific Group Thermodata Europe). The basic idea underpinning this work is the adoption of a universal approach which incorporates multiple physical contributions to the thermodynamic properties [2] and the use of a two state model to represent data for the liquid phase.

One question discussed at the Ringberg workshop was whether the Debye or the Einstein model should be used to represent the contribution to the heat capacity arising from harmonic lattice vibrations. It is well known that the Debye model gives a better description of the heat capacity at low temperatures, whereas the Einstein model always gives values which are too low. However, the expression for the heat capacity from the Debye function cannot be evaluated easily. Moreover, it is even more complicated to derive other thermodynamic functions such as the enthalpy, entropy and Gibbs energy. It should be noted that the Gibbs energy functions are stored within Calphad thermodynamic databases and that the minimization of Gibbs energy is the basis of all thermodynamic simulations. Furthermore, for practical purposes phase diagram calculations are useful for inorganic and metallic materials only above 100 K. The Einstein model should be more than adequate for this purpose.

Several other methods have been suggested over the past few years to form the basis for the creation of a new database for pure elements. One, in particular, was developed by the group at Bochum University based on the combination of the Debye model with a segmented function [3]. This method allowed precise descriptions of the thermodynamic properties of crystalline Cr, Fe and Ni to be made to very low temperatures 0–20 K. However, it is not clear if the model will work well for all elements over the whole temperature range, how the model can be integrated to yield expressions for other thermodynamic functions, and how this model can be used as a basis for descriptions of data for multicomponent systems. The complexity of the suggested model makes its implementation for wider practical use rather doubtful.

In the present work we have used the Einstein model with some additional parameters to take into account anharmonicity, electronic effects and the correction from constant volume to constant pressure properties. Our aim is to develop precise descriptions of the thermodynamic properties above 100 K consistent with the best experimental and ab initio data, but taking into account our need to use the resulting data as the basis for the modelling data for multicomponent systems. Precise description of the properties at very low temperatures will not be possible or even necessary. Attention will also be paid to maintain some physical meaning behind the data when extrapolating to 0 K as well as to very high temperatures.

Special attention has been paid in this work to the precise description of the following thermodynamic functions: S_{298}° , $H_{298}^{\circ}-H_{0}^{\circ}$,

* Corresponding author.

E-mail address: avkhvan@gmail.com (A.V. Khvan).

the heat capacity above 298.15 K, the melting temperature, and the entropy and enthalpy of fusion. In order to fulfil the need for a precise evaluation of S°_{298} we needed to use an additional technique, 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.

The extrapolation of the solid phase above the melting point is still an issue for discussion. It is important to constrain this as the extrapolation may indicate that the solid phase more stable than the liquid phase at very high temperatures. The simplest solution, which is similar to that used previously for the SGTE pure element database, is to merge the heat capacity function of the solid phase to that of the liquid phase at high temperatures. This is applied in the present work.

The two state liquid model is used in the present work to describe the thermodynamic properties of the liquid phase. The theoretical basis for this model was developed by Ågren [4] and later recommended during the first Ringberg workshop [5]. However, the application of this model requires a detailed analysis of the experimental data, and this is discussed in the present work.

These approaches were successfully applied by Chen and Sundman [6] for a description of the data for bcc, fcc, amorphous and liquid phases of pure Fe. More recently equivalent assessments have been carried out on data for Mn, Co and hcp Fe [7–9].

2. Literature analysis of the data for pure Pb

There have been several reviews of the experimental data for the thermodynamic properties of lead [10–15]. The data recommended by each of them differ slightly from the others for different temperature intervals (Fig. 1). The most recent review is from Arblaster [14]. The differences between the recommended data for the crystalline phase increases with increase in temperature. However this is within a 1.5 J/(mol K) corridor at high temperatures up to the melting point.

2.1. Heat capacity of crystalline Pb

A list of references relating to the experimental measurement of the heat capacity with methods applied, relative uncertainties and weights given in the present work is provided in Table 1.

2.1.1. Low temperature data

Meads et al. [16] carried out measurements of the heat capacity in the temperature interval 15.74–299.91 K using adiabatic calorimetry on lead samples with an iron impurity level not higher than 0.001% which had previously been melted with fused sodium hydroxide in order to remove any oxygen impurities. Their results are in good agreement with the experimental work of Keesom and Onnes [17].

Horowitz et al. [18] carried out measurements of the heat capacity on 99.99% purity lead specimens in both the normal and superconducting states over the temperature range (1–75 K) using adiabatic calorimetry. They claimed to use the more favourable Keesom and Kok [19] technique due to the absence of any drift in temperature either before or after the period of heating observed in the heating cycles. This enabled them to estimate the temperature differences with high accuracy without any need for a double extrapolation. The data of Horowitz et al. [18] for the normal (non-superconducting) state of Pb are in reasonable agreement with values obtained by Clement and Quinnell [20], Keesom and van den Ende [21] and Meads et al. [16].

Horowitz et al. [18] did not observe any anomaly in the heat capacity at very low temperatures associated with the transition to the superconducting state. This does not agree with the relatively high value of 2.20 K reported by Keesom and van den Ende [21] for the transition temperature.

In 1965 van der Hoeven and Keesom [22] reported their measurements on the specific heats of polycrystalline samples of lead of 99.9999% purity in the temperature interval between 0.4 and 4.5 K.

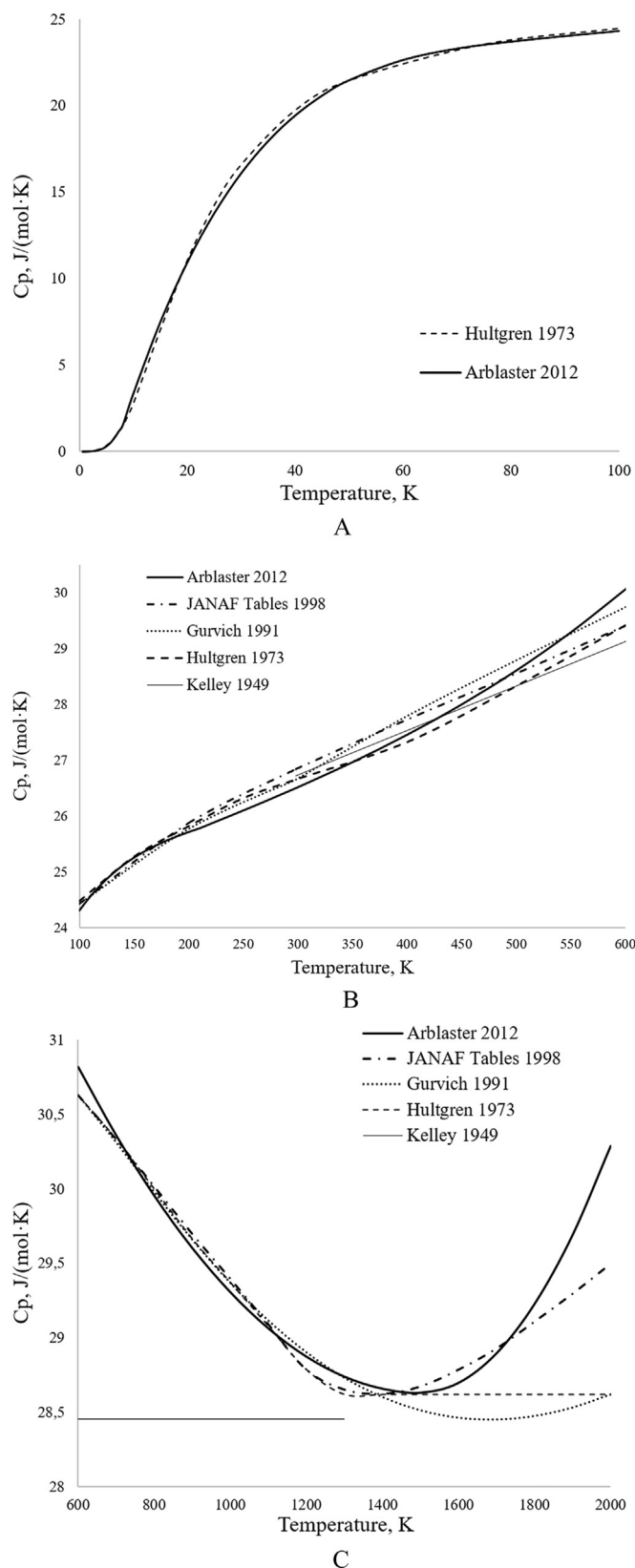


Fig. 1. Comparison of heat capacity calculated from assessed datasets: a) 0–100 K; b) 100–600 K; c) 600–2000 K. Please note that the curves are drawn from the values tabulated by the assessors and are therefore smooth.

The systematic error in the results was estimated to be less than 2% at the lowest temperature (due to difficulties in the calibration of the resistance thermometers) and 1% at 4 K. The values of the heat capacity

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