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A unified model for the cohesive enthalpy, critical temperature, surface tension and volume thermal expansion coefficient of liquid metals of bcc, fcc and hcp crystals

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Abstract

First the cohesive enthalpy of pure liquid metals is modeled, based on experimental critical temperatures of alkali metals. The cohesive enthalpies are scaled to the melting points of pure metals. The temperature coefficient of cohesive enthalpy is the heat capacity of the liquid metal. The surface tension and its temperature coefficient for pure liquid metals are modeled through the excess surface enthalpy, excess surface entropy and molar surface area supposing that the outer two surface layers of liquid metals are similar to the {1 1 1} plane of fcc crystals. The volumetric thermal expansion coefficient of liquid metals is scaled to the ratio of the heat capacity and cohesion enthalpy. From known values of melting point, heat capacity and molar volume the following calculated properties of liquid metals are tabulated: (i) cohesive enthalpy at melting point, (ii) cohesive energy of the solid metal at 0 K, (iii) critical temperature, (iv) surface tension at melting point, (v) volume thermal expansion coefficient, and (vi) temperature coefficient of surface tension. The present models are valid only for liquid metals of bcc, fcc or hcp crystals as only their structure and nature of bonding are similar enough to be treated together.

Keywords: Cohesive enthalpy; Cohesion energy; Metals; Critical point; Surface tension; Volumetric thermal expansion coefficient

1. Introduction

The cohesive enthalpy and surface tension of pure liquid metals were first modeled in a combined way by Skapski [1,2]. Since then, the same subject was considered in a number of papers [3–13] (see also monographs [14,15]). However, the main features of the model remained the same: the cohesive enthalpy and surface tension of pure liquid metals are modeled through the enthalpy of vaporization, while the obvious temperature dependency of the cohesive enthalpy is ignored. In the present paper the original model of Skapski is re-visited and improved. Some related properties of liquid metals are also modeled.

2. Cohesive enthalpy of liquid metals

Thermophysical properties of liquid metals are mostly influenced by the value of the cohesive enthalpy, bonding the atoms (ions) of the liquid metal. Classical thermodynamics works with relative enthalpy values, setting to zero the formation enthalpies of liquid Hg and all solid metals in their most stable crystal lattices under standard conditions. Thus, the absolute value of the cohesive enthalpies in liquid metals can be calculated only from first principles or by some model considerations. The cohesive enthalpy in liquids can be modeled by comparison of their behavior with that of a vapor, or a solid phase. In this paper, these two approaches will be applied and compared.

2.1. Estimation of cohesive enthalpy from the heat of evaporation

The simplest, and commonly used way to estimate standard cohesive enthalpy ($H^{\circ}_{c,i}$) in liquid i is to take it equal to the heat of vaporization ($\Delta_v H^{\circ}_i$) with an opposite sign:

$$H^{\circ}_{c,i} \cong -\Delta_v H^{\circ}_i \quad (1)$$

Eq. (1) is perfect only when the size, inner structure and inner bonds of the evaporating units (molecules or atoms) are not changed during evaporation. These conditions are mostly satisfied for non-ionic and non-metallic liquids, i.e. for organic

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liquids and water. However, the above conditions are not satisfied for metallic liquids, as during their evaporation a cation and one (or more) free electron(s) of the liquid metal are combined to form a neutral metallic atom. Moreover, for elements with high relative stability of their outer electron shells (such as s^2 for IIA metals) the vaporization enthalpy seriously underestimates the real cohesive enthalpy [6]. Nevertheless, the enthalpy of evaporation is taken as a direct measure of cohesive enthalpy of liquid metals [1,3–10,12,14,15]. Similarly, the cohesive energy in solid metals at 0 K is taken equal to the sublimation enthalpy of the metal in solid-state physics [16].

Finally, Eq. (1) can be considered only as first estimation for the cohesive enthalpy of liquid metals. The real cohesive enthalpy will be probably closer to that, calculated by Eq. (1) for large atoms (such as Cs) with weakly bonded outer electrons in the vapor phase, compared to small atoms (such as Li) with strongly bonded outer electrons.

2.2. The temperature dependence of cohesive enthalpy

The most negative consequence of the widespread use of Eq. (1) was that the temperature (T)-dependence of the cohesive enthalpy has been neglected in the literature, as the T-dependence of heat of evaporation appears to be not significant.

In reality, the heat capacity of any liquid i ($C^{\circ}_{\mathrm{p},i}$) should be taken as the T-coefficient of its cohesive enthalpy. Indeed, when a liquid is heated, thermal vibrations of its atoms work against the cohesive enthalpy. Thus, the cohesive enthalpy becomes weaker, i.e. more positive with temperature. Thus, the temperature dependence of the cohesive enthalpy of a liquid metal can be written as

$$H^{\circ}_{\mathrm{c},i} = H^{\circ}_{\mathrm{c},i,\mathrm{m}} + \int_{T_{\mathrm{m},i}}^{T} C^{\circ}_{\mathrm{p},i}\,\mathrm{d}T \tag{2}$$

with $H^{\circ}_{\mathrm{c},i,\mathrm{m}}$ the cohesive enthalpy of the liquid metal at its melting point.

2.3. Estimation of cohesion enthalpy from critical temperature

Above the critical point the gas cannot be converted into a liquid at any high pressure. This is mostly because at the critical point the cohesive enthalpy between the atoms of the liquid becomes approximately zero

$$H^{\circ}_{\mathrm{c},i,T_{\mathrm{cr},i}} \cong 0 \tag{3}$$

Combining Eqs. (2) and (3), the following equation is found

$$H^{\circ}_{\mathrm{c},i,\mathrm{m}} \cong -\int_{T_{\mathrm{m},i}}^{T_{\mathrm{cr},i}} C^{\circ}_{\mathrm{p},i}\,\mathrm{d}T \tag{4}$$

Reliable experimental data to apply Eq. (4) exist only for alkali metals and Hg.

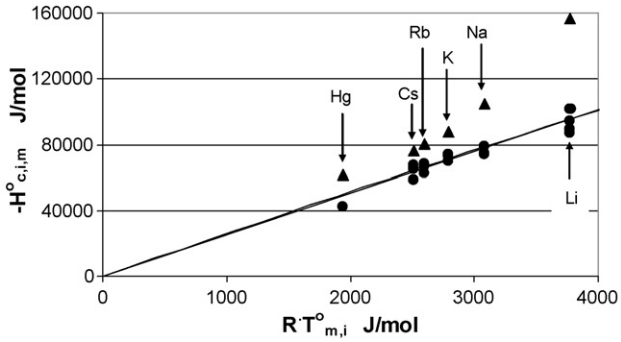

Fig. 1. Cohesive enthalpies of liquid alkali metals and Hg at their melting points as function of $RT^{\circ}_{\mathrm{m},i}$, calculated from the critical points [14,18–21] by Eq. (4) (circles) and from evaporation enthalpies [22] by Eq. (1) (triangles). The lines are drawn by Eq. (5). The solid line is drawn with $q_1 = 25.4$, $q_2 = 0$. The dashed line is drawn with $q_1 = 26.3$ and $q_2 = -2.62 \times 10^{-4}$ mol kJ (the two lines are hardly distinguishable).

2.4. The melting point, as a measure of cohesive enthalpy

The melting points of pure metals are usually accepted as being roughly related to cohesive enthalpy of liquid metals [11,13,14,17]. Indeed, if similar solid crystals are heated they will be stable against melting, if the cohesive enthalpy will keep the atoms together in the lattice against thermal vibrations. Thus, the melting point of similar metals will indeed characterize the cohesive enthalpy at the melting point. Due to restrictions of 'similar crystals' the validity of our model is limited to 'simple' liquid metals originated from bcc, fcc or hcp crystals. This is demonstrated in Fig. 1, showing the dependence of estimated cohesive enthalpies as function of $RT^{\circ}_{\mathrm{m},i}$ (with R being the gas constant) for alkali metals and mercury.

The following conclusions can be drawn from Fig. 1:

(i) the cohesive enthalpy values calculated from vaporization enthalpies deviate from those calculated using the critical points much more for Li compared to Cs, being in accordance with our theoretical expectations (see above),
(ii) As the crystal structure of Hg is very much different from that of alkali metals, the point for Hg falls out from the trend for alkali metals, as expected (i.e. Hg is not a 'simple' liquid metal).
(iii) The cohesive enthalpy of alkali metals can be described by the following semi-empirical equation:

$$H^{\circ}_{\mathrm{c},i,\mathrm{m}} \cong -q_1(RT^{\circ}_{\mathrm{m},i}) - q_2(RT^{\circ}_{\mathrm{m},i})^2 \tag{5}$$

with q_1 and q_2 being semi-empirical parameters. For the limited range of melting temperatures of alkali metals the first term of Eq. (5) is sufficient: $q_1 = 25.4 \pm 1.2$ (with $q_2 = 0$). The two-parameter version of Eq. (5) will be discussed later.

Summarizing Eqs. (2) and (5) the T-dependence of the cohesive enthalpy of 'simple' liquid metals can be approximately written as

$$H^{\circ}_{\mathrm{c},i,\mathrm{m}} \cong -q_1(RT^{\circ}_{\mathrm{m},i}) - q_2(RT^{\circ}_{\mathrm{m},i})^2 + C^{\mathrm{o}}_{\mathrm{p},i}(T - T^{\circ}_{\mathrm{m},i}) \tag{6}$$