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.
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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 ($H_{c,i}^{\circ}$) in liquid i is to take it equal to the heat of vaporization ($\Delta_v H_i^{\circ}$) with an opposite sign:

$$H_{c,i}^{\circ} \cong -\Delta_v H_i^{\circ} \tag{1}$$

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 ($C_{p,i}^{\circ}$) 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

$$H_{c,i}^{\circ} = H_{c,i,m}^{\circ} + \int_{T_{m,i}}^{T} C_{p,i}^{\circ}\, dT \tag{2}$$

with $H_{c,i,m}^{\circ}$ 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

$$H_{c,i,T_{cr,i}}^{\circ} \cong 0 \tag{3}$$

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

$$H_{c,i,m}^{\circ} \cong -\int_{T_{m,i}}^{T_{cr,i}} C_{p,i}^{\circ}\, dT \tag{4}$$

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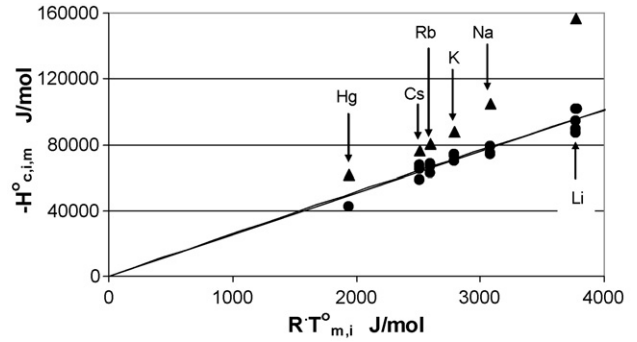

Fig. 1. Cohesive enthalpies of liquid alkali metals and Hg at their melting points as function of $RT_{m,i}^{\circ}$, calculated from the critical points [14,18–21] by Eq. (4) (circles) and from evaporation enthalpies [22] by Eq. (1) (triangles). The lines are drawn by Eq. (5). The solid line is drawn 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 $RT_{m,i}^{\circ}$ (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:

$$H_{c,i,m}^{\circ} \cong -q_1(RT_{m,i}^{\circ}) - q_2(RT_{m,i}^{\circ})^2 \tag{5}$$

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

$$H_{c,i,m}^{\circ} \cong -q_1(RT_{m,i}^{\circ}) - q_2(RT_{m,i}^{\circ})^2 + C_{p,i}^{o}(T - T_{m,i}^{\circ}) \tag{6}$$

By substituting Eq. (6) into Eq. (3), a new equation (see [14,23]) to estimate critical temperatures of 'simple' metals follows:

$$T_{\mathrm{cr},i}^{\circ} \cong (0.90 \pm 0.05) \frac{(q_1 R + C_{\mathrm{p},i}^{\circ}) T_{\mathrm{m},i}^{\circ} + q_2 (R T_{\mathrm{m},i}^{\circ})^2}{C_{\mathrm{p},i}^{\circ}} \qquad (6.a)$$

The coefficient (0.90 ± 0.05) takes into account the deviation from linearity in the proximity of the critical point.

3. Surface tension of liquid metals

The surface tension of liquids is defined as the ratio of the excess surface Gibbs energy (expressed through excess surface enthalpy $(\Delta H_{i/\mathrm{g}}^{\circ})$ and excess surface entropy $(\Delta S_{i/\mathrm{g}}^{\circ})$ divided by the molar surface area (ω_i°) [1]:

$$\sigma_i^{\circ} \equiv \frac{\Delta H_{i/\mathrm{g}}^{\circ} - T\,\Delta S_{i/\mathrm{g}}^{\circ}}{\omega_i^{\circ}} \qquad (7)$$

All three quantities of Eq. (7) will be modeled from the same assumption that the two outer surface layers of liquid metals are ordered (to minimize their surface tension) and are similar to the structure of the most closely packed crystal plane, namely the {1 1 1} plane of the fcc crystal [1].

3.1. The molar surface area of liquid metals

The molar surface area of a liquid metal i is usually modeled as [1]

$$\omega_i^{\circ} = f (V_i^{\circ})^{2/3} (N_{\mathrm{Av}})^{1/3} \qquad (8)$$

with N_{Av} is the Avogadro number $(6.022 \times 10^{23}\,\mathrm{mol}^{-1})$, V_i° the molar volume of metal i, and f is the geometrical constant [13]:

$$f = \left(\frac{3 f_{\mathrm{b}}}{4}\right)^{2/3} \frac{\pi^{1/3}}{f_i} \qquad (9)$$

with f_{b} and f_i is the volume and surface packing fractions.

The surface packing fraction of the {1 1 1} plane of the fcc crystal: $f_i = 0.906$ [1]. For fcc crystals $(f_{\mathrm{b}} = 0.740)$ $f = 1.09$ follows from Eq. (9). This value is used in the majority of models [1,3–10,12]. However, it is obviously overestimated, as the volume packing of liquid metals is surely below that of the solid fcc crystal.

The bulk packing fraction of a melted bcc crystal is obtained by lowering its crystal bulk packing fraction (0.68) by 9.6% due to volume expansion from 0 K till the melting point in liquid state (see Appendix A): $f_{\mathrm{b,bcc}} = 0.68/(1.096) = 0.62$. The same values for liquid metals, resulting from fcc and hcp crystals: $f_{\mathrm{b,fcc}} = 0.74/(1.12) = 0.66$ and $f_{\mathrm{b,hcp}} = 0.74/(1.086) = 0.68$ (see Appendix A). For an average 'simple' liquid metal: $f_{\mathrm{b}} = 0.65 \pm 0.02$. A similar value of 0.646 was obtained experimentally for random dense packing of macroscopic equal spheres [24]. The resulting value from $f_i = 0.906$ and $f_{\mathrm{b}} = 0.65 \pm 0.02$ and Eq. (9) is: $f \approx 1.00 \pm 0.02$.

3.2. The excess surface enthalpy of liquid metals

The excess surface enthalpy is the difference in the cohesive enthalpy values of bulk and surface atoms. If bulk and surface bonds are taken identical, the following equation can be obtained [1]

$$\Delta H_{i/\mathrm{g}}^{\circ} = \frac{H_{\mathrm{c},i}^{\circ}}{Z_{\mathrm{b}}} (Z_{\mathrm{i}} - Z_{\mathrm{b}}) = -\frac{\Delta Z_{\mathrm{i}}}{Z_{\mathrm{b}}} H_{\mathrm{c},i}^{\circ} = -\alpha H_{\mathrm{c},i}^{\circ} \qquad (10)$$

where Z_{b} and Z_{i} are the coordination numbers in the bulk and at the surface of liquid metals, while ΔZ_{i} and α are the number and ratio of broken bonds at the surface.

The average experimental bulk coordination number of 27 'simple' liquid metals: $Z_{\mathrm{b}} \cong 10.9 \pm 0.3$ [25]. The surface coordination number of the {1 1 1} plane of fcc crystal: $Z_{\mathrm{i}} = 9$. Then: $\Delta Z_{\mathrm{i}} = 1.9 \pm 0.3$ and $\alpha \cong 0.174 \pm 0.023$. Oriani [3] was the first to apply a similar value of $\alpha \cong 1/6 \cong 0.167$, while Skapski [1] used parameters for a quasi-fcc bulk liquid: $Z_{\mathrm{b}} \cong 12$, $\alpha \cong 0.25$.

3.3. The excess surface entropy of liquid metals

The excess surface entropy is the difference of the entropies of bulk and surface atoms. Skapski described it through the difference in oscillation frequencies of bulk and surface atoms [2] and obtained theoretically the vibrational excess surface entropy: $\Delta_{\mathrm{vib}} S_{i/\mathrm{g}}^{\circ} \cong 5.4 \pm 1.3\,\mathrm{J/(mol\,K)}$. A similar value was supposed by Eustathopoulos et al: $\Delta_{\mathrm{vib}} S_{i/\mathrm{g}}^{\circ} \cong 5.3\,\mathrm{J/(mol\,K)}$ [4,8], from a model made for Ni [26]. In this paper experimental values for surface Debye temperatures for 11 bcc and fcc metals [27] are used, resulting to: $\Delta_{\mathrm{vib}} S_{i/\mathrm{g}}^{\circ} \cong 5.8 \pm 1.3\,\mathrm{J/(mol\,K)}$. This value is in agreement with the previous estimations.

However, there is a second term of $\Delta S_{i/\mathrm{g}}^{\circ}$ neglected in previous literature, probably because this term is absent for solid metals. This term is connected with the transfer of an atom from the disordered bulk liquid to the ordered surface and it is called here the 'ordering' excess surface entropy $(\Delta_{\mathrm{ord}} S_{i/\mathrm{g}}^{\circ} < 0)$. It approximately equals the negative of the melting entropy of an average bcc metal. The bcc metal is chosen as it has the closest entropy to that of liquid metals [22]. The average numerical value: $\Delta_{\mathrm{ord}} S_{i/\mathrm{g}}^{\circ} \cong -7 \pm 1\,\mathrm{J/(mol\,K)}$ [22].

The total excess surface entropy of liquid metals is obtained as the sum of the two previous terms: $\Delta S_{i/\mathrm{g}}^{\circ} \cong \Delta_{\mathrm{vib}} S_{i/\mathrm{g}}^{\circ} + \Delta_{\mathrm{ord}} S_{i/\mathrm{g}}^{\circ} \cong -1.2 \pm 2.3\,\mathrm{J/(mol\,K)}$. In the first approximation this value will be used for all 'simple' liquid metals at any temperature.

3.4. Surface tension of 'simple' liquid metals at their melting points

Substituting Eqs. (8) and (10) into Eq. (7) with the estimated above parameter values the following equation is obtained for the surface tension of pure liquid metals at their melting points

$$\sigma_{i,\mathrm{m}}^{\circ} \cong \frac{-(0.174 \pm 0.023) H_{\mathrm{c},i,\mathrm{m}}^{\circ} + (1.2 \pm 2.3) T_{\mathrm{m},i}^{\circ}}{(1.00 \pm 0.02)(V_{i,\mathrm{m}}^{\circ})^{2/3} (N_{\mathrm{Av}})^{1/3}} \qquad (11)$$

Table 1
Comparison of calculated by Eqs. (1,11) and Eqs. (4,11) and experimental values for surface tension of alkali metals [28]

Me	$\sigma_{i,m}^{\circ}$ exp/(mJ/m²)	$-H_{c,i,r,m}^{\circ}$ (kJ/mol) Eq. (1)	$\sigma_{i,m}^{\circ}$ calc (mJ/m²) Eqs. (1) and (11)	Eq. (1) OK?	$-H_{c,i,m}^{\circ}$ (kJ/mol) Eq. (4)	$\sigma_{i,m}^{\circ}$ calc (mJ/m²) Eqs. (4) and (11)	Eq. (4) OK?
Li	398 ± 3	156.7 ± 1.0	581 ± 111	−	94.3 ± 7.1	354 ± 106	+
Na	198 ± 7	104.5 ± 0.7	259 ± 53	−	76.0 ± 2.6	190 ± 49	+
K	112 ± 11	96.3 ± 0.4	155 ± 33	+	72.0 ± 2.1	117 ± 29	+
Rb	94 ± 11	79.3 ± 0.4	112 ± 24	+	65.3 ± 2.9	93 ± 24	+
Cs	77 ± 9	72.1 ± 0.4	88 ± 19	+	63.0 ± 4.1	77 ± 23	+

In Table 1 the values calculated by Eq. (11) for the surface tension of alkali metals are compared with experimental results for the case when the cohesive enthalpy is calculated from Eq. (1) or Eq. (4). All reviewed experimental points [28] are taken into account for the possible range of surface tension. Melting point and enthalpy of vaporization data are from [22], molar volumes are from [14]. The evaluation of Eqs. (1) and (4) is marked by '+' and '−' signs in Table 1. If the intervals of calculated and experimental results overlap, the evaluation is '+', in the opposite case '−'. As follows from Table 1, Eq. (1) should be excluded for disagreement with Na and especially for Li. Thus, the method to calculate cohesive enthalpy from the evaporation enthalpy is excluded in this paper. As one can see from Table 1, acceptable values are obtained for all alkali metals if the cohesive enthalpy is calculated from the critical points and approximated through the melting temperature of metals, Eqs. (4) and (5).

Substituting Eq. (5) into Eq. (11) the following equation is obtained for the surface tension of pure liquid metals at their melting points:

$$\sigma_{i,m}^{\circ} \cong \frac{(0.174 \pm 0.023)[q_1(RT_{m,i}^{\circ}) + q_2(RT_{m,i}^{\circ})^2] + (1.2 \pm 2.3)T_{m,i}^{\circ}}{(1.00 \pm 0.02)(V_{i,m}^{\circ})^{2/3}(N_{Av})^{1/3}} \quad (12)$$

Particularly, if $q_1 = 25.4 \pm 1.2$ and $q_2 = 0$ (obtained from Fig. 1) are substituted into Eq. (12), the following simple equation is obtained

$$\sigma_i^{\circ} \cong (38 \pm 10) \frac{T_{m,i}^{\circ}}{(V_{i,m}^{\circ})^{2/3}(N_{Av})^{1/3}} \quad (12.a)$$

A similar semi-empirical equation was predicted first by Schytil [29]. Eq. (12.a) is tested against experimental data in Fig. 2. Only liquid metals classified as 'class A' metals [9] are shown, with ±5% of accuracy of all measured values [28]. Molar volume and melting point data are taken from [14,22].

As follows from Fig. 2, 'simple' liquid metals are quite well described by Eq. (12.a), while other liquid metals are not (see inserted figure). Upon a closer examination one can see that experimental data even for 'simple' liquid metals deviate from the calculated values to the negative direction as the melting point increases. One might explain this feature by the increasing difficulty to measure correct surface tension values for liquid refractory metals. However, if that was the only explanation for all the deviations in Fig. 2, the data points at high temperature would be expected to scatter increasingly around the thin line. As the scatter of data points around the thin line does not seem to depend on melting point, one should conclude that the deviation is mostly due to the oversimplified way in which the cohesive

enthalpy is expressed as a function of temperature using the single parameter q_1.

The two semi-empirical parameters of Eq. (5) were therefore optimized using the experimental surface tension data for 'simple' liquid metals shown in Fig. 2. During this optimization it was assumed that about 25% of high-temperature deviations in Fig. 2 are caused by experimental difficulties, while 75% of the deviations are caused by the oversimplified linearization of Eq. (5). The optimized parameters are as follows: $q_1 = 26.3$ and $q_2 = -2.62 \times 10^{-4}$ mol kJ with a slight change in parameter α from $\alpha \cong 0.174 \pm 0.023$ to $\alpha \cong 0.182 \pm 0.023$ (corresponding to the average coordination number of $Z_b = 11$ in bulk liquid metals). In this way both the cohesive enthalpies of alkali metals (see dotted line in Fig. 1) and surface tension of refractory metals are reasonably reproduced. Substituting the above new parameters into Eq. (12), the following final semi-empirical equation is obtained

$$\sigma_{i,m}^{\circ} \cong \frac{(41 \pm 10)T_{m,i}^{\circ} - (3.3 \pm 0.7) \times 10^{-3}(T_{m,i}^{\circ})^2}{(V_{i,m}^{\circ})^{2/3}(N_{Av})^{1/3}} \quad (12.b)$$

3.5. Temperature coefficient of surface tension of 'simple' liquid metals

Let us re-write Eq. (12) by taking into account the temperature dependence of the cohesive enthalpy and the molar volume of the liquid metals

$$\sigma_i^{\circ} \cong \frac{\alpha[q_1 RT_{m,i}^{\circ} + q_2(RT_{m,i}^{\circ})^2 - C_{p,i}^{\circ}(T - T_{m,i}^{\circ})] - \Delta S_{i/g}^{\circ}T}{f(V_{i,m}^{\circ})^{2/3}[1 + \beta_i^{\circ}(T - T_{m,i}^{\circ})]^{2/3}(N_{Av})^{1/3}} \quad (13)$$
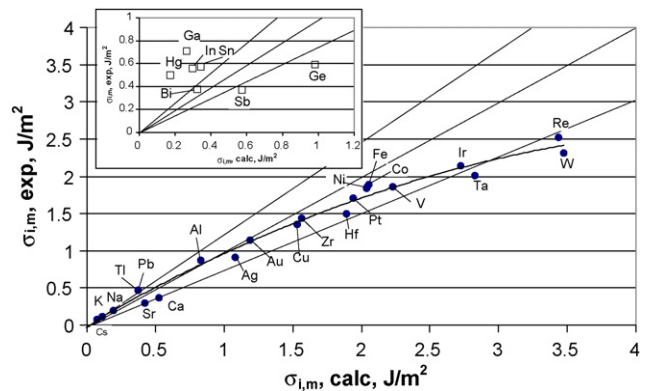

Fig. 2. Comparison of calculated by Eq. (12.a) and experimental surface tension values of liquid metals at their melting points for 'class A' metals [9]. Full circles: 'simple' liquid metals. Empty squares in the inserted figure: not 'simple' liquid metals.

Fig. 3. Comparison of calculated from Eq. (14) and experimental [9] values of the temperature coefficient of surface tension of some pure liquid metals. Full circles: 'simple' liquid metals. Empty squares in the insert: other liquid metals.

with β_i° the volume thermal expansion coefficient of pure liquid metal i. Although from Eq. (13) it is obvious that the surface tension of liquid metals is not a linear function of temperature, close to the melting point it can be taken as linear: $\sigma_i^\circ = \sigma_{i,m}^\circ + \sigma_i^{\circ,T}(T - T_{m,i}^\circ)$. Taking the derivative of Eq. (13) with respect to T and substituting the above parameter values, the temperature coefficient of surface tension is expressed as

$$\sigma_i^{\circ,T} \cong -\frac{(0.182 \pm 0.026)C_{p,i,m}^\circ - (1.2 \pm 2.3)}{(V_{i,m}^\circ)^{2/3}(N_{Av})^{1/3}} - \frac{2}{3}\beta_i^\circ \sigma_{i,m}^\circ \quad (14)$$

Eq. (14) is tested in Fig. 3 against the same 'class A' metals as in Fig. 2 [9]. Heat capacity values are from [30], volume thermal expansion coefficients are from [14], surface tension values at melting point are calculated by Eq. (12.b). From Fig. 3 one can see that the calculated and experimental values are in good agreement for 'simple' liquid metals of bcc, fcc and hcp crystals, while for other liquid metals the agreement is not acceptable. It should be noted that the good agreement for 'simple' liquid metals is mainly due to the heat capacity term and is much less due to the excess surface entropy term, contrary to what was claimed in previous publications [2–6,8–10].

4. Volumetric thermal expansion coefficients of liquid metals

According to Eq. (14), the value of β_i° is needed to calculate $\sigma_i^{o,T}$. Although there are hundreds of papers with original data on β_i° of liquid metals (see compilations [14,31]), the databank of β_i° is far from being complete, or free of contradictions.

β_i° for liquid metals has been correlated to the inverse of melting points [32], boiling points [33] and cohesive enthalpies (estimated from the velocity of sound) [14]. The idea behind these models is that the liquid metal is able to expand more if its atoms are bonded by weaker cohesive enthalpy. This idea will be improved further in what follows.

The relative molar volume and relative cohesive enthalpy of 'simple' liquid metals can be described by unique curves, as functions of T. The relative quantities are defined as the ratio of their value at any T to that at the melting point. These relative quantities can be normalized by subtracting unity from the relative values. The relative, normalized molar volume and cohesive enthalpy of pure liquid metal i will be denoted as $V_{i,r,n}^\circ$ and $H_{c,i,r,n}^\circ$, respectively, and can be written from the definition of β_i° and from Eqs. (5) and (6):

$$V_{i,r,n}^\circ \equiv \frac{V_i^\circ}{V_{i,m}^\circ} - 1 = \beta_i^\circ(T - T_{m,i}) \quad (15)$$

$$H_{c,i,r,n}^\circ \equiv \frac{H_{c,i}^\circ}{H_{c,i,m}^\circ} - 1 = \frac{C_{p,i,m}^\circ}{H_{c,i,m}^\circ}(T - T_{m,i}) \quad (16)$$

One can expect a unique functional relationship between $V_{i,r,n}^\circ$ and $H_{c,i,r,n}^\circ$ for all 'simple' liquid metals. In the vicinity of the melting point this functional relationship is supposed to be linear, and so the following equation follows:

$$V_{i,r,n}^\circ \cong -k_\beta H_{c,i,r,n}^\circ \quad (17)$$

where k_β is a dimensionless semi-empirical parameter. Substituting Eqs. (15) and (16) into Eq. (17), β_i° of 'simple' liquid metals is expressed as

$$\beta_{i,m}^\circ \cong -k_\beta \frac{C_{p,i,m}^\circ}{H_{c,i,m}^\circ} \quad (18)$$

The new Eq. (20) is similar to the model of [14], but it takes also into account the heat capacity of liquid metals. Heat capacity was recently used to scale volume expansion coefficient of solid metals by Garai [34]. Eq. (18) is checked against experimental data in Fig. 4. One can see a good linear correlation, with $R^2 = 0.91$ and $k_\beta = 0.62 \pm 0.23$.

5. Discussion and calculation for refractory metals

As one can see from Figs. 1–4, the same set of cohesive enthalpies coupled with appropriate theoretical equations and some semi-empirical coefficients is able to reproduce different thermophysical properties of 'simple' liquid metals of bcc, fcc and hcp crystals. Encouraged by this, the following properties of some 'simple' liquid metals have been calculated and tabulated

Fig. 4. Checking Eq. (18) against experimental data. Points on graph correspond to all 'simple' liquid metals given in the compilation of Ref. [14]. β_i° values of [14] are replaced for Al, Cu, Fe [35], Co [36], Ni [37], Pd [38] and Pt [39]. Additional β_i° values are given for Mo [40], W [41], Ru [42] and Rh [43]. Heat capacity is from [30], cohesive enthalpy is calculated by Eq. (5) with $q_1 = 26.3$ and $q_2 = -2.62 \times 10^{-4}$ mol kJ.

Table 2
Calculated properties for some 'simple' liquid transitional metals

Group	i	$T_{\mathrm{m},i}^\circ$ (K) [30] $\pm0.1\%$	$C_{\mathrm{p},i}^\circ$ (J/mol K) [30] $\pm2\%$	$V_{i,\mathrm{m}}^\circ$ (cm³/mol) Appendix $\pm2\%$	$-H_{\mathrm{c},i,\mathrm{m}}^\circ$ (kJ/mol) Eq. (5) $\pm15\%$	$-H_{\mathrm{c},i,0}^\circ$ (kJ/mol)* $\pm18\%$	$T_{\mathrm{cr},i}^\circ$ (K) Eq. (6.a) $\pm20\%$	$\sigma_{i,\mathrm{m}}^\circ$ (mN/m) Eq. (12.b) $\pm20\%$	$\beta_{i,\mathrm{m}}^\circ$ ($\times10^4$/K) Eq. (18) $\pm25\%$	$-\sigma_i^{\circ,T}$ (mN/mK) Eq. (14) $\pm30\%$
IIIB	Sc	1814	44.2	16.1	337	411	8,500	1180	0.81	0.191
	Y	1795	43.1	21.0	334	404	8,600	980	0.80	0.156
IVB	Ti	1939	46.3	11.6	356	431	8,700	1550	0.81	0.25
	Zr	2125	42.1	15.1	383	470	10,100	1400	0.68	0.19
	Hf	2500	44.0	14.5	433	545	11,100	1630	0.63	0.20
VB	V	2190	47.4	9.3	392	480	9,400	1980	0.75	0.30
	Nb	2750	41.8	11.8	464	577	12,500	2010	0.56	0.22
	Ta	3258	41.8	11.8	520	657	14,100	2250	0.50	0.22
VIB	Cr	2130	50.0	8.27	384	480	8,800	2100	0.81	0.34
	Mo	2896	42.6	10.2	481	613	12,800	2290	0.55	0.25
	W	3680	54.0	10.4	559	733	12,600	2640	0.60	0.32
VIIB	Re	3453	50.0	9.6	539	712	12,800	2680	0.58	0.31
VIIIB	Fe	1809	46.0	7.94	336	413	8,200	1890	0.85	0.32
	Ru	2523	51.9	8.8	436	559	9,800	2290	0.74	0.34
	Os	3300	50.0	9.1	524	679	12,400	2700	0.59	0.32
	Co	1768	40.5	7.6	330	405	8,900	1900	0.76	0.29
	Rh	2233	50.6	9.2	398	498	9,100	2030	0.79	0.32
	Ir	2716	59.4	9.5	460	589	9,400	2300	0.80	0.38
	Ni	1728	43.1	7.43	324	393	8,300	1900	0.83	0.31
	Pd	1825	41.2	10.2	339	407	9,000	1610	0.75	0.24
	Pt	2045	36.5	10.3	371	453	11,000	1750	0.61	0.21

(*) value of $H_{\mathrm{c},i,0}^\circ$ was calculated from the estimated value of $H_{\mathrm{c},i,\mathrm{m}}^\circ$, by subtracting the enthalpy change of the pure metals between the liquid (melting point) and solid (0 K) states [30]

in Table 2, based on the known values of their melting points [30], heat capacities [30] and molar volumes (see Appendix A):

(i) cohesive enthalpy at melting point $H_{c,i,m}^{\circ}$ by Eq. (5), $q_1 = 26.3$, $q_2 = -2.62 \times 10^{-4}$ mol kJ,

(ii) cohesive energy of solid metals at 0 K ($H_{c,i,0}^{\circ}$) by subtracting from $H_{c,i,m}^{\circ}$ the enthalpy change from solid metal at 0 K to liquid metal at melting point [30],

(iii) critical temperature $T_{cr,i}^{\circ}$ by Eq. (6.a),

(iv) surface tension at melting point $\sigma_{i,m}^{\circ}$ by Eq. (12.b),

(v) volume thermal expansion coefficient $\beta_{i,m}^{\circ}$ by Eq. (18), $k_\beta = 0.62$,

(vi) temperature coefficient of surface tension $\sigma_i^{\circ,T}$ by Eq. (14) using the calculated values of $\beta_{i,m}^{\circ}$ and $\sigma_{i,m}^{\circ}$.

The weakest agreement between calculated and experimental data appears for IIA metals (see Figs. 2 and 4). Thus, the relatively stable s^2 configuration of outer electron shells seems to disturb the cohesive enthalpy models for IIA metals calculated not only from enthalpy of vaporization but also from melting point values. That is why calculated values for IIA metals are not given in Table 2. Thermophysical properties of the transitional metals of IIIB–VIIIB groups are calculated in Table 2, as vacancies in databanks exist for these metals.

6. Conclusions

(i) The temperature coefficient of the cohesive enthalpy of liquid metals equals their heat capacity. The cohesive enthalpies of liquid alkali metals and Hg at their melting points are estimated through their critical temperature. The cohesive enthalpy of 'simple' liquid metals at their melting points is scaled to the melting point of the metals through two, semi-empirical parameters.

(ii) A theoretical model is developed for the surface tension of pure liquid metals. Using the best available experimental values, the above two semi-empirical parameters were deduced. The same theoretical model is developed further to derive the equation for the temperature coefficient of surface tension of liquid metals. The model describes experimental values with a reasonable accuracy.

(iii) The volume thermal expansion coefficient of pure liquid metals is shown to be proportional to the ratio of heat capacity and cohesive enthalpy of the liquid metal.

(iv) An approximate equation is derived for the critical temperature of metals using their melting points and heat capacities. The cohesive enthalpies of pure liquid metals are re-calculated to the cohesive energy at 0 K for solid metals.

(v) The above mentioned equations and parameters apply only to 'simple' liquid metals resulting from bcc, fcc or hcp crystals as the bulk and surface structure and type of bonding for these liquid metals are similar enough to be treated together.

Appendix A. Molar volume of liquid metals at their melting points

Original experimental data on the density of liquid metals are published in several hundreds of papers (see compilations [14,31]). However, there are missing or contradictory data for some refractory metals.

The most reliable data for solid metals are for their cell size at room temperature. Solid metals expand by about 6% [14] between 0 K and their melting points. Supposing that any given crystal lattice expands to the same ratio from 0 K to melting point in liquid state, the following equations is obtained:

$$V_{i,m}^{\circ} = k_{V,hkl} \frac{N_{Av} a_i^3}{n_{hkl}(1 + 0.06 \times (298/T_{m,i}^{\circ}))} \tag{A1}$$

where $k_{V,hkl}$ is the average expansion ratio for the hkl crystal from $T = 0$ K and melting point in liquid state, a_i is the cell dimension of metal i at 298 K [44], n_{hkl} is the number of atoms in a unit cell of the hkl crystal (2 for bcc, 4 for fcc and hcp crystals). For hcp crystals a_i^3 of Eq. (A1) should be replaced by $\sqrt{3}a_i^2 c_i$.

The semi-empirical coefficients $k_{V,hkl}$ have been found from known experimental values [14,31] for 9 bcc metals, 12 fcc metals and 15 hcp metals, resulting to: $k_{V,bcc} = 1.096$ ($R^2 = 0.9999$), $k_{V,fcc} = 1.12$ ($R^2 = 0.999$) and $k_{V,hcp} = 1.086$ ($R^2 = 0.996$). From these parameters the molar volumes for Nb, Ta, Mo, and W (bcc), Rh and Ir (fcc), Ru, Os, Zr, Hf, and Re (hcp) were estimated and included in Table 2, being in reasonable agreement with the known experimental values [38,40,42,43,45].

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