Applied Surface Science 257 (2011) 6372–6379

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Surface energies of metals in both liquid and solid states

Fathi Aqra*, Ahmed Ayyad

Department of Chemistry, Faculty of Science and Technology, Hebron University, P.O. Box 40, Hebron, West Bank, Palestine

ARTICLE INFO

Article history:
Received 21 January 2011
Received in revised form 25 January 2011
Accepted 26 January 2011
Available online 12 March 2011

Keywords:
Surface energies
Liquid metals
Modeling

ABSTRACT

Although during the last years one has seen a number of systematic studies of the surface energies of metals, the aim and the scientific meaning of this research is to establish a simple and a straightforward theoretical model to calculate accurately the mechanical and the thermodynamic properties of metal surfaces due to their important application in materials processes and in the understanding of a wide range of surface phenomena. Through extensive theoretical calculations of the surface tension of most of the liquid metals, we found that the fraction of broken bonds in liquid metals (f) is constant which is equal to 0.287. Using our estimated f value, the surface tension (γ_m), surface energy (γ_{SV}), surface excess entropy ($-\mathrm{d}\gamma/\mathrm{d}T$), surface excess enthalpy (H_s), coefficient of thermal expansion (α_m and α_b), sound velocity (c_m) and its temperature coefficient ($-\mathrm{d}c/\mathrm{d}T$) have been calculated for more than sixty metals. The results of the calculated quantities agree well with available experimental data.

1. Introduction

Mechanical and thermodynamic properties of surfaces such as surface tension, surface energy, surface entropy, surface enthalpy, etc. are very important. The surface tension and its temperature coefficient have been measured for most of the metallic elements. Surface tension is one of the fundamental and important quantities in the field of materials processing (such as welding and sintering), and surface tension temperature coefficient governs the Marangoni convection on the surface of melt. There are several characteristics of the liquid surface. It is known that liquid surface usually takes an equilibrium configuration with the minimum energy due to the high mobility of liquid molecules [1]. Because the liquid fails with respect to elastic deformation resistance, surface tension equals surface stress when surface adsorption is not taken into account, which is defined as the reversible work per unit area involved in forming a new surface of a substance plastically [1]. Although methods of surface tension measurement are precise, there is still uncertainty in its values and particularly regarding its temperature coefficient due to the effect of impurities. Therefore, efforts have been directed toward the experimental determinations of surface tension and its temperature coefficient of metals [2–4]. In contrast to the determination of the surface tension value, its temperature coefficient value is suffering a scatter and it is not well-known experimentally even for elemental metallic liquids [5]. Since the surface entropy is directly related to the value of the temperature coefficient of the surface tension in single component systems, it has been proposed that a real difference exists in the sign of the surface entropy (and therefore, in the degree of the surface ordering) in most of the liquid metal surfaces [6].

Computer simulations with Monte Carlo or molecular dynamics methods may be one of the reliable methods [7,8], but unfortunately suffer from high fluctuation and statistical uncertainty, and introduces additional complexity into the performance. Thus, the demand of developing reliable prediction methods has never declined. Semi-empirical predictions based on the correlation between the surface and bulk thermodynamic properties are always possible [9–13], such as linking surface tension to the heat of evaporation [9]. Also, surface tension of pure substances may be evaluated from values of critical temperature, using empirical equations [14]. In general, for liquids the surface tension decreases with increasing temperature (i.e. negative temperature coefficient $\mathrm{d}\gamma/\mathrm{d}T$) going to zero at the critical point: the variation often follows a linear function law over a limited temperature range [15]:

$$\gamma(T) = \gamma(T_m) + \frac{\mathrm{d}\gamma}{\mathrm{d}T}(T - T_m)(\mathrm{mJ\ m^{-2}}) \tag{1}$$

Therefore, when surface tension and its temperature coefficient, at melting point, values are known, surface tension as a function of temperature can be calculated. However, Eq. (1) has not been strictly examined. Thus, both surface tension and its temperature coefficient need to be further considered. In this paper, surface tension ($\mathrm{mJ\,m^{-2}}$), surface energy ($\mathrm{mJ\,m^{-2}}$), surface excess entropy ($\mathrm{mJ\,m^{-2}\,K^{-1}}$), surface excess enthalpy ($\mathrm{mJ\,m^{-2}}$), coefficient of thermal expansion ($\mathrm{K^{-1}}$), sound velocity ($\mathrm{m\,s^{-1}}$) and its temperature coefficient ($\mathrm{m\,s^{-1}\,K^{-1}}$) for most of the metallic elements are calculated. The predictions correspond to the available experimental or theoretical results.

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* Corresponding author.
E-mail address: fathiaqra2009@hotmail.com (F. Aqra).

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doi:10.1016/j.apsusc.2011.01.123

2. Theory and calculations

2.1. Surface tension

The present theory is based on classical statistical thermodynamics formulation of Eyring and co-workers [16–18]. The Eyring's approach in calculating the surface tension of a liquid metal was made by Schoutens [19], who calculated the surface tension of pure liquid Al. We, previously, derived an equation [20] for calculating the surface tension of pure liquid gallium [20], bismuth [21] and mercury [22], in wide temperature ranges. Here, this unified equation is applied for majority of liquid metals. The true form of this equation that is used to calculate the surface tension of any liquid metal at the melting point or at any temperature, is expressed as:

$$\gamma = \varphi^{-1}\left(\frac{V_s}{V}\right)^2 kT\left[\frac{E_s}{RT}(1-3f)+\frac{3}{2}\ln\frac{3}{4}(1+f)\right] \tag{2}$$

where γ is surface tension ($\mathrm{mJ\,m^{-2}}$), k is the Boltzmann constant ($1.38.10^{-23}\,\mathrm{J\,K^{-1}}$)), T is the absolute temperature (K), R is the universal gas constant ($8.31\,\mathrm{J\,k^{-1}mol^{-1}}$), V and V_s are molar volumes at any temperature and at the melting point ($\mathrm{cm^3\,mol^{-1}}$), respectively, φ is the area occupied by one atom ($\mathrm{cm^2\,atom^{-1}}$), E_s is the sublimation energy (its value is available in literature [23]) and f is a dimensionless constant which is equal to 0.287 for all metallic elements, except for less refractory metals such as Ga (0.292), Zn (0.24), Cd (0.24) and Hg (0.21) and semiconductors such as Si (0.297), Ge (0.297). The value of surface tension obtained from Eq. (2) should be multiplied by 10^7 to get γ in $\mathrm{mJ\,m^{-2}}$.

To identify the key assumptions underlying the model, it is important to clearly identify the physical origin of the term $(V_s/V)^2$ in the expression for the surface tension because it is an important issue, as the predicted temperature dependence of the surface tension arises entirely from the temperature dependence of the liquid density, through this term. The Eyring's significant structure theory is based on the accepted assumption that a liquid consists of two structures, one is solid-like and the other is gas-like. This is because the liquid is an intermediate state between a solid and a gas. X-ray studies of liquids indicate considerable short-range order with nearest-neighbor distances only slightly different from those of solids. So for liquids one can speak of a quasi-lattice structure with the typical 12% expansion of a liquid due to the introduction of vacancies or holes into the structure. The number of holes per mole of molecules is $(V-V_s)/V_s$. The chance that a vacancy confers gas-like properties on a neighboring molecule is assumed proportional to the fraction of neighboring positions populated by molecules. This fraction is V_s/V, if molecules and vacancies are randomly distributed. The mole fraction of gas-like molecules is $(V-V_s)/V$, and the remaining mole fraction (V_s/V) of molecules are solid-like. In the mathematical formulation of the model, the partition function is raised to the power of the neighboring probability of the molecule, which is proportional to V_s/V. In addition, the number of surface atoms is just the number of surface sites available multiplied by V_s/V. Therefore, we arrive at the term $(V_s/V)^2$ by combining Eqs. (17) and (18) described in the previous report [20].

The possible position available to a molecule is energetically favored over the other by the way the neighbors are organized about it. This difference in energy between the best position and the average for the neighboring available positions is proportional to the energy of sublimation. The sublimation energy of a surface molecule ($E_s{}'$) is proportional to the sublimation energy of a bulk molecule (E_s) multiplied by the term $3/4(1+f)$, which is given as follows [20]:

$$E_s{}' = \frac{3}{4}E_s(1+f) \tag{3}$$

Since f is assumed to be 0.287 for all metals, it follows that:

$$E_s{}' = 0.965E_s \tag{4}$$

So, the ratio of the E_s(surface)/E_s(bulk) is proportional to the f term. Eyring has theoretically indicated that the sublimation energy at the surface is equal to 0.75 of the sublimation energy of the bulk. Experimentally, many researchers have shown that the sublimation energy at the surface is in the range 0.99–0.75 of the bulk. Our value lies within this range. Moreover, the sublimation energy appears in the model as consequence of the partition function of the solid-like structure in the liquid. Therefore, f value is related to the difference of coordination number of the surface atoms compared to atoms in the bulk of the liquid (i.e. it is related to the ratio of the surface to bulk coordination numbers). By using the f value equal to 0.287, the temperature dependence of the surface tension of any liquid metal can be calculated provided that the temperature dependence of the density of the metal is available. Hence, the predictive value of the model is its power to study and calculate the temperature dependence of the surface tension of any liquid metal.

2.2. Fraction of broken bonds and coordination number

For liquids, a coordination number is defined as the average number of nearest neighbors about a given atom. The coordination number of a solid is defined as the number of atoms bonded to a central atom. The concept of coordination number for a liquid state can be related to solid state theory since solids and liquids have comparable densities and intermolecular separation. There is no unique value for the number of nearest neighbors in an irregular liquid, but a range within which the coordination number of any liquid can be found. It has been reported that the coordination number values to be nearly constant and independent of the element [24]. A number of experimental and theoretical data concerned with the coordination numbers of liquid metals near the melting point have been reported due to the importance of understanding the local structure of liquid metals [24–46]. This data indicate that the average coordination number for most liquid metals falls in the range 6–12, but most of the available data fall within the range 8–11. Therefore, due to this scattering in the value of coordination number of liquid metals, it is important to have a method that should be most subjective in arriving at a numerical value of the coordination number and the fraction of broken bonds.

In metals, the fraction of broken bonds (f), the ratio of coordination number of the surface to the bulk in liquid state (ξ) and in solid state (ξ_1) and the ratio of fraction of broken bonds in solid state to liquid state $(1-3f)$ are given by:

$$f = 1-\frac{CN_s}{CN_b},\ \text{and}\, f = \frac{N}{CN_b} \tag{5}$$

$$\xi = 1-f,\ \text{and}\,\xi\,\text{and}\,\xi_1 = \frac{CN_s}{CN_b} \tag{6}$$

$$(1-3f) = \frac{(1-\xi_1)}{(1-\xi)} \tag{7}$$

where CN_s and CN_b denote coordination numbers of the surface atom and that of the corresponding bulk one, respectively, N is the number of broken bonds. Some reported values [46–49] of these terms and our calculated values are given in Table 1. By extensive study of the surface tension of the majority of liquid metals, we found that the fraction of broken bonds (f) is 0.287, which is valid for most of the liquid metals, regardless the coordination number at the surface and in bulk. This value is explained in the following section.