STATISTICAL MECHANICAL CALCULATION OF THE EXCESS FREE ENTHALPY OF METAL SURFACES*

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Received June 27, 1989

Abstract

The excess free enthalpy of metal surfaces is calculated using Ising's model for both one- and two-dimensional surfaces. The result is in good agreement with experimentally obtained data.

Introduction

Many important properties of solid and liquid materials are related to their surface free enthalpy. Since Stefan's original study [1], which gave the molar surface energy as exactly half of the heat of vaporization, several attempts have been made to determine this quantity [2, 3].

We have derived the grand canonical partition function using a two-dimensional model that is suitable to describe a one-dimensional surface. An expression for the excess free enthalpy is obtained from the partition function. The calculation can be extended to a two-dimensional surface as well. Only the equilibrium structure is considered in this work.

The model

The model is shown on Figure 1. The square cells represent metal atoms which lie above each other. The uppermost layer is the surface layer, it has vacancies, i.e., missing atoms. The second layer is the semi-bulk layer, it has no vacancies, but some of its atoms are exposed to the gas phase. The other layers constitute the bulk, with none of their atoms being in contact with the gas phase. The surface configuration, determined solely by the surface layer,

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[*] Respectfully dedicated to Prof. János Giber, on his 60th birthday and to whom correspondence should be addressed.

is given as a one-dimensional array of numbers, (n_i). The value of n_i is zero if an atom is missing in the i-th position, and it is 1 if there is an atom. (The configuration of the surface on Figure 1 is 111010011.) Practically any surface configuration is possible on physical grounds. Surface atoms may enter the gas phase creating additional vacancies, and gas phase atoms may condense on the surface filling up vacancies. In addition, rapid surface jumps in the first layer are a frequent occurrence.

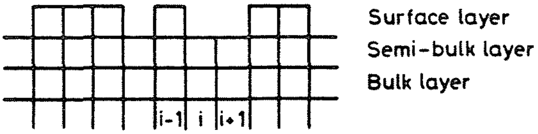

Fig. 1. Two-dimensional crystal structure with one-dimensional surface (cubic crystal)

It has been proved that the main contribution to the surface free enthalpy comes from the first two layers due to the large value of the molar heat of atomization of metals [4]. The latter quantity is almost equal to the internal energy of atomization since $\Delta E \gg \Delta\,(pV)$:

$$\Delta H \approx \Delta E \tag{1}$$

The excess energy of the i-th atom is given by

$$E_i(m) = \Delta E(8-m)/8 \tag{2}$$

where m is the coordination number defined as the number of neighbours of an atom. Obviously m is 8 for every atom in the bulk, 0 for gas phase atoms, 3, 4, or 5 for surface atoms, and 5, 6, 7, or 8 for an atom in the semi-bulk layer. The excess energy of the system is the sum of the individual excess energies:

$$E = \sum_{i=1}^{N} E_i \tag{3}$$

We assume that it is sufficient to take into account only the influence of the nearest neighbours, i.e., E_i will be the function only of n_{i-1}, n_i, and n_{i+1}. There are two possibilities depending on whether an atom is present or missing, i.e., whether $n_i = 1$ or 0:

$$E_i(n_{i-1}, 1, n_{i+1}) = (\Delta E/8)\,[(5-n_{i-1}-n_{i+1})+(2-n_{i-1}-n_{i+1})] \tag{4}$$

$$E_i(n_{i-1}, 0, n_{i+1}) = (\Delta E/8)\,(3-n_{i-1}-n_{i+1}) \tag{5}$$

due to (2). Eq.'s (4) and (5) can be combined, leading to the following general expressions:

$$E_i = E_i(n_{i-1}, n_i, n_{i+1}) = (\Delta E/8)\,[3+4n_i-(n_i+1)\,(n_{i-1}+n_{i+1})] \tag{6}$$

The canonical partition function for a surface containing N particles is [5]

$$Z_{\mathrm{N}}(T) = \sum \exp E(m_1, n_2, \ldots, n_{\mathrm{N}})] \tag{7a}$$

where

$$\sum \equiv \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots \sum_{n_N=0}^{1} \tag{7b}$$

and the summation includes all possible configurations. Substituting (6) into (7) and introducing $A \equiv \Delta E/8RT$, we obtain the following expression:

$$Z_N(T) = \exp(-3NA) \sum \exp\left\{ -A \sum_{i=1}^{N} [4n_{\mathrm{i}} - (n_{\mathrm{i}}+1)(n_{\mathrm{i}-1} + n_{\mathrm{i}+1})] \right\} \tag{8}$$

where the $\sum$ is defined in Eq. (7b) again. It can be simplified for very large N's, using

$$\sum_{i=1}^{N} (n_{\mathrm{i}} + n_{\mathrm{i}-1}) = \sum_{i=1}^{N} 2n_{\mathrm{i}} \quad \text{and} \quad \sum_{i=1}^{n} n_{\mathrm{i}} n_{\mathrm{i}-1} = \sum_{i=1}^{N} n_{\mathrm{i}} n_{\mathrm{i}+1} \tag{9}$$

leading to

$$Z_N(T) = \exp(-3NA) \sum \exp\left[-2A \sum_{i=1}^{N} (n_{\mathrm{i}} - n_{\mathrm{i}} n_{\mathrm{i}+1})\right] \tag{10}$$

If we introduce $s_{\mathrm{i}} = 2n_{\mathrm{i}} - 1$, (10) becomes a well known expression for the one-dimensional Ising model [6]:

$$Z_N(T) = \exp(-7NA) \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \cdots \sum_{s_N=\pm 1} \exp\left(a \sum_{i=1}^{N} s_{\mathrm{i}} s_{\mathrm{i}+1}/2 \right) \tag{11}$$

The explicit solution of an equality of this kind is received by making use of the equality [6]:

$$\sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \exp\left\{ \beta \sum_{i=1}^{N} [\varepsilon s_{\mathrm{i}} s_{\mathrm{i}+1} + F s_{\mathrm{i}} s_{\mathrm{i}+1}/2] \right\} =$$

$$= \langle \exp(\beta\varepsilon) \{\cosh(\beta F) + [\cosh^2(\beta F) - 2\exp(-2\beta\varepsilon)(\sinh(2\beta\varepsilon)]^{1/2}\} \rangle \tag{12}$$

In our case β, ε, and F correspond to A/2, 1, and 0, respectively, so the partition function acquires the following form:

$$Z_N(T) = \exp(-7NA/2)[\exp(A/2) + \exp(-A/2)]^N \tag{13}$$

Using [5]

$$G(T) = -RT \lim_{N\to\infty} [\ln Z_N(T)/N] \tag{14}$$

the free enthalpy excess of the surface is obtained from (13):

$$G^{\mathrm{S}}(T) = -RT] - 7A/2 + \ln[\exp(A/2) + \exp(-A/2)\} \tag{15}$$

Due to the high internal energy of atomization, i.e., 100—250 kJ/mol, the value of A is much greater than 1, so the $\exp(-A/2)$ term can be neglected from (15):

$$G^S(T) = 3\Delta E/8 \tag{16}$$

Discussion

Considering that our model is one-dimensional, and the most probable configuration is the flat surface (in average), we obtain also from (2) $\Delta E(8-5)/8 = 3\Delta E/8$. Even though the above treatment was applied to a two-dimensional Ising model with a one-dimensional surface, the calculation can be extended for a three-dimensional crystal having a two-dimensional surface. The analogous equations to (2) and (6) are (see ref. [9])

$$F_{i,j}(m) = \Delta E(26-m)/26 \tag{17}$$

and

$$E_{i,j} = [9 - \sum n_{i+a,j+b} + n_{i,j}(18 - \sum n_{i+a,j+b})]\Delta E/26 \tag{18a}$$

where

$$\sum \equiv \sum_{a=-1}^{1} \sum_{b=-1}^{1} \tag{18b}$$

i.e.: in Figure 2 the configuration of the column at (i, j) is $n_{i,j+1} = n_{i+1,j+1} = 1$, and every other n coordinate is zero. With these values (18) gives $E_{i,j} = 7\Delta E/26$. There is only one surface atom in that column at (i, j) (in the semi-bulk layer) having 19 neighbours, its energy is also $7\Delta E/26$ by (17) taking the $m = 19$ value. Similar but much longer derivation which has led to (16) gives that the flat surface is again the most probable configuration, a surface atom is missing 9 neighbours, while a bulk atom has all 26 of them. The multiplication factor (26—17)/26, and the expression for the excess free enthalpy becomes

$$G^S(T) = 9\Delta E/26 \tag{19}$$

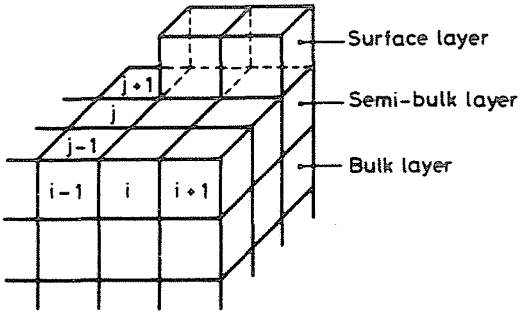

Fig. 2. Three-dimensional crystal structure with two-dimensional surface (cubic crystal)

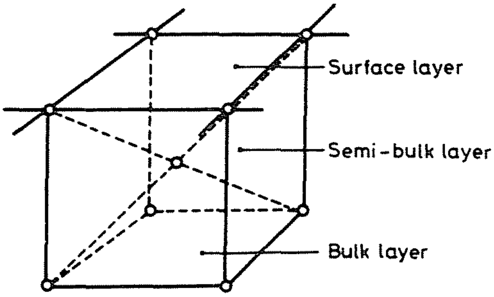

Fig. 3. Three-dimensional crystal structure with two dimensional surface (*bcc* crystal)

The value of the surface tension is calculated from (19) by dividing with the molar surface area. Experimentally obtained data [7] exhibit good correlation with the result, especially for hexagonal crystals too: The multiplication factor [10] is about 0.328 for Zn, and 0.369 for Cd. A certain degree of orientation dependence is also detectable [7, 8]. The equation (19) can be written as

$$G^S(T)=\alpha\Delta E \tag{20}$$

where α is $9/26=0.346$ for cubic crystals. For *bcc* crystal (Figure 3) the α constant can be calculated as follows: The flat surface is the most probable again. Let the atom in the center of the cube is *b* type atom and the others are the *a* type atoms. In the bulk, atoms of a type have 6 *a* type and 8 *b* type neighbours and atoms of *b* type have 8 *a* type and 6 *b* type neighbours. The number of atoms surrounding an atom is $8+6=14$ in the bulk. At the surface, atoms of a type have 5 *a* type and 4 *b* type neighbours, and atoms of *b* type have 8 *a* type and 5 *b* type neighbours. For *a* and *b* type atoms (similarly to equation (2) and (17), using the form of equation (20)) $\alpha(a)=[(6-5)+(8-4)]/14=$

Table 1

Experimental values of α in varions metals

Metal	Crystal type (ref. [12])	α (experimental, ref.[10])
Ag	fcc	0.213
Au	fcc	0204
Cu	fcc	0.206
Fe	bcc	0.234
K	bcc	0.18
Ni	fcc	0.189
U	bcc	0.237
W	bcc	0.179

$=0.3571$ and $\alpha(b)=[(8-8)+(6-5)]/14=0.0714$ and because the number of a type atoms and b type atoms are the same at the surface, the average value for α is $\alpha=(0.3571+0.0714)/2=0.214$. Similar calculation can be done for *fcc* crystals. The theoretical value for α correspond the experimental values at 298.2 K, see Table 1 for some elements (the experimental values for α are from ref. [10]). The values for ΔE can be found in ref. [11] and for G^S in J/m^2 unit in ref. [7].

It is also interesting that using the derivation which has lead to equation (16) and (19) an expression can be found [9] for the temperature dependence of α:

$$\partial\alpha/\partial T=-R\cdot\ln k/\Delta E \tag{21}$$

where k is the number of surface layers plus one, the semi-bulk layer.

It is 2 in Figure 1, 2 and 3, Equation (21) describes the experimental values very well [9]. α changes (decreasing) with the temperature very slowly, it is about $-10^{-5}\ K^{-1}$ for about 50 metals. The reason of decreasing of α is that at higher temperature the surface is rougher.

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