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Abstract

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APPROXIMATE CALCULATION OF THE SURFACE TENSION OF METALS

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The principal shortcoming of the existing calculations of the surface tension of metals ([1–7]), in our view, is the circumstance that the number of free electrons Z per metal atom, which enters into the theoretically obtained formulas, is taken by the authors to a certain extent arbitrarily. Some of them take as Z the maximum valence of the atom, others the mean value of the chemical valence, still others one free electron per metal atom, etc. However, such an important characteristic of a metal as the number Z should be determined above all on the basis of experiment, as was quite correctly pointed out in ([8]).

In addition, the majority of the indicated calculations of σ do not give the temperature dependence of the surface tension of metals, since the calculations of σ refer to absolute zero temperature. The question of the temperature dependence of σ for metals was considered in ([9–11]).

It seems to us desirable to construct such a theory of the surface tension of metals in whose final formulas for σ there would enter other physical constants of the metal that are readily accessible to experimental determination.

At various times a number of authors have proposed empirical and semiempirical formulas for calculating σ of metals through the work function of an electron from the metal ([12,13]), the heat of evaporation ([14]), etc. The values of σ calculated by these formulas agree better with experimental data than those found from theoretical formulas.

In the present work we wish to give an approximate calculation of σ of metals through their heat of evaporation.

We proceed from the following variant of the polar model of a metal. Let us consider a metal in the solid state at temperature T. We shall assume that the mean values of the coordinates of the positive ions of the metal coincide with the sites of the crystal lattice, while the mean values of the coordinates of the free electrons are distributed symmetrically within the crystal lattice in such a way that an "electron lattice" is formed of exactly the same structure as the lattice of positive ions, but shifted relative to the latter. In this case the volume elementary cells and basal planes of the metallic lattice must be neutral.

Consequently, in the polar model under consideration we shall have a coordinational ion-electron lattice of the metal which, for example, in the case of a metallic face-centered cubic lattice is represented in the form of a cubic lattice of the NaCl type with the shortest distance between the cation and the "anion" $a/2$, where a is the period of the metallic lattice.

In (^{11}) we gave the following formula for the coefficient of surface tension of metals:

$$\sigma = -n_s \frac{\Delta f}{f_{kv}} [3kT \ln 2 - 2(E_0' - E_0)], \tag{1}$$

where, for the polar model of a metal adopted by us, f_{kv} is the coordination number of a cation relative to an "anion" ; Δf is the number of nearest "anions" missing from a cation on the metal surface; E_0 and E_0' are the free energies at $T = 0$ that a particle inside the metal would have if its mean vibrational frequencies were, respectively, ν and $\nu/\sqrt{2}$, and if the coordination numbers were f_{kv} and $f_{kv}/2$. We calculate the values E_0 and E_0' in the following way. Since E_0 is the energy required to decompose the metal into free ions and free electrons at $T = 0$, then, by first imparting this energy to the metal, then the energy $\sum_{i=1}^{z} eV_i$, where $V_1, V_2, \ldots$ denote, respectively, the first, second, etc. ionization potentials of the atom, and, finally, by imparting the heat of sublimation at absolute zero L_0, we obtain the initial state of the metal. Hence it follows that

$$|E_0| = \sum_{i=1}^{z} eV_i + L_0, \tag{2}$$

$$|E_0'| = \sum_{i=1}^{z} eV_i + L_0'. \tag{3}$$

Substituting (2) and (3) into (1) and assuming, as in ($1'$), the free energy to be a linear function of f_{kv}, we find

$$\sigma = -n_s \frac{\Delta f}{f_{kv}} [3kT \ln 2 - L_0]. \tag{4}$$

Formula (4) makes it possible to find the value of σ for different faces of an ideal single crystal at temperature T.

Ya. I. Frenkel$^{(15)}$ showed that, owing to thermal fluctuations, the surface of a crystal in equilibrium possesses roughness. Therefore we shall assume that on the crystal surface only the short-range order is preserved, corresponding to the orientations of all the principal faces of the elementary electron-ion cell. In this case the surface tension of the crystal will be

$$\sigma = -\bar{n}_s \frac{\overline{\Delta f}}{f_{kv}} \, [3kT \ln 2 - L_0], \tag{5}$$

where $\bar{n}_s$ is the mean number of particles per unit surface; $\overline{\Delta f}/f_{kv}$ is the mean value of the relative number of missing neighbors (“anions”) of a positive metal ion on the surface. We find the values $\bar{n}_s$ and $\overline{\Delta f}/f_{kv}$ as follows. Let us consider some positive metal ion and compare the probability w'' of its being located per unit area on the metal surface with the probability w' of its being located per unit area of some plane parallel to the surface and passing inside the metal; we obtain

$$w''/w' = e^{-W_i/kT}, \tag{6}$$

where W_i is the work required for the transition of an ion from the bulk to the surface, proportional to the number of missing neighbors Δf_i on the surface. On the other hand, the ratio of the probabilities w''/w' must be equal to the ratio of the number of ions $n_i^{(s)}$ per unit area on the metal surface to the number of ions $n_0^{(s)}$ per unit area inside the metal. Therefore from (6) it follows that

$$n_i^{(s)} = n_0^{(s)} e^{-W_i/kT}. \tag{7}$$

Since on the metal surface there are $n_i^{(s)}$ particles per 1 cm^2 with excess energy W_i and, consequently, belonging to the i-th face of a cubic crystal, then

$$\sum_i \frac{n_i^{(s)}}{f_i^{(s)}} S_i = 1, \tag{8}$$

where S_i is the area of the i-th face; $f_i^{(s)}$ is the number of ions belonging to an elementary cell of the plane net for the same face. From (7) we find

$$\bar{n}_s = n_0^{(s)} \sum_i x_i, \tag{9}$$

where $x_i = \exp\left[-\frac{\alpha \Delta f_i}{kT}\right]$ (Δf_i is the number of missing neighbors for the i-th face).

The mean value of the relative number of missing neighbors on the surface of a metal will be

$$\frac{\overline{\Delta f}}{f_{kv}} = \frac{\sum_i \frac{\Delta f_i}{f_{kv}} x_i}{\sum_i x_i}. \tag{10}$$

It is known that in a crystal of the cubic system there are 6 faces (100), 12 faces (110), and 8 faces (111), for which the number of missing neighbors is respectively 1, 2, and 3 when these faces lie on the surface of the metal. For each of these faces $f_i^{(s)} = 2$. Consequently, expression (8), if (7) is taken into account, and also the fact that $S_{(100)} = a^2$, $S_{(110)} = a^2\sqrt{2}$, and $S_{(111)} = a^2\dfrac{\sqrt{3}}{2}$, may be written as follows:

$$\frac{n_0^{(s)}}{n_{(100)}^{(s)}}\left(6x_{(100)} + 12\sqrt{2}\,x_{(100)}^2 + 8\frac{\sqrt{3}}{2}\,x_{(100)}^3\right) = 1, \tag{11}$$

where $x_{(100)} = \exp\left[-\dfrac{\alpha\Delta f_{(100)}}{kT}\right]$ ($\Delta f_{(100)}$ is the number of missing neighbors for the face (100)); $n_{(100)}^{(s)}$ is the number of particles per 1 cm^2 of the face (100). Let us carry out the calculation for a surface parallel to the face (100) inside the crystal. Taking $n_0^{(s)} = n_{(100)}^{(s)}$, from (11) we find the value of $x_{(100)}$ satisfying the condition $0 \leq x_{(100)} \leq 1$: $x_{(100)} = 0.122$. From (9) and (10) we obtain $\overline{n}_s = 0.924\,n_{(100)}^{(s)}$ and $\overline{\Delta f}/f_{kv} = 0.201$. Differentiating equation (5) with respect to temperature and neglecting the temperature dependence of $\overline{\Delta f}/f_{kv}$, we find the value of the temperature coefficient γ of the surface tension of metals:

$$\gamma \equiv \frac{d\sigma}{dT} = -\left(3k\frac{\overline{\Delta f}}{f_{kv}}\,\overline{n}_s \ln 2 + 2\alpha\sigma\right), \tag{12}$$

Table 1

Metal	$n_{100}^{(s)} \cdot 10^{-14}$	$L_0 \cdot 10^{12}$erg/atom	Temp., °K	σ, erg $\cdot$ cm^{-2}calc.	σ, erg $\cdot$ cm^{-2}exp.	γ, erg $\cdot$ cm^{-2} $\cdot$ deg^{-1}calc.	γ, erg $\cdot$ cm^{-2} $\cdot$ deg^{-1}exp.
Ag	11.1	4.70 (20)	1268	898	751– 940923 (16)	–0.123	–0.13 (16)
Au	110.0	5.76	1473	1100	581– 14201120 (16)	–0.092	–0.10 (16)
Cu	14.6	5.27	1473	1380	1103– 14001154 (16)	–0.204	–
Pb	7.62	3.50	600	470	424– 536461 (16)	–0.078	–(0.06 –0.25) (16)

Metal	$n_{100}^{(s)} \cdot 10^{-14}$	$L_0 \cdot 10^{12}$erg/atom	Temp., °K	σ, erg $\cdot$ cm^{-2}calc.	σ, erg $\cdot$ cm^{-2}exp.	γ, erg $\cdot$ cm^{-2} $\cdot$ deg^{-1}calc.	γ, erg $\cdot$ cm^{-2} $\cdot$ deg^{-1}exp.
Al	11.5	4.15	973	832	520– 914860 (18)	−0.103	−(0.135 −0.35) (16)
Pt	12.0	8.75	2273	1815	1819 (16)	−0.097	−0.1
γ-Fe	14.0	7.43	1843	1970	950– 12101720 (21)	−0.12	–
Ca	6.61	2.71	1123	298	320	−0.048	–
β-Co	16.0	8.3	1763	2320	–	−0.142	–
β-Ni	16.2	6.97	1725	1957	1735 (19)	−0.132	–
β-Tl	8.50	3.03	573	454	436– 485 (16)	−0.086	–

where α is the thermal coefficient of linear expansion of the metal. The results of calculating the surface tension by formula (5) and the temperature dependence by formula (12) for metals of the face-centered cubic system are given in Table 1. The same table gives the experimental values of σ and γ for molten metals, the scatter of experimental data according to measurements by different authors, the most reliable values of σ according to the analysis of experimental data in (16), and the results of recent measurements. In all cases where this was possible, we took σ_{exp} from measurements in vacuum. As experimental values of the heat of sublimation, data recalculated by Rabinovich and Tilo (17) to absolute zero temperature are given, as well as data for Ag from (20).

It is seen from Table 1 that the calculated values of σ and γ, despite the crudeness of the adopted model of the metal and the approximate nature of the entire calculation, agree well with the most reliable experimental values, especially for Pb, for which the experimental value of σ is known with sufficient accuracy. In most of the remaining cases the deviation of σ_{calc} from σ_{exp} is no more than 5%, and only for Cu, γ-Fe, and β-Ni is it approximately 10–20%.

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