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LETTER TO THE EDITOR

Temperature dependence of the surface energy of mercury from 0 to 250 °C

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Abstract

The surface energy (SE) for mercury was calculated on the basis of the free electron model in which the electron density parameter, r_s, for bulk electrons was calculated from the density of mercury while the electron density parameter for surface electrons, r_{ss}, was assumed to be higher by a factor that is linearly dependent on temperature. Ideal agreement of calculated SE values with experimental data was attained for the temperatures 0–250 °C assuming that $r_{ss} = r_s \times 1.0021^{T/100\,^\circ\mathrm{C}}$.

Recently we have published a simple formula for the surface energy (SE) of a metal, which was derived on the basis of the free electron model [1]. In this model the SE is expressed solely in terms of the electron density parameter (the Wigner–Seitz radius, r_s). At temperatures close to 273 K, the SEs of a number of metals obey the following relationship with the r_s-parameter (see figure 2 in [1]):

$$\mathrm{SE} = 44.06 r_s^{-5} + 94.49 r_s^{-3.5} - 121.7 r_s^{-4}. \tag{1}$$

To give a clearer understanding of the meaning of the three terms in the above formula, it may be rewritten in the following form:

$$\mathrm{SE} = [44.06 r_s^{-3} + 94.49 r_s^{-1.5} - 182.6(r_s^{-2} - \tfrac{1}{3} r_s^{-2})]/r_s^2. \tag{2}$$

The first term in the brackets is proportional to the energy of the surface dipole layer, the second term is the contribution of the electron vibrational energy, whereas the third term results from the difference in electron kinetic energy between the bulk and the surface. All the above contributions are per unit surface. A careful inspection of the derivation of formula (2), given in a previous paper [1], leads us to the conclusion that r_s should be replaced in the first and second terms by a value of the electron density parameter more appropriate for the surface layer. The third term was previously calculated assuming identical density parameters for

Table 1. The comparison of calculated SEs for mercury with experimental data for temperatures 0–250 °C.

T (°C)	ρ (g cm^{-3})[a]	SE_{exp} (mJ m^{-2})	SE_{calc} (mJ m^{-2})
0	13.5951	485.5	485.4
50	13.4723	477.3	475.3
100	13.351	467.8	465.4
150	13.232	456.8	455.9
200	13.113	444.3	446.1
250	12.994	430.5	436.7

[a] After [5].

surface and bulk electrons, which may not be appropriate over a broad temperature range. Therefore the formula (2) should be rewritten in the following form:

$$\mathrm{SE} = [44.06r_{ss}^{-3} + 94.49r_{ss}^{-1.5} - 182.6(r_s^{-2} - \tfrac{1}{3}r_{ss}^{-2})]r_s^{-2}, \tag{3}$$

where r_{ss} is the electron density parameter at the surface and r_s retains its previous meaning. A linear relationship between r_{ss} and r_s may be assumed for a rather broad temperature range. The basis of this assumption comes from consideration of the top-layer relaxation of a metal crystal as a function of temperature, which for $0 < T < 600$ K may be represented by a parabola [2].

In order to test the above idea, liquid mercury was selected, because its thermal expansion and surface tension are very well determined experimentally. The density of mercury as a function of temperature is given in table 1. The appropriate experimental values of SE were tabulated using the following empirical formula [3]:

$$\mathrm{SE} = 485.5 - 0.149T - 2.84 \times 10^{-4}T^2, \tag{4}$$

where SE is expressed in mJ m^{-2} (=erg cm^{-2} = dyn cm^{-1}) and T in °C.

The electron density parameters for bulk electrons were calculated using the following formula [4]:

$$r_s = 1.3882\left(\frac{A}{z\rho}\right)^{1/3}, \tag{5}$$

where A is the atomic mass of mercury ($A = 200.59$ g), z stands for the effective number of free electrons per atom ($z = 2.5$ [4]), ρ is density of mercury in g cm^{-3}, given in table 1.

The electron density parameter for surface electrons was calculated from the following formula:

$$r_{ss} = r_s(1+\varepsilon)^{T/100\,^\circ\mathrm{C}} = r_s\left[1 + \varepsilon\frac{T}{100} + \mathrm{O}(\varepsilon^2)\right], \tag{6}$$

where T is in °C. The calculation of the SE for temperatures from 0 to 250 °C was performed with ε ranging from 0.001 to 0.003. The best agreements of calculated SE values with experimental data were found for $\varepsilon = 0.0021$; see table 1. The value $\varepsilon/100$ is about a third of the linear expansion coefficient at normal temperature.

In conclusion, one may state that the free electron model is very useful not only in the calculation of SEs of metals but also in the calculation of their temperature dependence. For this calculation the electron density parameters for the surface and bulk electrons have to be used. The same effective numbers of free electrons per atom are used as in the case of the work-function calculation [4].

Another important conclusion is that for the 16 univalent and divalent metals for which the SE was calculated in a previous paper [1], r_s and r_{ss} are nearly the same at normal temperatures.

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