DENSITY DEPENDENCE OF THE SURFACE TENSION OF LIQUID METALS

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Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, Vol. 7, No. 4, pp. 139–141, 1966

The surface tension can be caluclated from the equation [1]

$$\sigma=\int_{-1/2\delta}^{1/2\delta}(p_n-p_t)\,dz$$

if the normal p_n and tangential p_t components of the pressure in an interphase layer of thickness δ are known.

Remote from the critical point the entire change in density is virtually confined to a layer of thickness equal to the interatomic distance d, i.e., $\delta = d$. In this case $p_n = 2p_t$ and

$$\sigma = {}^1/_2\, p_n d\,. \qquad (1)$$

Equation (1) is valid for the case of spherically symmetrical forces [1].

We calculate the pressure in the liquid as follows. As the temperature increases from T = 0° K around each molecule of liquid, there develops a free volume element v. Let the number of volume elements dn in the interval from v to v + dv be described by the ordinary distribution function

$$dn=A\left(\exp\frac{-W}{kT}\right)dv\,.$$

Here W is the energy of free volume formation, k Boltzmann's constant, and T the absolute temperature. We assume that the work of formation of a volume element v is equal to $W = p_n v$. From the normalization condition $\int dn = N$, where N is the total number of atoms per mole (Avogadro's number), we obtain $A = Np_n/kT$. Then, using the expression for the total free volume (equal to the total increase in the volume of the body from 0 to T° K), for the pressure we obtain

$$V-V_0=\int_0^N v\,dn=\int_0^\infty\frac{Np_n}{kT}\exp\frac{-p_n v}{kT}\,v\,dv=\frac{NkT}{p_n}\,,$$

$$\text{or}\qquad p_n=\frac{NkT}{V-V_0}\,.$$

Here V is the molar volume at the given temperature, and V_0 the molar volume at 0° K in the liquid. As the temperature increases, a change is observed in the density and the ratio p_n/p_t in the interphase layer. At the critical point p_n becomes equal to p_t, and the surface tension vanishes. Equation (1) should take the form $\sigma = p_n d\Psi(\rho)/2$. Here $\Psi(\rho)$ is a certain function of the density of the liquid ρ, taking into account the change in pressure (ρ) in the interphase layer. As a first approximation we assume that $\Psi(\rho)$ is a linear function of the density. Keeping in mind that $\Psi(\rho) \to 0$ when $\rho \to \rho_*$, where ρ_* is the density at the critical point, we write Eq. (1) in the form

$$\sigma=\frac{p_n d}{2}\left[1-\frac{1-\rho/\rho_0}{1-\rho_*/\rho_0}\right]\quad \rho_0\text{ — density at } 0^\circ\text{ K}. \qquad (2)$$

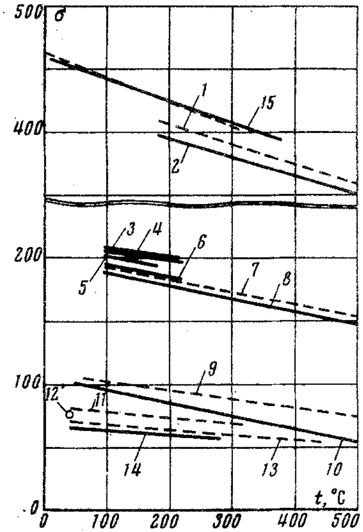
For many liquids $\rho_0/\rho_* \approx 3$–4. Then, selecting $\rho_0/\rho_* = 3$, we obtain

$$\sigma=\frac{p_n d}{2}\left[1-\frac{3}{2}\left(1-\frac{\rho}{\rho_0}\right)\right]=\frac{NkT\,d}{2(V-V_0)}\left[1-\frac{3}{2}\,\frac{V-V_0}{V}\right].\ (3)$$

Selecting the value 4 for ρ_0/ρ_* has little effect on the result, since in the relatively small temperature intervals (for metals) considered the second term of the equation is small as compared with unity.

Equation (3) does not contain empirical constants and directly relates the surface tension with the density. The mean interatomic distance

$$d=\left[\frac{\mu m(H)}{\rho}\right]^{1/3}\qquad\left(\rho=\frac{1}{V}\,,\quad m(H)=1.67\cdot10^{-24}\,\mathrm{g}\right).$$



Comparison of calculated and experimental data on the surface tension of liquid metals. Lithium: 1) theoretical relation; 2) data of [6]; sodium: 3) data of [10]; 4) [11]; 5) [12]; 6) [13]; 7) theoretical relation; 8) [6]; potassium: 9) theoretical relation; 10) [6]; rubidium: 11) theoretical relation; 12) [14]; cesium: 13) theoretical relation; 14) [15]; mercury: 15) theoretical curve; 16) [20].

Here μ is the molecular weight, ρ the density of the liquid and m(H) the mass of a hydrogen atom. After substituting practical numerical values of N, k, and m(H) in Eq. (3), for the surface tension we obtain the formula

$$\sigma=0.247\,T\left(\frac{\rho}{\mu}\right)^{2/3}\frac{3\rho/\rho_0-1}{1-\rho/\rho_*}\,,\qquad\sigma=\left(\frac{\rho}{\mu}\right)^{2/3}\frac{0.247}{\alpha}\left(\frac{3\rho}{\rho_0}-1\right).\ (4)$$

Here α is the temperature coefficient of the density. The table presents values of the surface tension σ_1 at the solidification point for 19 metals, calculated from equation (4) in dynes/cm; σ_2 are experimental values.

The density used in the calculations was taken from [2–4]. For comparison, the table also presents the most reliable experimental data from handbook [5], as well as the results of the theoretical calculations of several authors [16–19]. For most metals the agreement between the calculated and experimental data is quite satisfactory.

The figure shows calculated and experimental data for the alkali metals and mercury as a function of temperature. It is clear that eq. (4) also gives a satisfactory description of the temperature dependence of the surface tension.

Noteworthy is the difference between the calculated value of dσ/dt and the experimental values of Taylor [6] for liquid potassium. It has already been suggested [7] that Taylor's temperature coefficient was apparently incorrectly determined, since extrapolation to σ = 0 gives a much reduced value of the critical temperature (1250° K instead of 1770° K [8]).

	σ_1	σ_2	$\frac{\Delta\sigma}{\sigma_1}\%$	σ_1 [16]	σ_1 [17]	σ_1 [18]	σ_1 [19]
Li	413	398	3.6	—	—	302.9	—
Na	194	191	1.5	297	196	206.04	208
K	105	101	4.0	148	86.8	90.2	114.6
Rb	82	78.5	4.2	123	59.8	—	—
Cs	71	67.8	4.5	111	48.0	—	—
Ag	910	923	1.4	734	—	903	810
Au	1280	1130	13	930	—	925.7	814
Cu	1380	1356	1.5	1150	—	1156	1168
Mg	665	572	15	658	530	—	204
Zn	782	772	1.2	760	—	—	1100
Cd	622	630	1.2	595	—	—	880
Hg	460	466	1.2	—	—	796.8	—
Al	775	520—865	10	610	—	668	829
In	580	570	1.6	569	—	—	—
Tl	510	401	27	356	—	—	—
Si	702	700	0.5	—	—	—	—
Ge	960	960	0	—	—	—	—
Sn	520	540	3.5	—	—	845	—
Pb	475	465	2	392	—	463	—

Thus, in spite of the highly simplified assumptions upon which Eq. (3) is based, calculations give satisfactory agreement with experiment. We note that for calculating the surface tension it is necessary to know the density in both the liquid and solid phases (at least at T = = 0° K). Ordinarily, ρ_0 is found by extrapolation, which may quite easily involve an error of 1.0–1.5%, and this gives an error in determining σ of 10–15% at the melting point. In most cases it is difficult to check the formula for organic liquids on account of the lack of sufficiently reliable data on the density in the solid state. Equation (4) can easily be transformed to the form

$$\sigma\left(\frac{\mu}{\rho}\right)^{2/3} = c\,(T'_* - T),\quad c = \frac{R\,[m\,(H)]^{1/3}}{2\alpha T_*'} \qquad (5)$$

if it is assumed that the density is a linear function of temperature. Here $T'_* = T_* + \delta$ is the temperature corresponding to $\rho = \rho_*$.

Equation (5) coincides with the well-known Eötvös formula, the Eötvös constant being equal to

$$c = \frac{0.494\cdot 10^{-6}}{\alpha T_*'}.$$

In conclusion, we will demonstrate one more property of Eq. (5). Keeping in mind that [9]

$$\left(\frac{\mu}{\rho}\right)^{2/3} \sim d^2, \quad \beta = \frac{V - V_0}{V_0} \sim d$$

we can write (4) in the form

$$\sigma d^3 = k\,\frac{V - V_*}{V_*}.$$

The quantity σd^3 can be treated as the energy of part of the interphase layer with an area proportional to the square of the interatomic distance and a thickness proportional to that distance, i.e., as the energy of the interphase layer corresponding to the volume of a single atom. In [9] Solov'ev introduced the idea of "atomic" electrical resistance $\rho_a = \rho d_a^2$, which was found to be the same for a group of similar (alkali) metals, if ρ_a is calculated at the same values of the reduced volume $V_0^{-1}\Delta V$. Equation (6) shows that the quantity $\sigma d^3 = = \sigma_a$, which may be called the "atomic" surface tension, is also a universal function of the reduced volume for similar substances.

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8 October 1965 Novosibirsk