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ESTIMATIONS OF SURFACE FREE ENERGIES FOR SOLID METALS

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ABSTRACT. Experimental methods rarely give reliable values of the free surface energies/surface tensions for solid metals and just few data exist. Therefore correlations between surface and bulk thermodynamic properties are important in order to obtain estimated values for the surface quantities. From experimental values, molar free surface energies are calculated on the basis of molar volumes or atomic radii of metallic elements. The bulk properties considered here are melting point, enthalpy of atomization, free enthalpy of atomization and inner free enthalpy of atomization. Different correlations are investigated and the results are discussed and compared with the predictions of the rule of broken bonds between first neighbour atoms. The deviations of some elements from the regression lines are examined. From the correlations, a set of calculated free surface enthalpies for 69 solid elements is proposed.

Keywords: metals, surface free energy, enthalpy of atomization, correlations

Introduction

Surface free energy is one of the most important properties of solid state and particularly of solid metals. It determines the equilibrium shape of crystals and plays a decisive role in surface phenomena and processes, such as surface faceting, roughening, surface segregation in binary alloys, crystal growth, formation of grain boundaries, growth and stability of thin films, the shape of small crystallites in a supported catalyst, adsorption, sintering. The surface free energies between two interacting surfaces control processes like the stability of aqueous colloidal suspensions, the dynamics of molecular self-assembly, wetting, spreading, deinking, adhesion. Many mineral processing techniques, e.g. froth flotation, selective flocculation, filtration and thickening depend on the solid/liquid interfacial interaction [1].

Surface free energy, γ is defined as the excess Helmholtz energy (free energy), or the excess Gibbs energy (free enthalpy) per unit area:

$$\gamma = F_s = G_s = \Delta F/A_s = \Delta G/A_s \qquad (1)$$

For liquids it is numerically and dimensionally equal to the *surface tension* (*interfacial tension*), Some authors consider the two notions to be synonymous for solids too and related to the work spent in forming the surface,

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and introduce the *surface stress* or *stretching tension* in order to describe the work spent in stretching the surface [2, 3]. The first is a scalar quantity, the second - a tensor. The difference comes from the reduced mobility of atoms in solids, which prevents them to quickly rearrange to an equilibrium position when a new surface is created, while liquids cannot maintain a strain. However, this mobility is increased near the melting point, where this difference should disappear. As the temperature is approaching the melting point, a roughening of the surface occurs and even a “surface melting” can take place.

The temperature dependence of the surface free energy is related to the surface entropy, $S_s = \Delta S/A_s$, A_s being the surface area, the entropy variation involved in the creation of the unit area of the solid-vapour interface, by the obvious relation:

$$S_s = -\left(\frac{\partial G_s}{\partial T}\right)_p = -\left(\frac{\partial \gamma}{\partial T}\right)_p \tag{2}$$

and the surface enthalpy (or energy) can be obtained from the Gibbs-Helmholtz equation:

$$H_s = \gamma - T\frac{\partial \gamma}{\partial T} \tag{3}$$

So-called “molar“ surface quantities are defined as products of the above functions with the “molar” surface, $V_M^{2/3}$ (V_M – the molar volume of the solid), e.g. the “molar” surface free energy $\gamma V_M^{2/3}$. For liquids, a linear decrease of surface tension with temperature increase is generally assumed, i.e. surface entropy is constant, independent of temperature. In the case of solid metals, exact measurements on the temperature dependence of surface free energy are missing, but here also a decrease of γ with increasing temperature is observed.

Since experimental methods rarely give reliable values of the free surface energies for solid metals and just few data exist, there were many attempts to calculate the surface energy. They range from empirical correlations between this quantity and some bulk properties of the metal to the use of *ab-initio* techniques, passing through semi-empirical methods, among them many applications of the law of corresponding states and statistical mechanics [4].

Empirical Correlations Between Free Surface Energy and Other Properties of Solid Metals

In order to find correlations between free surface energies and other properties of the metals, experimental values were used (Table 1), taken mostly from the compilation of Kumikov and Khokonov [5]. The authors have selected, compared and evaluated experimental values, obtained by various methods. These measurements were made at different, most of

Table 1.

Surface free energies and other properties of solid metals

Element	γ^{exp} [mJ.m^{-2}]	γ^{TM} [mJ.m^{-2}]	T_m[K]	ΔH_a [kJ/mol]	V[cm^3]	R [pm]
Li	---	472	454	159.4	13.096	156
Be	1000	1298	1551	324.3	4.875	113
Na	---	234	370.9	108.4	23.686	186
Mg	---	688	922	147.7	13.981	160
Al	1140	1020	933.5	326.4	9.985	143
Si	1200	940	1683	455.6	12.051	117
K	---	129	337	89.2	45.348	231
Ca	---	425	1112	178.3	25.851	197
Sc	---	---	1814	377.8	15.033	161
Ti	1938	1749	1941	469.9	10.546	145
V	2900	2301	2173	514.2	8.782	131
Cr	2090	2006	2130	396.6	7.230	125
Mn	1400	1298	1518	280.7	7.393	137
Fe	2170	2123	1808	416.3	7.095	125
Co	2424	2218	1768	424.7	6.621	125
Ni	1940	2080	1726	429.7	6.594	124
Cu	1520	1566	1356.4	338.3	7.123	128
Zn	868	896	693	130.7	9.158	133
Ga	767	845	302.9	277	11.70	122
Ge	820	748	1210.4	376.6	13.64	123
Rb	---	104	312.2	80.9	55.856	243
Sr	---	358	1041	164.4	33.7	215
Y	---	---	1795	421.3	19.888	180
Zr	1850	1687	2125	608.8	14.055	161
Nb	2400	2313	2741	725.9	11.059	147
Mo	2630	2510	2883	658.1	9.405	136
Tc		---	2445	678	8.513	135
Ru	3400	2655	2607	642.7	8.217	132
Rh	2800	2325	2239	556.9	8.298	134
Pd	2000	1743	1825	378.3	8.868	138
Ag	1205	1086	1235	384.6	10.272	144
Cd	675	698	594.1	112	12.995	149
In	633	658	429.3	243.3	15.869	163
Sn	673	661	505	302	16.306	140
Cs	---	84	301.6	76.1	70.955	265
Ba	---	326	998	180	39.122	210
La	---	---	1193	427	20.731	187
Nd	---	812	1297	328	20.605	181
Pm	---	---	1312	301	22.380	183
Sm	---	---	1345	206.7	19.941	180
Eu	---	---	1095	178	28.895	204
Gd	900	---	1586	398	19.936	179
Yb	---	---	1097	152	24.790	194

Lu	---	---	1936	428	17.781	174
Hf	---	1923	2495	669	13.521	154
Ta	2480	2493	3269	782	10.900	143
W	2900	2765	3683	849.4	9.476	137
Re	2200	3133	3453	769.9	8.854	138
Os	---	2950	3327	790.8	8.492	134
Ir	---	2655	2637	665.2	8.573	136
Pt	1950	2203	2045	565.3	9.094	139
Au	1410	1333	1337.6	369	10.210	144
Tl	562	550	576.7	182.2	17.710	170
Pb	560	540	601	196	18.271	175
Bi	501	446	544.5	207.1	21.324	155
Ra	---	---	973	161.9	44.403	132
Th	---	---	2023	598.3	19.832	181
Pa	---	---	1873	606.7		161
U	---	1780	1405	535.6	12.494	138

γ^{exp} – experimental values for free surface energy [5], γ^{TM} – Tyson and Miller values [6], T_m – melting point, ΔH_a – enthalpy of atomization, V – molar volume, R – metallic radius

them at relatively high, temperatures, near the melting point of the metal. The preferred values are mostly those obtained by the compensated zero-creep method. The scatter of the values is important, the relative errors of the measurements reach 10-20%, but only 1-3% in the zero-creep method. We selected the most probable values (most of them recommended by the authors) along with some values from other sources. Insofar as possible, we selected values obtained at lower temperature, where the peculiarities of the solid metals are more pronounced.

In literature the „experimental“ values of Tyson and Miller [6] are often used. As a matter of fact, these are extrapolated from the values for liquid metals at the melting point, γ_L which are reasonable well known quantities. They inferred that the ratio of free surface energies for solids γ_S and for liquids should be approximately constant for metallic elements:

$$\gamma_S / \gamma_L = 1.18 \pm 0.03 \tag{4}$$

The values given by Tyson and Miller are also included in Table 1.

Since surface free energy of a pure solid is determined by the strength of cohesive forces between the adjacent particles, it seems logically to expect correlations between it or other surface properties and some physico-chemical bulk properties of the materials, that are also the result of forces of this kind. Of course, this should apply only to pure materials, inasmuch as even the smallest amounts of surface active contaminants have a strong influence on the values of surface tension, while the bulk properties are only slightly modified. The bulk properties considered here are melting temperatures and standard enthalpies of atomization.

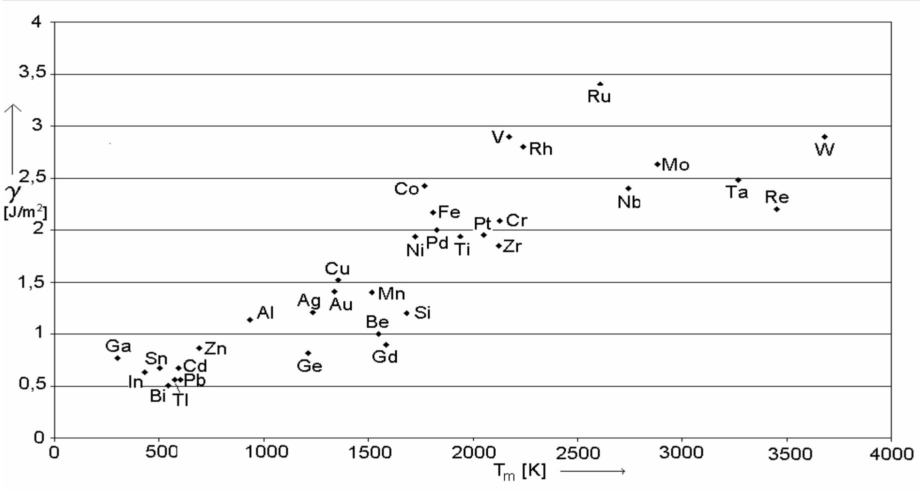

Figure 1.
Surface free energies of solid metals versus melting temperatures

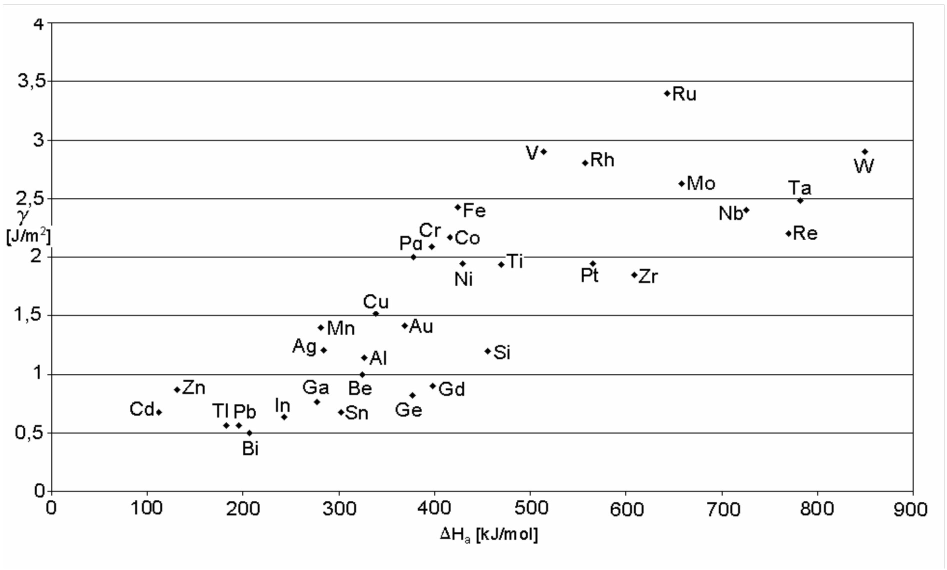

Figure 2.
Surface free energies of solid metals versus enthalpies of atomization

Experimental values for the surface free energies of solid metals were plotted versus melting points T_m in Figure 1. The two properties appear to be related, but there is not a strong linear correlation. Particularly, metals with high melting points (Nb, Mo, Ta, Re, W) don't have correspondingly high γ-values. The same is the case for the semi-metals Ge and Si. On the other hand, the surface free energy for Ga is unexpectedly high for its melting point. The correlation line for 33 experimental values corresponds to the equation:

$$\gamma\ [\mathrm{mJ/m^2}] = (313\pm157) + (0.791\pm0.083)T_m[\mathrm{K}],\quad r = 0.864 \qquad (5)$$

Another measure of cohesion forces in the metal lattice could be the standard enthalpy of atomization, ΔH_a (the values are also given in Table 1). As in the case of the temperature dependence, an increase of the free surface energies with increasing ΔH_a-values is evident from Figure 2, but there is no linear correlation, the scatter of the points is even higher than in Fig.1. The equation of the correlation line, passing through the origin, is:

$$\gamma[\mathrm{mJ/m^2}] = (3.80\pm0.18)\ \Delta H_a[\mathrm{kJ/mol}]\quad r = 0.819,\ n = 33 \qquad (6)$$

One of the reasons for the poor correlation is that, while surface free energies refer to the surface unit, the enthalpies of atomization are molar quantities. Therefore, „molar" surface tensions $\gamma.V^{2/3}$ should be used, where V stands for the molar volume of the solid metal, calculated as the ratio of the atomic weight to the density of the solid, M/ρ_S. Calculated values for the molar volumes are given in Table 1. The plot of this quantity versus melting point is given in Figure 3. The correlation is somewhat better as in Fig.1 (eq. 5), but not satisfactory. The equation of the correlation line is:

$$10^4\gamma.V^{2/3}\ [\mathrm{mJ}] = (2160\pm580) + (3.16\pm0.31)\,T_m\ r = 0.880\ \ n = 33 \qquad (7)$$

The greatest deviations form the fitting line are those for Be and Re (negative deviations) and for V, Ru (positive deviations). Excluding the evidently wrong values for Be and Re, the equation of the new correlation line is:

$$10^4\gamma.V^{2/3}\ [\mathrm{mJ}] = (950\pm460) + (3.44\pm0.25)\,T_m\ \ r = 0.931\ \ n = 31 \qquad (7a)$$

and without the uncertain values for V and Ru also:

$$10^4\gamma.V^{2/3}\ [\mathrm{mJ}] = (2100\pm350) + (3.22\pm0.20)\,T_m\ r = 0.953\ n = 29 \qquad (7b)$$

i.e. a quite good correlation.

Subsequently „molar“ surface tensions were plotted versus enthalpies of atomization (Figure 4). The correlation line is given by the equation:

$$10^4\gamma.V^{2/3}\ [\mathrm{mJ}] = (17.12 \pm 0.57)\ \Delta H_a[\mathrm{kJ/mol}] \quad r = 0.894 \quad n = 33 \tag{8}$$

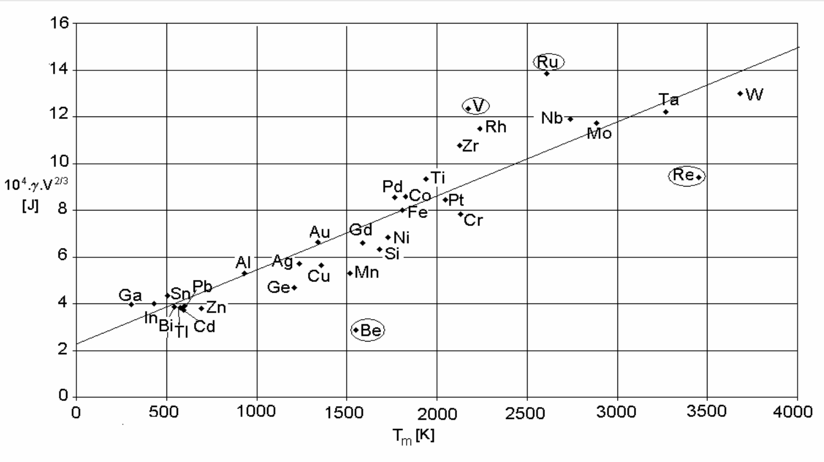

Figure 3.
„Molar“ surface tensions of solid metals versus melting points

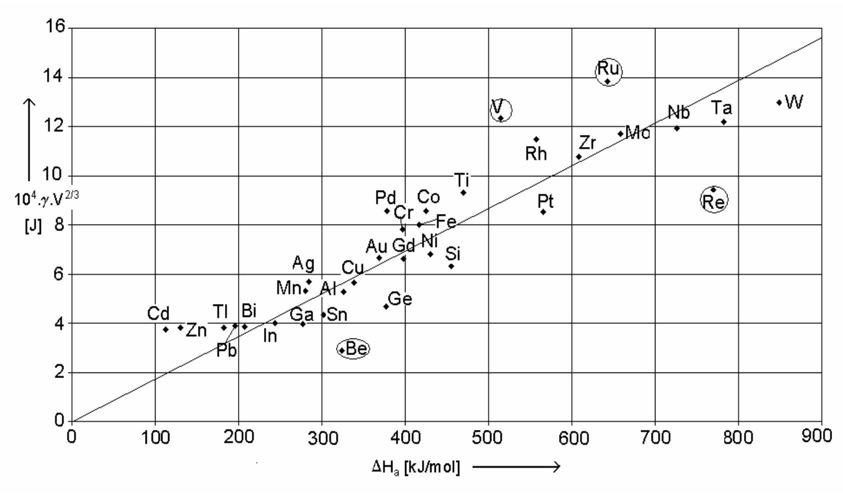

Figure 4.
„Molar“ surface tensions of solid metals versus enthalpies of atomization

The most important deviations are caused by the same elements as in the previous representation. Without Be and Re, the equation becomes:

$$10^4\gamma.V^{2/3}\ [\mathrm{mJ}] = (17.70\pm0.51)\ \Delta H_a[\mathrm{kJ/mol}]\quad r = 0.923,\ n = 31 \qquad (8a)$$

and letting apart V and Ru too:

$$10^4\gamma.V^{2/3}\ [\mathrm{mJ}] = (17.14\pm0.45)\ \Delta H_a[\mathrm{kJ/mol}]\quad r = 0.946,\ n = 29 \qquad (8b)$$

The general appearance of the plot is very similar to that on Figure 3, the correlation is quite the same. The introduction of molar surface tensions leads therefore to a better correlation as compared to surface tensions, but the scatter of the points is still important. Some reasons could be the imprecision of experimental values, the different types of crystal lattices in different metals, the fact that the experimental data were measured at temperatures sometimes quite far from the standard temperature, and the nature of molar surface tensions, these being essentially *free* energies, other than the enthalpies of atomization.

Two metals giving here deviations (but not in Fig.2) are Zn and Cd: their $\gamma V^{2/3}$-values appear to be too high as compared to their enthalpies of vaporization. This could be related to peculiarities of their crystal structure. They have a hexagonal closest packed structure, but the height of their unit cell is some 15% larger than normal for this type of crystals, i.e. the 6 adjacent atoms in the basal plane are nearer to one another as the other 6, in the next planes above or bellow. The interatomic distances are 2.660 and 2.907 Å for Zn, respectively 2.973 and 3.287 for Cd [7]. This could diminish the cohesion energy, i.e the enthalpy of atomization, while in the surface layer, these greater distances probably vanish. Besides, $V^{2/3}$ could give here a too large evaluation for the molar surface.

For comparison, the correlations were tested also with the values proposed by Tyson and Miller (Table 1). The corresponding „molar“ quantities $\gamma^{TM}V^{2/3}$ were calculated for 45 elements and plotted versus melting points (Figure 5). The correlation line is described by the equation:

$$10^4\gamma^{TM}V^{2/3}\ [\mathrm{mJ}] = (1350\pm330) + (3.42\pm0.18)\ T_m\quad r = 0.944,\ n{=}45 \qquad (9)$$

The corresponding representation against standard enthalpies of atomization is given in Figure 6. The equation of the correlation line is:

$$10^4\gamma^{TM}V^{2/3}\ [\mathrm{mJ}] = (16.60\pm0.31)\ \Delta H_a[\mathrm{kJ/mol}]\quad r = 0.969,\ n = 45 \qquad (10)$$

The much better correlation in both cases is a consequence of the higher precision of experimental data for liquid metals, the values of Tyson and Miller are based on, and of the disappearance of differences contingent on the crystal lattice near the melting point as well. Some larger deviations are those for Be, Ge and Si, accountable by their semi-metallic character and the presence of covalent binding. In Fig. 5 the large deviation for U is striking; caused by the unusual high melting temperature of this metal. In Fig. 6 this point is not longer an outlier; enthalpies of atomisation are better correlated to surface tensions than melting points.

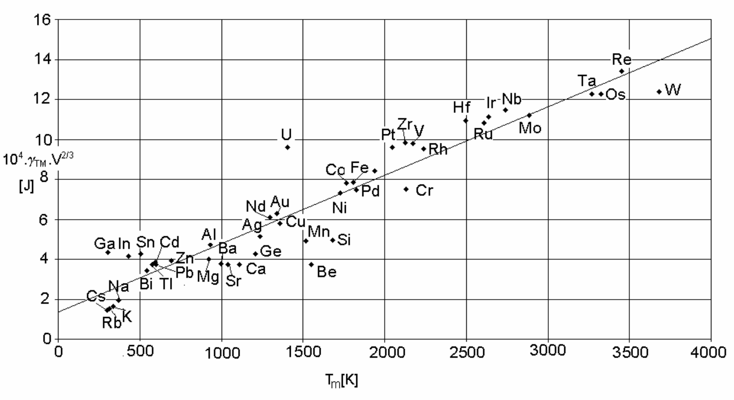

Fig.5.
Molar surface tensions (Tyson and Miller) versus melting points

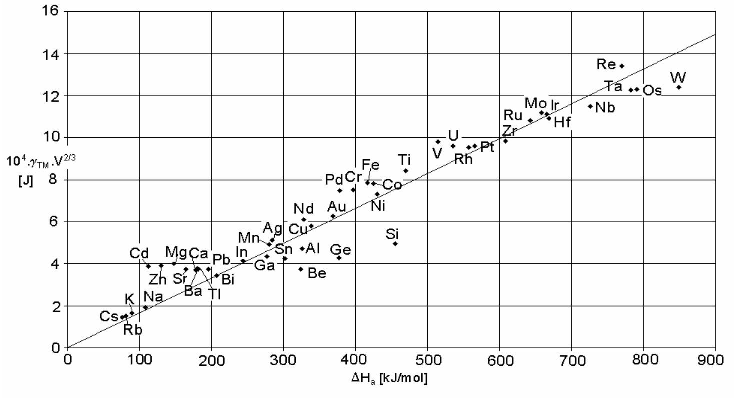

Fig.6.
Molar surface tensions (Tyson and Miller) versus enthalpies of atomization

The points for 2nd group elements in the periodic system (Mg, Ca, Sr, Ba) and for 12th group elements (Zn, Cd) are somewhat apart, over the correlation line; they all correspond to nearly the same value of „molar“ surface tension. Such deviations appear also for the melts of these metals, in the correlation of their molar surface tensions with enthalpies of vaporization [8].

The experimental value for berrylium (γ = 1000 mJ/m^2) is evidently to low; it was determined by a single method [5] and is much under the value given by Tyson and Miller (1298). But even with this value, the point is clearly under the correlation line. Mezey and Giber [9] calculated for Be a γ-value of 1117; the value of Tyson and Miller extrapolated for 0 K is 1628, Boer et al. [10] estimated a value as high as 2700, while an *ab initio* calculation [11] gives γ = 1834.

The point for rhenium in Fig. 3 and 4 is far under the line, while the calculated value of Tyson and Miller gives a point near the line (Fig. 5, 6). The experimental value (2200 mJ/m^2) coming from a single determination (FEM) [5] is apparently wrong, the value extrapolated by Tyson and Miller (3133), and that calculated by Mezey [9] (3109) are much higher. Even larger are the values given by Boer [10]: 3600 and calculated ab initio [11]: 4214.

For V and Ru the points in Fig. 3 and 4 are far above the correlation line, while with the values of Tyson and Miller there are not such deviations. For both metals the experimental γ-values [5] are much higher than those given by Tyson and Miller and even than those given by Boer, but are in good agreement with the calculations of Mezey and ab initio (for V), while the results of the ab initio calculation for Ru are still higher. Therefore, our linear regression calculations were conducted as well without these four elements.

As a measure for the area occupied by an atom in the surface layer, we could select also the square of the metallic radius of the element R (Table 1), even though in the surface shell the positions of the atoms are somewhat different to those inside the metal lattice. The differences resulted from the reconstruction of the surface should however affect interatomic distances between different planes rather than distances within the same plane. The product $\gamma.R^2$ as an alternative to the “molar” surface tension, was thus plotted against the enthalpy of atomization in Figure 7, with experimental γ-values. The equation of the correlation line is:

$$10^{24}.\gamma.R^2[\mathrm{J}] = (71.9 \pm 2.9)\Delta H_a[\mathrm{kJ}] \quad r = 0.86,\ n = 33 \qquad (11)$$

This correlation is slightly worse than the corresponding one with $\gamma.V^{2/3}$ (Fig. 4, eq. 8), but the distribution of the points is very similar. The great deviations of the point for Ge and Si from the correlation line are evident. The reason could consist in the use of covalent radii for these elements, while metallic radii were used for all the other elements.

Excluding again Be, Re, V and Ru, the equation becomes:

$$10^{24}.\gamma.R^2[J] = (71.7 \pm 2.8)\Delta H_a[kJ] \quad r = 0.88,\ n = 29 \qquad (11a)$$

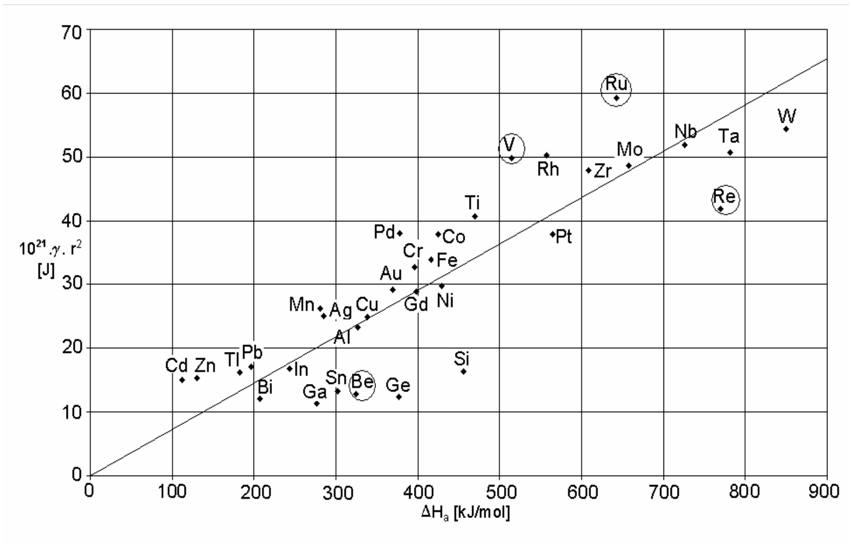

Fig.7.
$\gamma.R^2$ products against enthalpies of atomization

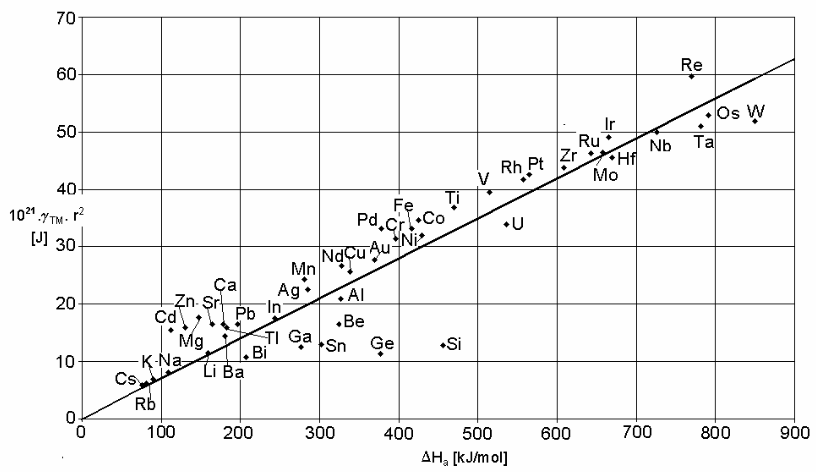

Fig. 8.
$\gamma.R^2$ products against enthalpies of atomization (γ from Tyson and Miller)

without a significant improvement for this once.

The similar plot with the values given by Tyson and Miller (Figure 8) corresponds to the correlation line:

$$10^{24}\gamma^{TM}.R^2[J] = (67.9 \pm 2.2)\Delta H_a[kJ] \quad r = 0.90,\ n = 45 \qquad (12)$$

The correlation is also somewhat worse than for „molar“ surface tensions (Fig. 6, eq. 10), while the general form is the same. The greater deviations correspond again to elements whose radii don’t fit the pattern of metallic radii (Ge, Si).

Many approaches in the evaluation of surface energy make use of the broken-bond rule, according to which the surface energies scale with the number of broken bonds between first neighbours, when bulk atoms become surface atoms [12]. If only interactions between pairs of adjacent atoms are considered, the energy needed to bring atoms from the bulk to the surface should be proportional to the fraction α of broken bonds. Usually the ratio of surface energy (or enthalpy) to the enthalpy of vaporization for liquids or the enthalpy of atomization for solids is considered to be given by α. But above, we had free surface energies correlated to bulk energies. In order to have the same kind of quantities, we could either use instead of the molar surface free energies (surface tensions) the molar surface enthalpies (3) or energies

$$U_{sM} = \gamma_M + T.S_{sM} \qquad (13)$$

or instead of standard enthalpies of atomisation the corresponding free enthalpies

$$\Delta G_a = \Delta H_a - T\Delta S_a \qquad (14)$$

S_{sM} is the molar surface entropy (cf. Eq.(2)). In correlating surface and bulk properties of melted metals, the first way was chosen [8], since the temperature coefficients of the surface tension were reasonable well known and the molar surface entropy is nearly a constant, whatever the metal or the temperature were [13]. However for solid metals the temperature coefficient of surface tension was rarely determined and its constancy is questionable. For liquids, this constancy is related to constant value of the entropies of vaporization (Trouton‘s rule), while melting entropies are not constant, and atomization entropies should not be expected to be constant. The calculation of surface energies of solid metals would thus be very intricate. We preferred therefore the second way, to estimate free enthalpies of atomization (10).

The standard atomization entropy for solid metals can be calculated as the difference:

$$\Delta S_a = S_{298}^0\ (\text{gas}) - S_{298}^0\ (\text{solid}) \qquad (15)$$

Standard entropies of solid metals are well known quantities and are given in Table 2. The entropies for gaseous metals can be calculated

Table 2.

Experimental and calculated properties of solid metals

Ele-ment	$S_{298,s}^0$ [J.mol^{-1}.K^{-1}]	$S_{298,g}^0$ [J.mol^{-1}.K^{-1}]	ΔS_a [J.mol^{-1}.K^{-1}]	ΔG_a [kJ/mol]	γ_{298} [mJ/m^2]	ΔG_a^i [kJ/mol]	k	γ_M [kJ]	$\alpha/f = \gamma_M/\Delta G_a^i$
Li	29.1	138.8	109.7	126.7	---	---	---	---	---
Be	9.5	142.0	132.5	284.8	1096	305.92	10.30	26.62	0.087
Na	51.3	153.7	102.4	77.9	---	---	---	---	---
Mg	32.7	154.4	121.7	111.4	---	---	---	---	---
Al	28.3	155.7	127.4	288.4	1180	307.77	17.78	46.22	0.150
Si	18.8	156.2	137.4	414.7	1200	433.53	14.55	53.26	0.123
K	64.7	160.3	95.6	60.7	---	---	---	---	---
Ca	41.6	160.6	119.0	142.7	---	---	---	---	---
Sc	34.6	162.1	127.5	339.8	---	---	---	---	---
Ti	30.7	162.8	132.1	430.5	2211	449.72	23.64	89.78	0.200
V	28.9	163.6	134.7	474.1	2900	493.71	25.00	104.24	0.211
Cr	23.76	163.9	140.1	354.8	2488	374.98	24.81	78.55	0.209
Mn	32	164.6	132.6	241.2	1400	261.28	20.33	44.87	0.172
Fe	27.3	164.8	137.5	375.3	2550	395.52	23.80	79.50	0.201
Co	30	165.4	135.4	384.3	2859	404.69	24.90	85.11	0.210
Ni	29.9	165.4	135.5	389.3	2304	409.69	19.77	68.41	0.156
Cu	33.2	166.4	133.2	298.6	1770	318.78	20.55	55.33	0.174
Zn	41.6	166.7	125.1	93.4	976	112.96	37.83	36.08	0.319
Ga	40.9	167.5	126.6	239.3	762	258.20	15.21	33.16	0.128
Ge	31.1	168.0	136.9	335.8	966	354.40	15.57	46.60	0.131
Rb	76.8	170.1	93.3	53.1	---	---	---	---	---
Sr	52.3	170.4	118.1	129.2	---	---	---	---	---
Y	44.4	170.6	126.2	383.7	---	---	---	---	---
Zr	39	170.9	131.9	569.5	2215	587.99	22.01	109.27	0.186
Nb	36.4	171.1	134.7	685.8	2667	704.84	18.78	111.79	0.159
Mo	28.7	171.5	142.8	615.5	3124	635.02	21.92	117.59	0.185
Tc	33.5	171.8	138.3	636.8	---	---	---	---	---
Ru	28.5	172.2	143.7	599.9	3400	619.70	22.15	116.91	0.189
Rh	31.5	172.4	140.9	514.9	2800	534.71	21.46	96.91	0.181
Pd	37.6	172.8	135.2	337.9	2000	357.54	23.96	72.36	0.202
Ag	42.6	173.0	130.4	245.7	1393	265.01	24.83	55.58	0.210
Cd	51.8	173.5	121.7	75.7	745	94.42	43.59	34.76	0.368
In	57.8	173.7	115.9	208.8	668	226.95	18.58	35.61	0.157
Sn	51.2	174.2	123.0	265.4	727	283.47	17.36	39.48	0.139
Cs	85.2	175.6	90.4	49.2	---	---	---	---	---
Ba	62.8	176.0	113.2	146.3	---	---	---	---	---

La	56.9	176.1	119.2	391.5	---	---	---	---	---
Nd	71.5	176.6	105.1	296.7	---	---	---	---	---
Pm	---	176.7	---	---	---	---	---	---	---
Sm	69.6	177.1	107.5	174.7	---	---	---	---	---
Eu	77.8	177.2	99.4	148.4	---	---	---	---	---
Gd	68.1	177.7	109.6	365.3	900	382.96	17.28	55.88	0.146
Yb	59.9	178.9	119.0	116.5	---	---	---	---	---
Lu	51	179.0	128.0	389.9	---	---	---	---	---
Hf	43.6	179.3	135.7	628.6	---	---	---	---	---
Ta	41.5	179.4	137.9	740.9	2957	760.01	19.13	122.76	0.162
W	32.76	179.6	146.9	805.6	3198	825.10	17.36	120.95	0.147
Re	36.9	179.8	142.9	727.3	2679	746.95	15.35	96.81	0.130
Os	32.6	180.1	147.5	746.9	---	---	---	---	---
Ir	35.5	180.2	144.7	622.1	---	---	---	---	---
Pt	41.6	180.4	138.8	523.9	2318	543.51	18.58	85.31	0.157
Au	47.4	180.5	133.1	329.3	1641	348.62	22.15	65.20	0.187
Tl	64.2	180.9	116.7	147.4	616	165.32	25.33	35.37	0.214
Pb	64.8	181.1	116.3	161.3	619	179.17	23.96	36.26	0.202
Bi	56.7	181.2	124.5	170.0	547	187.45	22.43	35.50	0.189
Ra	71.1	182.0	110.9	128.9	---	---	---	---	---
Th	51.8	182.5	130.7	559.3	---	---	---	---	---
Pa	51.9	---	---	---	---	---	---	---	---
U	50.2	182.8	132.6	496.1	---	---	---	---	---

Standard entropies of solid, $S_{298,s}^0$, and gas, $S_{298,g}^0$; ΔS_a - standard entropies of atomization, ΔG_a – free enthalpies of atomization, γ_{298} - γ values extrapolated for 298 K, ΔG_a^i – internal free enthalpies of atomization, $k = \gamma_{298}V^{2/3}/\Delta G_a^i$, γ_M – molar surface free energy.

by the methods of statistical thermodynamics. Since gaseous metals are monoatomic, the equation of Sackur und Tetrode [14] can be applied:

$$S(T,p) = \frac{5}{2}R\ln T - R\ln p + \frac{5}{2}R + R\ln\frac{(2\pi m)^{3./2}k^{5/2}g_0}{h^3} \qquad (16)$$

The entropies calculated by this formula are given in Table 2, together with the calculated values for the entropy of atomization (15) and the standard free enthalpies of atomization (14)

The plot of molar free surface energy against these calculated free enthalpies of atomization is similar to that in Fig. 4. The correlation line corresponds to the equation:

$$10^4\gamma V^{2/3}\ [\text{mJ}] = (18.53 \pm 0.66)\Delta G_a[\text{kJ/mol}] \quad r = 0.893,\ n = 33 \qquad (17)$$

The correlation is just the same as for enthalpies of atomisation (8), the introduction of free enthalpies did not improve it. The most important deviations are again for Be and Re (wrong experimental data) and for V and Ru (uncertain experimental values). Without the first two elements we obtain:

$$10^4\gamma V^{2/3}\ [\mathrm{mJ}] = (19.20\pm0.60)\Delta G_a[\mathrm{kJ/mol}] \quad r = 0.922,\ n = 31 \qquad (17a)$$

and excluding all the 4 elements:

$$10^4\gamma V^{2/3}\ [\mathrm{mJ}] = (18.60\pm0.56)\Delta G_a[\mathrm{kJ/mol}] \quad r = 0.945,\ n = 29 \qquad (17b)$$

The same correlation was verified for the values proposed by Tyson and Miller. The equation of the correlation line is:

$$10^4\gamma^{TM} V^{2/3}\ [\mathrm{mJ}] = (17.92\pm0.39)\Delta G_a[\mathrm{kJ/mol}] \quad r = 0.969,\ n = 45 \qquad (18)$$

The image is very similar to the one in Figure 6 and the coefficient of correlation is just the same.

The correlation with free enthalpies of atomization was also tested using R^2 as a measure of atomic surface. The correlation described by the equation:

$$10^{24}\gamma.R^2[\mathrm{J}] = (77.89 \pm 3.23)\Delta G_a[\mathrm{kJ}] \quad r = 0.860,\ n = 33 \qquad (19)$$

does not differ from the one using ΔH_a (Fig. 7, eq. 11). The exclusion of the 4 doubtful values (for Be, Re, V. Ru) does not result in an obvious improvement:

$$10^{24}\gamma.R^2[\mathrm{J}] = (77.85 \pm 3.20)\Delta G_a[\mathrm{kJ}]\ r = 0.881,\ n = 29 \qquad (19a)$$

Even though correlation is not improved by using free enthalpies of atomization instead of enthalpies of atomization, this treatment is theoretically legitimate.

The experimental values of surface free energies for solid metals were determined at very different temperatures. In order to compare them with ΔG_a it would be appropriate to refer them all to the standard temperature (298K). On the basis of the theory of corresponding states, Digilov [15] deduced an equation for the temperature dependence of surface tensions for solid metals, starting with the surface tension of the liquid at the melting point:

$$\gamma_s(T) \cong 1{,}2\gamma_L\left[1-0{,}229\left(\frac{T}{T_m}-1\right)+0.01\left(\frac{T}{T_m}-1\right)^2\right] \qquad (20)$$

Actually, this relation should hold only for medium temperatures, about 0,6 T_m, but one may assume that the errors should not be important if extrapolated to the standard temperature. Thus the experimental data were recalculated for 298 K, inasmuch the temperature of their determination was found in literature, by an extension of equation (20):

$$\gamma_s(298) \cong \gamma_s(T)\frac{1-0,229\left(\dfrac{298}{T_m}-1\right)+0.01\left(\dfrac{298}{T_m}-1\right)^2}{1-0,229\left(\dfrac{T}{T_m}-1\right)+0.01\left(\dfrac{T}{T_m}-1\right)^2} \qquad (21)$$

These values were also enlisted in Table 2; of course, they are somewhat higher than the experimental values, determined at higher temperatures.

The values of free surface energies, recalculated for the standard temperature, were used to calculate the “molar” quantities γ_{298} $V^{2/3}$. These were plotted against free enthalpies of atomization (Fig. 9) and the correlation line has the equation:

$$10^4\gamma_{298}V^{2/3}\ [\mathrm{mJ}] = (20.66\pm0.65)\Delta G_a[\mathrm{kJ/mol}] \quad r = 0.916,\ n = 33 \qquad (22)$$

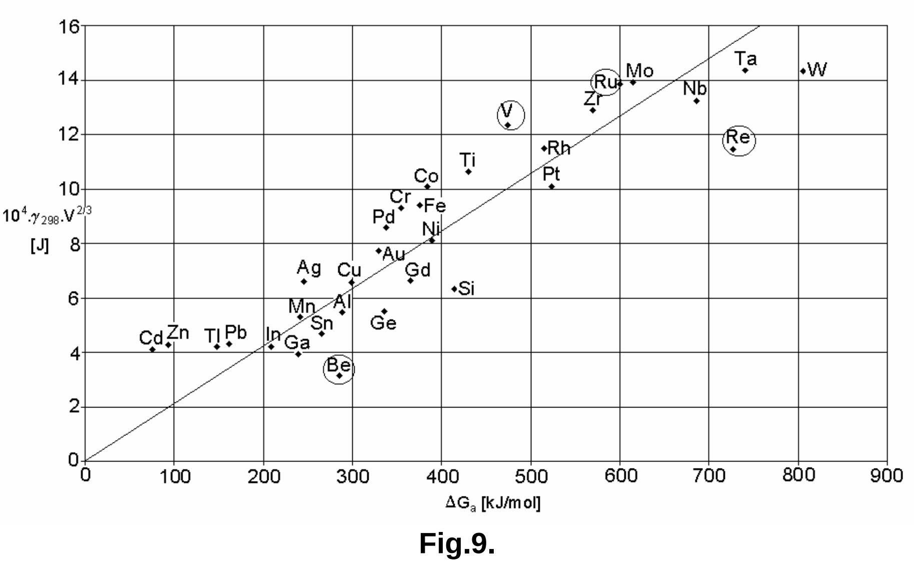

Fig.9.
„Molar“ free surface enthalpy (standard temperature) against free enthalpy of atomization

Now the correlation is somewhat improved, but not in such a degree to justify all the amount of calculations necessary. The points for Be and Re remain here also far from the field of the other values, and without them the equation becomes:

$$10^4\gamma_{298}V^{2/3}\ [\mathrm{mJ}] = (21.28 \pm 0.61)\Delta G_a[\mathrm{kJ/mol}]\quad r = 0.936,\ n = 31 \qquad (22a)$$

and after exclusion of V and Ru also:

$$10^4\gamma_{298}V^{2/3}\ [\mathrm{mJ}] = (20.92 \pm 0.63)\Delta G_a[\mathrm{kJ/mol}]\quad r = 0.940,\ n = 29 \qquad (22b)$$

Among the other elements, higher deviations are observed for Si (nonmetal), Zn and Cd (their specific structure was discussed above) and W, whose very high free enthalpy of atomization should demand a higher value for the free surface energy also.

A possible improvement according to Mezey and Giber [9], is to use so-called "internal" free enthalpies of atomisation ΔG_a^i. These values are enthalpies of atomization corrected for the expansion work of the gas resulted by splitting all the bonds in the metal, from the (very small) volume of the metallic crystal to the volume of the monoatomic ideal gas. This work is missing in the case of the partial splitting of the bonds, associated with the conversion of a bulk atom into a surface atom. Since this work of expansion is negative, internal free enthalpies of atomisation have larger numerical values than ΔG_a:

$$\Delta G_a^i = \Delta G_a + RT\ln\frac{V_G}{V_S} = \Delta G_a + RT\ln\frac{RT}{p_0 V_S}. \qquad (23)$$

The molar volume of the gas was calculated from the law of ideal gases for the standard state, and the molar volume of the solid metal from the atomic mass and density, in the same state. These ΔG_a^i values are given in Table 2. The difference to the uncorrected values of the enthalpy of atomization is not important (some 10%) and it does not affect substantially the sequence of these values.

The plot of „molar" free surface enthalpies at 298K against the corrected ΔG_a^i-values is almost the same as in Fig. 9, and the correlation coefficient is also nearly unchanged.

$$10^4\gamma_{298}V^{2/3}\ [\mathrm{mJ}] = (19.90 \pm 0.60)\Delta G_a^i\,[\mathrm{kJ/mol}]\quad r = 0.917,\ n = 33 \qquad (24)$$

The corresponding equations without Be and Re:

$$10^4\gamma_{298}V^{2/3}\ [\mathrm{mJ}] = (20.48 \pm 0.55)\ \Delta G_a^i\,[\mathrm{kJ/mol}]\quad r = 0.937,\ n = 31 \qquad (24a)$$

and when V and Ru are also excluded:

$$10^4\gamma_{298}V^{2/3}\ [\mathrm{mJ}] = (20.13\pm0.57)\ \Delta G_a^i[\mathrm{kJ/mol}]\quad r = 0.941,\ n = 29 \qquad (24b)$$

remain also quite unchanged.

It is interesting, that for both, the highest and the lowest values of free enthalpy of atomization, there are important deviations from the line of correlation. A sigmoidal curve seems to fit better the experimental points than a straight line (Fig. 10). Only the points for Be, Si and Re are now far outside the curve. It may be assumed that for high values of the surface energy, a more important surface relaxation and reconstruction process takes place, in order to reduce tensions, so that the surface energy represents a smaller fraction of the bulk energy than the average for all metals. For low energies, the rearrangement of the atoms on the surface occurs to a lower degree and surface energy is a higher fraction of bulk energy.

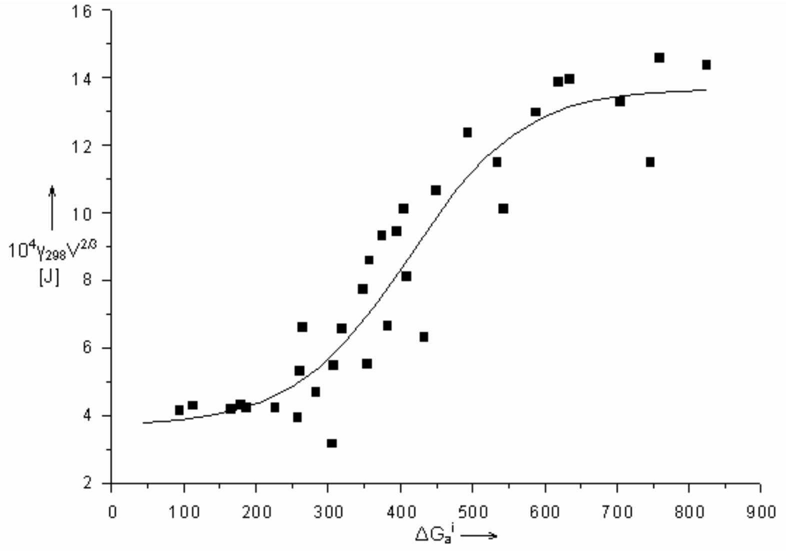

Fig.10.

Sigmoidal representation of $\gamma_{298}V^{2/3}$-values versus internal enthalpy of atomization

Estimation of Surface Free Energies for Solid Elements

In order to compare for different metals the ratio of „molar" surface free enthalpy to the enthalpy of atomization, its value: $k = \dfrac{\gamma_{298}V^{2/3}}{\Delta G_a^i}$ was calculated (Table 2). The values are quite different, between 10.3 for Be and 43.6 for Cd.

The mean value is 21.57, the standard deviation 6.15, and the standard error of the mean 1.07. By excluding the extreme values for Be, Si (semi-metals), Re (uncertain value), Zn, Cd (exceptional cases), the span of the remaining 28 values is much narrower (from 15.6 to 25.3); the mean value is 21.08, the standard deviation 2.98 and the standard error of the mean: 0.56.

The “molar” surface quantities used above were conventional ones. In order to estimate the actual molar surface free energies, let us consider the atomic volume in the solid, Ω as the molar volume of the solid divided to Avogadro’s number, V_S/N_A. The area assigned to an atom in the surface layer is:

$$s = f\Omega^{2/3} = f\,\frac{V_S^{2/3}}{N_A^{2/3}} \qquad (25)$$

and the area occupied by a mole of atoms of this kind is $A_M=N_A s$. The molar surface free energy is therefore given by:

$$\gamma_M=fN_A^{1/3}\gamma V^{2/3} \qquad (26)$$

f is a packing coefficient, a little greater then 1, depending on the crystalline structure. Ignoring this factor, the $\gamma V^{2/3}$-values should be multiplied by $N_A^{1/3}$ = $8{,}445.10^7$ to give molar surface free energies. The ratio of these values to the enthalpies of atomization, α, should represent, according to the model of broken bonds, the fraction of broken bonds with the nearest neighbours, when an bulk atom goes to the surface of the crystal. Actually, for unknown f-values, the ratio of the two energies is equal to α/f. These values are also given in Table 2.

The statistical analysis of the results is similar to that of the *k*-values. The extreme values are 0.087 (Be) and 0.368 (Cd). For the 33 elements, the mean value is 0.182, the standard deviation 0.052, and the standard error of the mean 0.09. Without the values for Be, Si, Re, Zn and Cd, the range of the remaining 28 values is restrained to 0.128… 0.214; the mean value is 0.177, the standard deviation 0.026 and the standard error of the mean 0.005.

The α-value is therefore about 1/5. If we assume, with Mezey and Giber [16], that the effect of the relaxation and reconstruction in the surface layer were equivalent to the recovery of one of the broken bonds, the transition of an atom from the bulk to the surface should thus bring about the splitting of about ¼ of its bonds to the nearest neighbours.

In the case of melted metals, for 64 elements, the average ratio found between molar surface energy and enthalpy of vaporization was 0.18 [8], i.e. the same as here for α/f. This speaks for the model of the broken bonds, and shows that the situation is similar in the case of metal melts and of polycrystalline solid metals.

Among the metals with different crystal structures, no significant differences were found: the mean α/f-value is 0.182 for the 7 metals with body centred cubic lattice and 0.181 for the 9 metals with cubic close packed lattice. There are probably too few available data. According to the theoretical estimations of Mezey and Giber [9] the ratio should be in these two cases 0.184 and 0.192 respectively.

The same ratios calculated from the data of Tyson and Miller [6], the range of values is narrower: the k-values go from 11.40 (Si) to 40.86 (Cd). Other values far from the average are those for Ge (12.06), Be (12.20) and Zn (34.72). For the other elements k varies between 15.00 and 30.72 (α/f between (0.127 and 0.260). The mean value is somewhat lower: k = 19.52 and α/f = 0.165 for 46 elements. Without the extreme values for Si, Ge, Be, Zn and Cd, the mean values become 19.186 and respectively 0.162. These lower ratios can be explained by the fact that the values of the surface free energies refer to the melting point of the solid elements, while the internal free enthalpies of atomization were calculated at 298 K. According to Mezey [9], this ratio should not vary with the temperature, but both quantities should refer to the same temperature.

On the basis of the relations found here, free surface energies for 69 elements were estimated, in three variants:

- from $\gamma_M = k\Delta G_a^i$, with the mean value k = 21
- from $\gamma_M = k\Delta G_a^i$, taking for k the slope of the straight line in eq. (20b): k = 20,1
- from the γ_M-values read on the sigmoidal representation (Fig. 14).

These free surface energies are given as γ_1, γ_2 and γ_3 in Table 3.

By comparison with experimental data (if available) and with calculated values from different authors (cf. Table 1), the most plausible values were selected (as recommended values printed in bold characters in Table 3). Insofar as possible, for elements of the same group in the periodic table the same kind of values was selected.

For non-metals and semi-metals, as Si, Ge, Be, Sb, Te none of the calculated values are suitable. The sigmoidal correlation gives better values for elements of the main groups: group 2 (Mg - Ra), groups 13 (Al - Tl), 14 (Sn - Pb), but also for groups 12 (Zn,Cd) and 15 (V - Ta), or for transition metals with highest values of surface tensions: W, Re. This correlation works also for the bivalent lanthanoides Yb and Eu, whose similarities to elements of the groups 2 and 12 are known, and also for Th and U.

For alkali metals (1st main group) the linear correlation with the lower k-value (γ_2) seems to fit the best; as well as for lanthanoides (except Eu and Yb), elements of group 15 (Sb, Bi) and for Ni and Mo.

The linear correlation with the higher k-value (γ_1) seems to work best for transition metals of the groups 3 (Sc, Y), 4 (Ti - Hf), Mn, groups 8-10 (except Ni), 11 (Cu - Au).

For some elements (Po, At, Ac) there is no possibility to select the best values, since both experimental and calculated values are missing.

Table 3.

Free surface energies (mJ/m^2) of solid metals at standard temperature, estimated from linear correlations for k=21 (γ_1) and for k = 20,1 (γ_2) and from sigmoidal correlation (γ_3). Recommended are the bold values

Element	Li	Be	Na	Mg	Al	Si	K	Ca	Sc
γ_1	550	2230	240	470	1390	1730	130	380	**1230**
γ_2	**530**	2140	**230**	450	1330	1660	**120**	370	1180
γ_3	730	2030	470	**690**	**1280**	1780	300	**470**	1162
Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
γ_1	**1960**	2440	**2110**	**1450**	**2250**	**2410**	2450	**1810**	540
γ_2	1880	2330	2020	1380	2150	2310	**2340**	1730	520
γ_3	2050	**2610**	2020	1320	2220	2390	2450	1640	**900**
Element	Ga	Ge	Rb	Sr	Y	Zr	Nb	Mo	Tc
γ_1	1050	1300	100	290	**1150**	**2120**	2980	2990	**3310**
γ_2	1010	1250	**95**	280	1100	2030	2850	**2860**	3170
γ_3	**960**	1220	260	**390**	1150	2180	**2710**	2950	3180
Element	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
γ_1	**3200**	**2740**	**1750**	**1180**	360	750	930	730	500
γ_2	3060	2620	1680	1130	340	720	890	700	480
γ_3	3200	2910	1650	1080	**700**	**730**	**830**	690	570
Element	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd
γ_1	80	300	1140	1140	950	880	550	370	1090
γ_2	**75**	283	**1090**	**1090**	**910**	**840**	**530**	350	**1050**
γ_3	220	**360**	1140	1140	880	790	590	**440**	1060
Element	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta
γ_1	1100	820	860	910	670	330	1260	**2390**	3250
γ_2	**1050**	**780**	**820**	**870**	**640**	320	**1200**	2290	3110
γ_3	1060	740	770	830	640	**470**	1260	2330	**2750**
Element	W	Re	Os	Ir	Pt	Au	Tl	Pb	Bi
γ_1	3870	3660	**3870**	**3220**	**2620**	**1560**	510	540	510
γ_2	3700	3510	3700	3080	2510	1490	490	520	**490**
γ_3	**3040**	**3160**	3260	3140	2760	1440	**610**	**610**	560
Element	Po	At	Ra	Ac	Th	U			
γ_1	330	220	240	1010	1650	2010			
γ_2	320	210	230	970	1580	1920			
γ_3	500	530	**320**	990	**1710**	**2150**			

Conclusions

The scarcity of direct experimental data for the surface tensions or surface free energies of solid metals make necessary their semi-empirical estimation or the theoretical calculation. Using selected experimental values, their correlation with melting points and standard enthalpies of atomization was verified. „Molar" surface free energies, calculated by means of molar volumes or metallic radii gave acceptable linear correlations with the enthalpies of atomization. With standard free enthalpies of atomization, calculated with the entropies of atomization, obtained as differences between the entropies of gaseous and solid metals, the correlations are almost the same as with standard enthalpies.

In order to improve the calculations, surface free energies at standard temperature were estimated from the experimental values and internal free enthalpies of atomization were calculated, but not significantly better correlations were obtained. The deviations of some elements from the correlation lines can be explained by errors in the experimental data or by peculiarities in their structure.

The results can be interpreted in terms of the theory of broken bonds between neighbouring atoms in the metallic crystals. The correlations found here could be used to estimate values of free surface energies for 69 solid elements.

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