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On the limitations of the applicability of Young's equations temperature

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Abstract

The article uses the thermodynamics of interfacial phenomena to justify the fact that Young's equations can correctly describe the three-phase equilibrium with any type of interatomic bonds.

Wetting, adhesion, dissolution, surface adsorption, and other surface phenomena are important characteristics, which largely determine the quality and durability of materials, and the development of a number of production techniques, including welding, soldering, baking of metallic and non-metallic powders, etc. Therefore, it is important to study them.


Using experimental data regarding surface energies of liquids (melts) and contact angles available in the literature, we calculated the surface energies of many solid metals, oxides, carbides, and other inorganic and organic materials without taking into account the amount of the interfacial energy at the solid-liquid (melt) interface. Some researchers assumed that in case of an acute contact angle the interfacial energy is low. Therefore, they neglected it and assumed it to be zero. Others knew that this value could not be measured, that is why they measured and calculated the difference between the surface energy of a solid and the interfacial energy of a solid and a liquid (melt), which is equal to the product of the surface energy of this liquid by the cosine of the contact angle. It is obvious that these methods of determining the surface energy based on such oversimplified assumptions result in poor accuracy.

Through the use of examples this paper shows how the surface energies of solids were previously calculated and how the shortcomings of previous calculations can be corrected.

Keywords: Surface energy, Interfacial energy, Wetting angle, Nickel, Cobalt, Graphite, Titanium carbide

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1. Introduction

Since T. Young derived the two equations named after him, some researchers of interfacial phenomena have subjected them to revision. Some of them have denied their validity, others have noted their limited applicability, and yet others have tried to derive new alternative equations.

As we know, the first of Young's equations associates the work of adhesion W_A with the surface energy of the liquid (melt) σ_{LV} and the contact angle Θ :

$$W_A = \sigma_{LV} (1 + \cos \Theta). \quad (1)$$

Equation (1) is theoretically and practically reasonable, however, some authors do not recognize the validity of Young's first equation. In [1], N. K. Adam wrote in regards to it that Young not only formulated equation (1) with adhesion, but he also indicated its meaninglessness when W_A is more than $2\sigma_{LV}$.

According to Yu. V Naidich [2], in other words, Young also pointed out the limitations of the applicability of equation (1), although this is sometimes forgotten, and the equation is unjustly criticised due to its inapplicability at $\Theta = 0$.

The second equation derived by Young is represented as following:

$$\cos \Theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}, \quad (2)$$

where σ_{SV} , σ_{SL} , σ_{LV} are the surface energies on the respective three interphase boundaries: solid – vapour, solid – melt, and melt – vapour.

In the case of equation (2) things are more complicated. Despite the fact that equation (2) is over 215 years old, that there are numerous works devoted to its theoretical derivation, and that it is widely applied in practice during analyses of the wettability phenomena, the equation (in the case of solid – liquid – vapour) has still not been experimentally verified. The latter circumstance is due to the fact that to date there are no sufficiently reliable methods to determine the absolute values of the interfacial energies. All this means that Young's equation (2) has regularly been a matter of debate since the moment it was derived [2].

The purpose of this work is to show that in general Young's equations correctly describe the three-phase equilibrium.

2. Methods for calculating the surface energy of solid titanium carbide and graphite

[3] analysed the existing measurement methods and results regarding the surface energy of solid carbides obtained by various authors with the help of Young's equation (2).

The authors of [3] examined the liquid nickel – titanium carbide system (Ni-TiC). The wetting angle of nickel on titanium carbide equals 4° in a vacuum at a temperature of 1728 K. Assuming that σ_{SL} is zero, and the surface energy of nickel equals 1934 mJ/m², the authors inserted the respective values in Young's equation (2) and found the surface energy of titanium carbide:

$$\sigma_{SV} = 0 + 1934 \cdot 0.998 = 1930 \text{ mJ/m}^2 \quad (3)$$

The authors then pointed out that their assumption that $\sigma_{SL} = 0$ may be wrong, and the surface energy of titanium carbide can be expected to have higher values of σ_{SV} .

Similar calculations were performed by the authors of [3] to determine the minimum surface energy of graphite. Pure liquid cobalt with graphite in a vacuum at a temperature of 1773 K has a contact angle of 35° . The authors assumed that the surface energy of liquid cobalt was equal to 1942 mJ/m² and σ_{SL} was equal to zero, and according to equation (2) the value for the minimum surface energy of graphite in an atmosphere of cobalt vapour was equal to 1590 mJ/m². In this case, this value was also underestimated by the unknown value of σ_{SL} .

Until recently, researchers were unable to calculate the interfacial energy σ_{SL} . Therefore, they had to be satisfied with calculating either the difference of $\sigma_{SV} - \sigma_{SL}$ or they assumed that at the contact angle of $\sigma < \pi/2$ the interfacial energy was low and neglected it as stated above, for example in [3–7].

Earlier in [8], a thermodynamic formula was obtained to calculate σ_{SL} using the known values of the surface energy of the liquid (melt) σ_{LV} and the wetting angle Θ :

$$\sigma_{SL} = \sigma_{LV} \left(\frac{2 - 3 \cos \Theta + \cos^3 \Theta}{4} \right)^{1/3}. \quad (4)$$

If we insert the above-mentioned numerical values in formula (4) or use a table based on formula (4), then for the Ni-TiC system [8–9]:

$$\sigma_{SL} = 1934 \cdot \left(\frac{2 - 3 \cdot 0.9976 + 0.9976^3}{4} \right)^{1/3} = 32 \text{ mJ/m}^2. \quad (5)$$

A similar calculation for the system of cobalt-graphite will have a result where $\sigma_{SL} = 553 \text{ mJ/m}^2$.

During calculations, we used a previously prepared table of relative values of σ_{SL}/σ_{LV} depending on the contact angle.

Taking into account the recent results for σ_{SL} , the surface energies of solid titanium carbide and graphite will be equal to 1962 and 2144 mJ/m² respectively.

The work of adhesion of nickel to titanium carbide and cobalt to graphite can be calculated by two identical equations: by equation (1) and by the Dupré equation:

$$W_A = \sigma_{SV} + \sigma_{LV} - \sigma_{SL}. \quad (6)$$

By inserting numerical values, for example, in (6), we will obtain the following:

$$W_{A1}(\text{Ni-TiC}) = 3864 \text{ mJ/m}^2,$$

$$W_{A2}(\text{Co-graphite}) = 3532 \text{ mJ/m}^2.$$

Inserting numerical values in (1) with an accuracy of $\pm 1 \text{ mJ/m}^2$ produced results consistent with the results obtained from equation (6).

And here is another example:

[4] studied the influence of silicon on the interfacial properties of low-carbon liquid steel. The researchers calculated the contact angles formed by steel on a substrate of chromium oxide Cr_2O_3 depending on the silicon concentration in the steel.

In [4], we were interested in the numerical values of contact angles, but the authors presented them in the form of graphs, so based on the differences of $\sigma_{SV} - \sigma_{SL}$ provided by the authors and their experimental data regarding the surface tension of liquid steel, we calculated contact angles Θ for each concentration of silicon in steel. The differences of $\sigma_{SV} - \sigma_{SL}$ for a substrate of Cr_2O_3 not only decreased with increasing silicon concentration, but even changed the sign, which indicates the good wettability by liquid silicon and chromium oxide melts. Then, knowing the contact angles and the surface tensions of melts, we were able to calculate the interfacial characteristics: σ_{SL} , σ_{SV} , and W_A . What is more, σ_{SV}

and σ_{SL} were calculated as separate values rather than as differences.

Hereinafter, we will consider another aspect of the problem concerning the determination of interfacial energy at the solid-liquid (melt) interface. For this purpose, we will use the data of the surface energy of solid chromium oxide provided in [10]. The authors provided the value for the surface energy of chromium oxide at $T = 0 \text{ K}$: $\sigma_{SV} = 1400 \text{ mJ/m}^2$. The value of the temperature coefficient is $d\sigma_{SV}/dT = -0.25 \text{ mJ}/(\text{m}^2 \cdot \text{K})$. If we combine these data with the data obtained in [4], namely the isotherm of contact angles Θ , and use the concentration relation of the surface tension of liquid silicon at the measurement temperature for contact angles $T_{\text{mes}} = 1823 \text{ K}$, then:

$$\begin{aligned} \sigma_{SV}(1823 \text{ K}) &= 1400 - 0.25(1823 - 0) = \\ &= 1400 - 456 = 944 \text{ mJ/m}^2. \end{aligned}$$

After that, we will find the interfacial energy at the solid oxide - liquid steel interface by formula (2) using the value of $\sigma_{SV} = 944 \text{ mJ/m}^2$ and compare them with our calculations.

Tables 1 and 2 show the results obtained.

3. Discussion

It follows from the above that until recently, it was impossible to take into consideration the interfacial energy σ_{SL} when calculating the surface energy of solids since it was not experimentally measurable and there was no separate formula to calculate it. The formula derived by us allows determining σ_{SL} within the range of the contact angle starting from 1° up to 180° . A wetting angle equal to zero is a singular point at which the interfacial energy σ_{SL} is zero, which also follows from formula (4).

For this three-phase system the smaller the contact angle, the lower the interfacial energy at the solid-liquid (melt) interface. In case of ($\Theta < 90^\circ$) the value of the surface free energy of a solid at the interface with saturated vapour of a liquid is determined as a sum of the interfacial energy σ_{SL} and $\sigma_{LV} \cdot \cos \Theta$, wherein with an increasing contact angle the contribution of σ_{SL} grows much faster than that of σ_{LV} . At ($\Theta > 90^\circ$), on the contrary, the closer to 180° , the smaller the surface energy of a solid is. If a wetting angle of 180° was achievable, the surface energy of the solid would be equal to zero.

Table 1. The dependence of the interfacial characteristics on the silicon concentration in the system of solid chromium oxide - low carbon liquid steel

Si, at%	Cr ₂ O ₃ substrate					W _A , mJ/m ²
	σ _{LV} , mJ/m ²	Θ, degree	-(σ _{SV} - σ _{SL}), mJ/m ²	σ _{SL} , mJ/m ²	σ _{SV} , mJ/m ²	
1.0	1430	110	490	1297	808	940
4.0	1360	98	190	1150	960	1170
9.5	1300	87	-65	1004	1072	1365
18.0	1200	87	-63	927	990	1263
25.4	1040	76	-250	713	964	1291
34.0	820	62	-385	458	843	1205
45.0	715	48	-460	299	777	1193

Table 2. Deviation of Δσ_{SV} and Δσ_{SL} from the initial calculations

1	Δσ _{SL1} = 136
2	Δσ _{SV1} = 136
3	Δσ _{SL2} = -86
4	Δσ _{SV2} = -86
5	Δσ _{SL3} = -128
6	Δσ _{SV3} = -128
7	Δσ _{SL4} = -46
8	Δσ _{SV4} = -46
9	Δσ _{SL5} = -20
10	Δσ _{SV5} = -20
11	Δσ _{SL6} = 101
12	Δσ _{SV6} = 101
13	Δσ _{SL7} = 167
14	Δσ _{SV7} = 167

Table 2 implies the most interesting fact that an increase in σ_{SL} means a similar increase in σ_{LV}. The reduction in σ_{SL} results in a similar reduction in σ_{LV}. At the same time, the work of adhesion remains unchanged. This is understandable, since in the Dupré expression the surface energy of a solid and the interfacial energy at the solid - liquid (melt) interface have different signs. The changing surface energy of a solid is compensated with interfacial energy. This surprising phenomenon is probably due to the effect of the adsorption of liquid vapours on the surface energy of a solid which causes a simultaneous modification of σ_{LV} and σ_{SL} when the contact angle changes.

4. Conclusions

1. The validity of Young’s equations was shown by examples of contact between highly energetic surfaces.

2. Interfacial energies of titanium carbide at the interface with liquid nickel and graphite with liquid cobalt were calculated for the first time.

3. Surface energies of solid titanium carbide and graphite were determined considering the interfacial energies of the respective systems.

4. The work of adhesion of liquid metals to titanium carbide and graphite were calculated respectively.

5. The deviations between interfacial energies σ_{SL} and surface energies σ_{SV} calculated using a constant value and by our method were found.

6. It was shown that the larger the contact angle is, the greater is the contribution of interfacial energy to the surface energy of solids within an acute contact angle.

Conflict of interests

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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