From our readers

NEGATIVE SURFACE ENERGY — CLEARING UP CONFUSION

To the editor – We noted with interest the results of Lodziana *et al.*[1] regarding surface energy for θ-alumina. Their use of the provocative term "negative surface energy" can and has caused confusion in the scientific community. Here we offer a clarification in order to present the appropriate context for their work.

In a single-component system, the 'surface energy' of the solid is, to be precise, the interfacial energy of the solid in equilibrium with a vapour of the same chemical species. In thermodynamic terms this quantity is the reversible work, that is, the change in Gibbs free energy of the system (at constant temperature and pressure), per unit new surface area. In this system, the Gibbs dividing surface can be located arbitrarily so that there is no 'surface excess' quantity, which is to say that because the solid is surrounded by its own vapour, there are no chemical effects to consider. For all stable solids then, energy input is required for creating new surface area and hence all clean solids have positive surface energies. As such, references to a solid's 'surface energy' in literature, unless noted, refer to a single-component system, that is, a clean solid surface without adsorbed components.

The situation is slightly more complicated in a multicomponent system (such as θ-alumina + water), where chemical effects must be considered. In such a system, the Gibbs dividing surface can be located such that there is no excess term for one component, but this only leads to non-zero excess quantities for the other components, which alters the solid's surface energy. Physically, this is a result of the interaction energies between the solid surface and the other components. So, in addition to reversible work for creation of new (clean) surface area, surface energy here also includes chemical interactions between the newly formed surface and the surroundings. Adsorption on solid surfaces is typically an exothermic process and it reduces the solid's surface energy in this manner; if energy of adsorption is large enough, it can result in a negative surface energy. Others have indeed shown that chemical effects can lead to negative surface energies[2,3].

It is therefore possible to predict positive and negative surface energies for any number of multicomponent systems, whereas surface energy in a single-component system is positive for all stable solids, including clean θ-alumina[1].

References

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AUTHORS' RESPONSE

In their comment, Mathur, Sharma and Cammarata nicely summarize and clarify definitions of surface energies for single- and multicomponent systems. Surface energy for single-component systems is always positive, whereas for multicomponent systems it can become negative under certain conditions. It is an important conclusion from our density functional theory calculations that the surface energy of θ-alumina can become negative in the presence of water.

Mathur, Sharma and Cammarata go on to discuss whether the single- or multicomponent surface energy is the critical parameter. We agree that in idealized situations (like in an ultra-high vacuum experiment, for instance) the surface energy (or surface stress) without effects due to interactions with the surroundings is the quantity of interest, but for most conditions (including those where transition aluminas are synthesized) the effect of the surroundings is very important and cannot be neglected. Indeed, the other new result of our paper is that for such multicomponent systems a negative surface energy can lead to porous equilibrium structures or small stable nanoparticles.

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