The chemical (not mechanical) paradigm of thermodynamics of colloid and interface science

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Abstract

In the most influential monograph on colloid and interfacial science by Adamson three fundamental equations of "physical chemistry of surfaces" are identified: the Laplace equation, the Kelvin equation and the Gibbs adsorption equation, with a mechanical definition of surface tension by Young as a starting point. Three of them (Young, Laplace and Kelvin) are called here the "mechanical paradigm". In contrary it is shown here that there is only one fundamental equation of the thermodynamics of colloid and interface science and all the above (and other) equations of this field follow as its derivatives. This equation is due to chemical thermodynamics of Gibbs, called here the "chemical paradigm", leading to the definition of surface tension and to 5 rows of equations (see graphical abstract). The first row is the general equation for interfacial forces, leading to the Young equation, to the Bakker equation and to the Laplace equation, etc... Although the principally wrong extension of the Laplace equation formally leads to the Kelvin equation, using the chemical paradigm it becomes clear that the Kelvin equation is generally incorrect, although it provides right results in special cases. The second row of equations provides equilibrium shapes and positions of phases, including sessile drops of Young, crystals of Wulff, liquids in capillaries, etc. The third row of equations leads to the size-dependent equations of molar Gibbs energies of nano-phases and chemical potentials of their components; from here the corrected versions of the Kelvin equation and its derivatives (the Gibbs-Thomson equation and the Freundlich-Ostwald equation) are derived, including equations for more complex problems. The fourth row of equations is the nucleation theory of Gibbs, also contradicting the Kelvin equation. The fifth row of equations is the adsorption equation of Gibbs, and also the definition of the partial surface tension, leading to the Butler equation and to its derivatives, including the Langmuir equation and the Szyszkowski equation. Positioning the single fundamental equation of Gibbs into the thermodynamic origin of colloid and interface science leads to a coherent set of correct equations of this field. The same provides the chemical (not mechanical) foundation of the chemical (not mechanical) discipline of colloid and interface science.

Keywords: thermodynamics; fundamental equation; colloids; interfaces; Gibbs