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A Coherent Definition of Henry Constant and Isothermic Heat at Zero

Loading for Adsorption in Solids

An Absolute Accessible Volume

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Abstract

We present a new analysis of the Henry's law constant and isothermic heat at zero coverage for gas adsorption on solid surfaces, which removes the ambiguities inherent in earlier definitions [1]. A new definition of accessible volume ensures physical self-consistency between these two properties. We show that an earlier definition of accessible volume, as the volume within which the adsorbate-adsorbent potential energy is non-positive, is too restrictive because it neglects the penetration of molecules with large kinetic energies into the highly repulsive (positive) regions of the potential, which occurs more frequently at higher temperatures. The new definition has been tested for a number of adsorbents, and for a wide range of adsorbates commonly used in the characterization of porous solids. In particular, we have highlighted the differences between the old and new definitions of the Henry constant and the isothermic heat at zero loading. Our analysis also reveals that, contrary to a common assumption made in the adsorption literature, the van't Hoff plot is non-linear, and linearity is only satisfied over a narrow range of temperature.

Keywords: Adsorption; Henry constant; Isothermic heat; Accessible volume

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