Consistent Approach to Adsorption Thermodynamics on Heterogeneous Surfaces Using Different Empirical Energy Distribution Models

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Adsorption on heterogeneous surfaces with three basic energy distribution models (uniform model, exponential model, and normal-like model) is studied. Exact analytical solutions of the adsorption isotherms and the heats of adsorption are derived for the uniform and exponential models, and, with these solutions including a numerical solution for the normal-like model, the behavior of the differential heat of adsorption and the "apparent" standard adsorption entropy concerning the overall surface is described as a function of coverage and temperature. The approximations underlying the isotherms and heats of adsorption in the Temkin, Freundlich, and Langmuir−Freundlich types of adsorption are rationalized. By comparing these empirical formulas to the exact solutions, the level of these approximations is found to be identical, which is similar to the "condensation approximation". Their preconditions are that either the temperature is low enough, or the surface is strongly heterogeneous. Generally, they are suitable for the middle coverage range. The exact solutions provide a method to obtain more information on the heats, entropy, and heterogeneity of the catalyst surface from the calorimetric measurement of the heat of adsorption.