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 underlining 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.

1. Introduction

The direct description of adsorption on a heterogeneous surface is to regard the surface as being composed of different types of homogeneous sites with a certain normalized distribution function of energy, assuming that there is no interaction between the adsorbates on the different types of adsorption sites and that there is no transformation of adsorption sites during adsorption. With a stable differential distribution \( f(\epsilon) \) of the number of adsorption sites corresponding to adsorption energy \( \epsilon \),

\[
\int_{\varOmega} f(\epsilon) \, d\epsilon = 1
\]  

(1)

the overall coverage is given by

\[
\Theta = \int_{\varOmega} \theta(\epsilon)f(\epsilon)\,d\epsilon
\]  

(2)

where \( \theta(\epsilon) \) is the equilibrium coverage on energetically homogeneous sites with adsorption energy \( \epsilon \), \( \Theta \) is the averaged equilibrium coverage on energetically heterogeneous sites, and \( \varOmega \epsilon \) is the domain of \( \epsilon \). The associative adsorption on local sites with identical energy is of the Langmuir type:

\[
\theta = \frac{K_p}{1 + K_p f(\epsilon)}
\]  

(3)

where \( K \) is the Langmuir coefficient. So the key problem is to solve the integral eq 2 with different \( f(\epsilon) \) and the kernel of eq 3, especially to obtain the empirical isotherms dealing with chemisorption on a heterogeneous surface. There are two directions relating these isotherms to energy distributions: either to obtain an exact solution from a simple \( f(\epsilon) \), or to derive an exact \( f(\epsilon) \) from an empirical isotherm. The exact \( f(\epsilon) \) functions were obtained from the Langmuir—Freundlich isotherm, from another generalized Freundlich isotherm, from the Dubinin—Radushkevich isotherm, and from a generalized Dubinin—Radushkevich isotherm, but these \( f(\epsilon) \) forms are too complicated for the description of a real surface.

On the other hand, several empirical isotherms are proposed based on simple \( f(\epsilon) \): the Freundlich isotherm is related to an exponential \( f(\epsilon) \), and the Temkin isotherm is related to a uniform \( f(\epsilon) \), which can be deduced approximately either from the relation between \( \Theta \) and the differential heat of adsorption \( q^{\text{diff}} \) or from \( f(\epsilon) \). The only exact solution for the isotherm from these simple distributions was derived for the uniform \( f(\epsilon) \). Da Rocha et al. tried to solve the isotherm for the exponential \( f(\epsilon) \), but they did not obtain a final solution. Because of the difficulties encountered when solving eq 2, the “condensation approximation” (CA) method was proposed and applied. With this method, Rudziński et al. obtained the Temkin isotherm from the uniform \( f(\epsilon) \), the Freundlich isotherm from the exponential \( f(\epsilon) \), and the Langmuir—Freundlich isotherm from a normal-like \( f(\epsilon) \).