LATTICE MODELS OF THE ADSORPTION OF DIATOMIC MOLECULES

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In the study of physical adsorption on solid adsorbents, the orientation of the adsorbed molecules relative to the surface is usually not taken into account. However, in the construction of the theoretical model of the adsorption of nonspherical molecules one must take into account the possibility of the different orientations of the adsorbed molecules and also their reorientation with a change in the equilibrium pressure (occupancy). A reorientation must obviously be reflected in the thermodynamic characteristics of the system — for example, in the shape of the adsorption isotherms and the dependence of the heat of adsorption on the occupancy. It is desirable to investigate the question of the influence of the reorientation of adsorbed molecules on the properties of a system by the methods of statistical mechanics, beginning with a lattice model which, apparently, describes the most fundamental features of the phenomenon in qualitatively correct fashion. To describe the system, use has been made of the statistical sum of the states $\mathcal{Z}$, which in the case of a lattice model is a function of the chemical potential $\mu$, the temperature $T$, and the number of active centers $B$ [1]. The monolayer adsorption of $N$ molecules on a system of $B$ centers forming a regular lattice has been considered. As is customary in lattice models, the adsorption was assumed to be equal to the total number of molecules on the surface, and not the Gibbsonian excess. The interaction of the adsorbed molecules with one another was not taken into account. In the present work, the reorientation of diatomic molecules, which can be adsorbed both "vertically" (occupying one center) and "horizontally" (occupying two centers) has been investigated. One of the main assumptions was that the distance between the centers of the lattice was taken to be close to the interatomic distance in the adsorbed molecules. The state of the system is defined by the numbers $n_1$ and $n_2$ (the number of vertically and horizontally adsorbed molecules with adsorption energies equal to $\varepsilon_1$ and $\varepsilon_2$, respectively).

It must be noted that to obtain the correct thermodynamic characteristics it is necessary to consider an infinitely large system with fixed intensive parameters (temperature, chemical potential, etc.). In all conclusions, explicitly or implicitly, the method of the maximum term is used; i.e., in essence it contains a transition to the thermodynamic limit at $B \to \infty$, $N \to \infty$ (N/B=const).

1. One-Dimensional Model

In the case of the one-dimensional model it is possible to write an accurate expression for the total statistical sum of the system considered. One of the possible (equivalent) variants of this expression has the form

$$\mathcal{Z}(\mu, T, B) = \sum_{N=0}^{B} Q(N, B, T) y^N = \sum_{N=0}^{B} \sum_{n_1=0}^{N} \sum_{n_2=0}^{N} \frac{(N + n_1)!}{n_1! n_2! n_3!} \prod_{i=1}^{3} r_i^{n_i} y^N,$$

where $Q(N, B, T)$ is the canonical sum, $y = e^{\mu/kT}$ is the absolute activity, $n_0$ is the number of free centers, and $j_1 = \int J_1 e^{-\varepsilon_1/kT} d\varepsilon$, $j_2 = \int J_2 e^{-\varepsilon_2/kT} d\varepsilon$, where $j_1$ and $j_2$ are the sums over the states of the internal degrees of freedom of the adsorbed molecules and for the degrees of freedom connected with the motion of the molecules in the neighborhood of an adsorption center (for molecules adsorbed vertically and horizontally, respectively). The combinatorial member shows what number of methods can be used for $B$ centers of a one-dimensional...
lattice of $n_1$ vertically and $n_2$ horizontally adsorbed molecules. The variables appearing in the total statistical sum are connected by the relations

$$n_1 + n_2 = N; \quad B - n_1 - 2n_2 = \nu.$$  

Consequently, the summation in (1) is performed with respect to two variables the choice of which is arbitrary and is determined by convenience in the solution of the concrete case.

**Derivation of the Equation of the Adsorption Isotherm**

The equation of the adsorption isotherm can be represented in two equivalent forms: $p = \rho(\Theta_\Sigma)$ and $\Theta_\Sigma = \Theta_\Sigma(p)$, where $p$ is the equilibrium pressure of the gas undergoing adsorption and $\Theta_\Sigma = N/B$ is the total degree of occupancy. Both forms are obtained from expression (1) with the appropriate choice of variables in the summation.

a) Derivation of the Equation $p = \rho(\Theta_\Sigma)$. The replacement of the summation with respect to $n_2$ in Eq. (1) by the maximum term of the sum enables the most probable number of horizontally adsorbed molecules to be determined as a function of the total number of adsorbed molecules $N$:

$$n_2 = \frac{1}{2} \left( B - \sqrt{B^2 - 4N(B - N)\frac{I_2}{I_1 + I_2}} \right).$$

An analogous substitution in the sum with respect to $N$, corresponding to the condition $\partial (\ln \Theta_\Sigma^N/\partial N) = 0$, taking into account the relation $n_2 = n_2(N)$ obtained leads to the equation of isothermal adsorption in the form

$$y = \frac{2N - B + \beta'}{I_1(B - 2N + \beta')},$$

where

$$\beta' = \sqrt{B^2 - 4N(B - N)\frac{I_2}{I_1 + I_2}}.$$  

If the numerator and denominator are divided by $B$, we obtain

$$y = \frac{2\theta_2 - 1 + \beta}{I_1(1 - 2\theta_2 + \beta)},$$

where

$$\beta = \beta'/B = \sqrt{1 - 4\theta_2(1 - \theta_2)\frac{I_2}{I_1 + I_2}}.$$