Simulation of BET Type Adsorption

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With 2 figures and 3 tables

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Two adsorption models, Langmuir type and BET type (1), are most frequently used in the field of colloid science. In a previous paper (2), the author has shown that the Monte Carlo calculation can be successfully applied to the Langmuir type adsorption kinetics. This paper deals with the similar calculation applied to the BET adsorption.

The adsorption model can be simulated in a digital computer only when the number of allowable adsorption layers is limited to a finite value because the computer cannot treat properly a mathematical infinity. In principle, therefore, the present method cannot be applied to an ordinary BET adsorption, in which the number of adsorption layers increases infinitely at the condensation pressure of the adsorbate. This theoretical drawback is not prominent at the adsorbate pressure sufficiently lower than the condensation pressure, or to the partial pressure \( p \) in the case of a gas phase. The adsorption probability for a molecule that has collided with a bare site, \( a_0 \), is a constant dependent on the species of the adsorbate and the surface. The adsorption probability of a molecule that has collided with a site already occupied with one or more (up to 8) molecules, \( a \), is a constant dependent on the species of the adsorbate alone. If we denote the number of bare sites by \( n_0 \), the number of singly occupied sites by \( n_1 \), the number of doubly occupied sites by \( n_2 \), and so on, the number of adsorptions per unit time onto the bare sites is given by

\[
A_0 = a_0 n_0
\]

and that onto the occupied sites by

\[
A = \alpha n (n_0 + n_1 + \ldots + n_8).
\]

The mean lifetime of a molecule in the first layer (not covered with the second layer), \( \tau_1 \), is a constant dependent on the species of the adsorbate. The number of molecules which collide with one site per unit time, \( n \), is proportional to the concentration \( C \) in the coexisting phase, or to the partial pressure \( p \) in the case of a gas phase. The adsorption probability \( a_0 \) for a molecule that has collided with a bare site is a constant dependent on the species of the adsorbate and the surface. The adsorption probability of a molecule that has collided with a site already occupied with one or more (up to 8) molecules, \( a \), is a constant dependent on the species of the adsorbate alone. If we denote the number of bare sites by \( n_0 \), the number of singly occupied sites by \( n_1 \), the number of doubly occupied sites by \( n_2 \), and so on, the number of adsorptions per unit time onto the bare sites is given by

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adsorbate and the surface. The number of desorptions per unit time from the first layer is given by \( D_1 = \frac{n_1}{\tau} \). Similarly, that from the second and higher layers is given by \( D = \frac{(n_2 + n_3 + \ldots + n_b)}{\tau} \), where \( \tau \) is the mean lifetime of a molecule in the top of a pile of 2 \( \sim \) 9 adsorbate molecules and is a constant dependent on the species of the adsorbate alone.

Defining \( a_0' = a_0 n \) (\( \propto C \) or \( p \)), \( a' = \alpha n \) (\( \propto C \) or \( p \)), \( d_1' = \frac{1}{\tau} \) (constant), and \( d' = \frac{1}{\tau} \) constant), we get

\[
A_0 = a_0' n_0, \quad A = a' (n_1 + n_2 + \ldots + n_b) \\
D_1 = d_1' n_1, \quad D = d' (n_2 + n_3 + \ldots + n_b) \\
n_0 + n_1 + n_2 + \ldots + n_b = 1000. \tag{1}
\]

Here, \( a_0' \) means the number of adsorptions per unit time onto a bare site\(^1\). The meanings of \( a' \), \( d_1' \), and \( d' \) are apparent and need no explanation.

The two kinds of adsorptions and two kinds of desorptions are perpetually taking place at all one thousand sites, but we cannot specify a priori where and in what order individual processes occur. These processes occur quite at random, although the ratio of their occurrence must be statistically \( A_0 : A : D_1 : D \). Now let us choose a positive number (including zero) \( n_0' \) provisionally, and define \( a_0, a, d_1, d, \) and \( n_0 \) so as to make (2) hold.

\[
\begin{align*}
\frac{a_0'}{a_0} &= \frac{a'}{a} = \frac{d_1'}{d_1} = \frac{d'}{d} = \frac{n_0'}{n_0} \\
 &= \frac{a_0' + a' + d_1' + d'}{1000} \\
a_0 + a + d_1 + d + n_0 &= 1000 \tag{2}
\end{align*}
\]

From (1), we get

\[
\begin{align*}
A_0 &= a_0 n_0 (a_0' + a' + d_1' + d' + n_0')/1000 \\
A &= a (n_1 + n_2 + \ldots + n_b) (a_0' + a' + d_1' + d' + n_0')/1000 \\
D_1 &= d_1 n_1 (a_0' + a' + d_1' + d' + n_0')/1000 \\
D &= d (n_2 + n_3 + \ldots + n_b) (a_0' + a' + d_1' + d' + n_0')/1000. \tag{3}
\end{align*}
\]

The following procedure is applied to simulate the adsorption reaction. A three-digit random number ranging from 000 to 999 is picked out and \( a_0 \) is added to it. 1. If a carry or overflow to the fourth digit occurs, an adsorption-onto-vacant-site trial is carried out. A three-digit random number is picked out again. If the storage addressed by this number contains a numeral 0, it is replaced by 1 because the site is vacant and able to adsorb a molecule. The number of adsorbed molecules is increased by one. Alternatively, if the storage contains a numeral from 1 to 9, it is left as such because the site is already occupied. 2. If the carry does not occur, \( a \) is added to the sum of \( a_0 \) and the (first) random number. If the carry occurs at this stage, an adsorption-onto-occupied-site trial is tried. Namely, if the storage specified by the second random number contains a numeral from 1 to 8, it is increased by one. The number of adsorbed molecules is increased by one, too. 3. If the carry does not occur when \( a_0 \) and \( a \) are added to the first random number, \( d_1 \) is added to their sum. In a similar manner as above, a desorption-from-first-layer trial or a desorption-from-higher-layer trial may be carried out. The former desorption is realized if the carry occurs at the stage where \( d_1 \) is added and if the storage specified by the second random number contains 1. The latter desorption is realized if the carry occurs at the stage where \( d \) is added and if the storage specified by the second random number contains 1. The number of executed trials is increased by one. To save calculation time, one may alter the order of additions of the four parameters at will. In the program shown in table 1, these parameters are added to the random number in the order of \( d, a, a_0, \) and \( d' \).

If the order is, for example, \( a_0 \rightarrow a \rightarrow d_1 \rightarrow d \), an adsorption-onto-vacant-site trial should be carried out when the first random number is one of the numbers between 999 and 1000 \(- a_0 \). The probability of this trial executed is \( a_0/1000 \). The probability that the storage specified by the second random number contains a numeral 0 is \( n_0/1000 \). Therefore, the probability that the adsorption-onto-vacant-site is realized by one trial, is equal to \( a_0 n_0/10^6 \). Similarly, an adsorption-onto-occupied-site trial is carried out for the first random number in the range from

\(1\) The same symbol \( a_0' \) was used to represent the number of adsorptions per unit time onto 10000 bare sites in the previous paper (2). Care must be taken if one reads through the previous and present papers.