AN ADSORPTION ISOTHERM OF MULTI-SITE OCCUPANCY MODEL FOR HETEROGENEOUS SURFACE

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An adsorption isotherm for a heterogeneous surface is described on the basis of a multi-site occupancy model followed by a group-contribution assumption. Equations of single- and multi-component adsorptions are derived for systems of molecules consisting of several functional groups and a surface composed of active sites of different energies interacting with the groups independently. The isotherm equation reduces to the expression derived by Sparnaay in the special case where a molecule occupies one site of the surface.

The theory is applied to adsorption equilibria for systems of oxygen, nitrogen, and carbon monoxide on Molecular Sieves 5A and 10X. Correlations of single-component isotherms are excellent for nitrogen and oxygen and fairly good for carbon monoxide; predictions of adsorption isotherms of binary gas mixtures are made satisfactorily by means of parameters determined from the best fit to each single-component isotherm.

1. Theory
1.1 Theoretical framework
To simplify the theoretical treatment, single-component adsorption isotherm is the decrease of the slope of adsorption against pressure. Sparnaay suggested many types of isotherms having a low slope of adsorption by assuming different kinds of active sites; however, the fundamental equation is based on the Langmuir model, characterized as a localized monolayer in which a molecule occupies one active site.

In a previous paper concerning a multi-site occupancy model, the authors pointed out that the slope of an adsorption isotherm decreases with increasing number of sites occupied by a molecule even when a homogeneous surface is assumed. An extension to a heterogeneous surface of the multi-site occupancy model is given here, which may be characterized as a method of group contributions. Numerical examples and an application to adsorptions on Molecular Sieves are included.
where \( N_{ai} \) is the number of adsorption-pairs of sites \( a \) and a group \( i; \{N_{ai}\} \) is a distribution of adsorption pairs \( \{N_{a0}, N_{a1}, \cdots, N_{am}\} \) where the subscript \( a0 \) stands for the site \( a \) to be empty; \( g(N, M, \{N_{ai}\}) \) is a combinatorial factor, which is the number of distinguishable ways of distributing the \( N \) molecules on the \( M \) sites under the condition of a specified distribution \( \{N_{ai}\} \); \( g(N, M, \{N_{ai}\}) \) is the internal and vibrational partition function of a molecule, which is assumed to be independent of the frequency of molecular vibration on the surface.

It is difficult to find a rigorous expression of \( g(N, M, \{N_{ai}\}) \) by taking into consideration the mutual correlations between neighboring sites and neighboring groups in a molecule. A simple expression is obtained by assuming that each pair of adsorptions \( \{ai\} \) is independent under constraints for a distribution of \( \{N_{ai}\} \). The assumption and procedure are similar to the quasi-chemical approximation presented by Guggenheim for molecule-molecule interactions (cf. chapter 14 of Hill’s text \(^3\)). The expression is given as

\[
\ln g(N, M, \{N_{ai}\}) = \ln g_0(N, M) - \sum_{a=a_0}^{m} \sum_{i=0}^{k} \ln \left( \frac{N_{ai}}{N_{ai}^*} \right) \tag{2}
\]

where \( g_0 \) is the combinatorial factor for a homogeneous surface and the superscript \( * \) stands for the random distribution corresponding to the homogeneous surface. The expression for \( g_0 \) is given as

\[
g_0(N, M) = \frac{M!}{N!(M-nN)!} \cdot \frac{\zeta^N}{M^{(n-1)N}} \tag{3}
\]

where \( \zeta \) is a constant relating to flexibility and the symmetric number of a molecule; \( n \) is the number of sites occupied by a molecule, given by the sum of all \( n_i \)’s \( (i=1, 2, \cdots, k) \). Substituting Eq. (2) into Eq. (1) and replacing the summation by the maximum term on the right-hand side of Eq. (1), we obtain the expression of \( \ln Q \) as

\[
\ln Q = N \ln j_a + \ln g_0 + \sum_{a=a_0}^{m} \sum_{i=0}^{k} \left\{ \ln \left( \frac{N_{ai}}{N_{ai}^*} \right) + \frac{N_{ai}}{kT} \beta_i \right\} \tag{4}
\]

There are constraint conditions for the numbers of adsorption pairs \( \{N_{ai}\} \).

\[
\sum_{a=a_0}^{m} N_{ai} - n_i N = 0 \quad (i = 1, \cdots, k) \tag{5}
\]

\[
\sum_{j=0}^{k} N_{aj} - M_a = 0 \quad (a = a, \cdots, m) \tag{6}
\]

The problem to be solved may now be expressed as that of determining the adsorption-pairs distribution \( \{N_{ai}\} \) which minimizes the Helmholtz energy of the system (or maximizes \( Q \)) subject to constraints of Eqs. (5) and (6); thereafter, thermodynamic properties such as the chemical potential, the spreading pressure, the internal energy, etc. are derived from partial differentiations of \( \ln Q \) with respect to \( N, M, \) or \( T \). The method of undetermined multipliers is used to determine the distribution \( \{N_{ai}\} \). From the condition of the maximum point with respect to variables \( \{N_{ai}\} \), we obtain the relations as

\[
-\ln \left( \frac{N_{ai}}{M_a - \sum_{j=1}^{k} N_{aj}} \right) + \frac{\beta_i}{kT} = 0 \tag{7}
\]

where \( \beta_i \) is a Lagrange multiplier relating to a group \( i \) originated from Eq. (5).

1.2 Chemical potential, spreading pressure, and internal energy

The chemical potential of an adsorbate \( \mu^* \), the spreading pressure of an adsorbed phase \( \Phi \), and the internal energy \( U \) are derived from the partition function \( Q(N, M, T) \) according to a conventional procedure. Analytical expressions for each thermodynamic property are summarized here; some additional relations are needed in the derivations, the details of which are given in Appendix 1.

Chemical potential:

\[
\frac{\partial \ln Q}{\partial N} = -\frac{\mu^*}{kT} \tag{8}
\]

Surface pressure:

\[
\Phi = \frac{\partial \ln Q}{\partial M} \tag{9}
\]

Internary energy:

\[
U = kT \left( \frac{\partial \ln Q}{\partial T} \right) = -NK \left( \frac{\partial j_a}{\partial (1/T)} \right) - \sum_{a=a_0}^{m} \sum_{i=0}^{k} N_{ai} \left[ \frac{\partial \beta_i}{\partial (1/T)} \right] \tag{10}
\]

1.3 Surface coverages, definitions and calculation

Three kinds of surface coverages, \( \theta, \{\theta_i\} \) and \( \{\theta_{ai}\} \), are defined as follows:

\[
\begin{align*}
\theta & = \frac{1}{m} \sum_{a=a_0}^{m} \frac{N_{ai}}{M_a} \\
\{\theta_i\} & = \left\{ \frac{1}{m} \sum_{a=a_0}^{m} \frac{N_{ai}}{M_a} \right\}
\end{align*}
\]
The constraint condition of Eq. (5) and the stationary-point condition of Eq. (7) are rewritten by use of surface coverages as follows.

\[ \sum_{\alpha} f_{\alpha} \theta_{\alpha} = \theta_i \quad (i = 1, \cdots k) \]  
\[ \theta_{\alpha i} = \frac{\theta_{\alpha i} r_{\alpha i}}{1 - \sum_{j=1}^{k} \theta_{s j}} \quad (\alpha = a, \cdots m; i = 1, \cdots k) \]

where

\[ r_{\alpha i} = \exp \left( \frac{\epsilon_{\alpha i} - \epsilon_{\alpha}}{kT} \right) \]

Equations (12) and (13) are \( m \cdot k \) simultaneous equations of \( m \cdot k \) variables \( \{ \theta_{\alpha i} \} \). Since \( \theta_{\alpha i} \) approaches zero when \( \theta_{i} \) approaches zero, positive non-zero variables, \( \{ Y_{\alpha i} \} \), are defined through Eq. (15).

\[ Y_{\alpha i} = \frac{\theta_{\alpha i} \theta_{i}}{1 - \sum_{j=1}^{k} \theta_{s j}} \]

Then the surface coverage of a pair of a site \( \alpha \) and a group \( i \), \( \theta_{\alpha i} \), is transformed by means of \( \{ Y_{\alpha i} \} \) and \( \{ \theta_{i} \} \) as

\[ \theta_{\alpha i} = \frac{\theta_{i} Y_{\alpha i}}{1 + \sum_{j=1}^{k} \theta_{j} Y_{s j}} \]

Substituting Eq. (16) into Eq. (12), using the relation that \( Y_{\alpha i} = r_{\alpha i} Y_{\alpha} \) for all pairs of \( \{ \alpha \} \) and abbreviating \( Y_{\alpha i} \) as \( Y_{i} \), we obtain \( k \) simultaneous equations of \( k \) variables \( \{ Y_{i} \} \).

\[ \sum_{\alpha} f_{\alpha} Y_{i} = 0 \quad (i = 1, \cdots k) \]

The above simultaneous equations are solved by means of the Newton–Raphson method, details of which are described in Appendix 2.

1.4 Adsorption isotherm

The chemical potential for an ideal gas of pressure \( P \) is

\[ \mu_{g} = \ln \left( \frac{PA^3}{j_{g}kT} \right) \]

where \( A \) is the thermal de Broglie wavelength; \( j_{g} \) is the internal molecular partition function for a gas phase. From the equilibrium condition that \( \mu_{g} = \mu_{s} \), we obtain an adsorption isotherm, written in surface-coverage expression as

\[ \ln nKP = \ln \theta - n \ln (1 - \theta) + \sum_{i=1}^{k} n_{i} \ln \left( \frac{\theta_{\alpha i}}{1 - \sum_{j=1}^{k} \theta_{s j}} \right) \]

where \( K \) is an adsorption equilibrium constant defined by Eq. (20).

\[ K = \frac{j_{g}A^3}{kT} \exp \left\{ \sum_{i=1}^{k} n_{i} \epsilon_{s i} \right\} / n \]

The last term of Eq. (19) is equivalent to \( \sum_{i=1}^{k} n_{i} \ln (Y_{i} / Y_{i}^{*}) \); \( Y_{i}^{*} \) is given as \( 1/(1 - \theta) \). The molar energy of adsorption on a hypothetical homogeneous surface consisting of sites \( a \), \(-E_{a}\), is obtained from temperature dependence of \( \ln K \).

\[ E_{a} = R \frac{\partial \ln K}{\partial (1/T)} + \frac{1}{2} RT \]

The isotherm of Eq. (19) reduces to Henry’s law as the surface-coverage approaches zero. When Henry’s constant \( H \) is defined by Eq. (22), the analytical expression of \( H \) is given as Eq. (23).

\[ H = \lim_{\theta \to 0} \frac{P}{\theta} \]
\[ \ln H = -\ln (nK) - \sum_{i=1}^{k} n_{i} \ln \left( \frac{m}{\sum_{\alpha} f_{\alpha} r_{\alpha i}} \right) \]

It is noteworthy that the adsorption–isotherm equation (19) combined with Eq. (17) reduces to the fundamental equation derived by Sparnaay7) in the special case of \( n = 1 \).

1.5 Multi-component adsorptions

Consider the adsorbed phase containing molecules of \( C \) components on a heterogeneous surface of \( m \) different site-groups, numbering different functional-groups in the components such that \( i = 1, 2, \cdots k \). Let \( s_{i} \) be the number of sites occupied by a functional-group \( i \) and \( l_{iA} \) be the number of the group \( i \) in a molecule \( A \). Then, the number of sites occupied by the group \( i \) in the molecule \( A \), \( n_{iA} \), is \( s_{i}l_{iA} \); that is,

\[ n_{iA} = s_{i}l_{iA} \]

Let \( N_{A}, N_{B}, \cdots N_{C} \) be the number of adsorbed molecules of \( A, B, \cdots C \), respectively, and \( N_{s} \) be the number of adsorption pairs of sites \( \alpha \) and a group \( i \); the adsorption energy per site for the pair \( \alpha - i \) is denoted as \( -\epsilon_{s i} \).

The partition function of the system \( Q(\{ N_{A} \}, M, T) \) may be written as

\[ Q = \left\{ \prod_{A} \left( \sum_{N_{s}} g(N_{s}) \right) \right\} \times \exp \left\{ \sum_{\alpha} \sum_{i} N_{s} \epsilon_{s i} / kT \right\} \]
The combinatorial factor $g$ is expressed by Eq. (2); $g_0$ is extended to a multi-component system as

$$
\ln g_0 = \ln \frac{M!}{(M - \sum \frac{n_A N_A}{A})!} + \sum A \ln \left( \frac{1}{N_A} \cdot \frac{C_{n_A}^{m n_A}}{M^{m n_A - 1} n_A} \right)
$$

(26)

where $n_A$ is the number of sites occupied by a molecule A.

$$
n_A = \sum_{i=1}^{k} n_{iA}
$$

(27)

Let $N$ be the total number of adsorbed molecules and $n_i$ be the average number of sites occupied by a group $i$, which is defined by Eq. (28).

$$
n_i = \sum_A n_{iA} N_A / N = \sum_A n_{iA} z_A
$$

(28)

where $z_A$ is a mole fraction of component A in the adsorbed phase. The constraint equations for $\{N_A\}$ are just the same as Eqs. (5) and (6) given for a single-component system; therefore, derivations of thermodynamic functions are easily performed for the multi-component system. The adsorption isotherm for a component A, corresponding to Eq. (19), is given here.

$$
\ln (n_A K_A p_A) = \ln \theta_A - n_A \ln \left( 1 - \sum_B \theta_B \right)
$$

$$
+ \sum_{i=1}^{k} n_{iA} \ln \left( Y_i / Y_i^* \right)
$$

(29)

The value of $K_A(T)$ is the same as that determined from a single-component adsorption isotherm for the component A, Eq. (20). The variables of $\{Y_i\}$ are determined by solving $k$ simultaneous equations, Eq. (17).

The partition function, Eq. (25), used for the multi-component system is a consequence of the assumption of independent interactions between an active site and a group in any molecules; therefore, we can expect to correlate and predict the parameters, decomposing them into site-group characteristics, then specifying the number $l_{iA}$ for a molecule A, if the assumptions in the theory are reasonable.

2. Calculation Examples of Adsorption Isotherms

To illustrate how the surface heterogeneity affects the behavior of adsorption isotherms, two examples of single-component adsorptions are shown first. Comparisons of the theory with experiment will be given later for the systems of nitrogen, oxygen, and carbon monoxide on Molecular Sieves.

2.1 Effect of the parameter $r$

Figure 1 shows the calculated results of the surface coverage $\theta$ against $\log (nKP)$ in cases where a molecule consists of unigroup occupying four sites and the surface has two different sites a and b; the assigned parameters are such that $n = 4$, $r_{A} = 1.0$, $r_{B} = 1, 10$, or 100. The solid lines are the isotherms calculated at equimolar site-fraction ($f_a = f_b = 0.5$). When the value of $r$ increases, the slope in Fig. 1 decreases gradually, giving a stepped isotherm for large values of $r$. The broken lines are those calculated at the site-fraction where $f_a = 0.9$ and $f_b = 0.1$. The isotherms are close to the line for homogeneous surface ($r = 1$), having a stepped point at the surface coverage of 0.1 for large $r$.

2.2 Effect of the ratio of site-fraction to group-fraction in a molecule

Figure 2 indicates the results calculated in cases where a molecule consists of 2 groups, 1 and 2, varying the group-fractions in a molecule under the condition that $n_1 + n_2 = 4$; two different sites a and b of equal amounts are considered ($f_a = f_b = 0.5$). The values for $r_{51}$ is assumed to be unity; $r_{82}$ is fixed at 100.

An important conclusion deduced from Fig. 2 is that when $f_b \geq n_2 / n$, the isotherms resemble that for a homogeneous surface in shape, being parallel to each other. This is because the group 2 in a molecule occupies the more active site b without competition with each other, being accompanied by pairs a–1 in stoichiometric amounts corresponding to the b–2.
Table 1. Parameters determined for oxygen, nitrogen, and carbon monoxide on Molecular Sieve 10X

\[ W^* = 8.10 \text{ mmol} \cdot \text{g}^{-1}; \quad f_a = 0.78, \quad f_b = 0.22 \]

<table>
<thead>
<tr>
<th>gas</th>
<th>( n )</th>
<th>( \Delta e^*/k )</th>
<th>( K ) (at -200°F) ( [\text{K}] )</th>
<th>( K ) (at -150°F) ( [\text{kPa}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>1.106</td>
<td>0.0</td>
<td>( 2.19 \times 10^{-2} )</td>
<td>( 4.16 \times 10^{-3} )</td>
</tr>
<tr>
<td>N₂</td>
<td>1.455</td>
<td>584.7</td>
<td>( 5.38 \times 10^{-2} )</td>
<td>( 7.02 \times 10^{-3} )</td>
</tr>
<tr>
<td>CO</td>
<td>1.364</td>
<td>893.2</td>
<td>0.184</td>
<td>( 1.76 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

\* \( \Delta e = e_{b0} - e_{a1} \).

Table 2. Parameters determined for oxygen, nitrogen, and carbon monoxide on Molecular Sieve 5A

\[ W^* = 7.84 \text{ mmol} \cdot \text{g}^{-1}; \quad f_a = 0.67, \quad f_b = 0.33 \]

<table>
<thead>
<tr>
<th>gas</th>
<th>( n )</th>
<th>( \Delta e^*/k )</th>
<th>( K ) (at -200°F) ( [\text{K}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>1.375</td>
<td>0.0</td>
<td>0.108</td>
</tr>
<tr>
<td>N₂</td>
<td>1.624</td>
<td>326.5</td>
<td>0.412</td>
</tr>
<tr>
<td>CO</td>
<td>1.564</td>
<td>500.**</td>
<td>2.26</td>
</tr>
</tbody>
</table>

\* \( \Delta e = e_{b0} - e_{a1} \).
\** Estimated from the values obtained for MS 10X.

Fig. 3. Single-component adsorption isotherms on Molecular Sieve 10X at -200°F: \( P^* = 1 \text{kPa} \).

Fig. 4. Single-component adsorption isotherms on Molecular Sieve 5A at -200°F: \( P^* = 1 \text{kPa} \).

Fig. 5. Adsorption equilibria of binary gas mixtures on Molecular Sieve 10X at -200°F and 760 mmHg. Data points are taken from Danner and Wenzel (1969). Broken lines show ideal adsorbed solution theory; solid lines show results in present theory.

Fig. 6. Adsorption equilibria of binary gas mixtures on Molecular Sieve 5A at -200°F and 760 mmHg. Data points are taken from Danner and Wenzel (1969). Broken lines show ideal adsorbed solution theory; solid lines show results in present theory.

2.3 Application of the theory to adsorption on Molecular Sieves

Adsorption equilibrium data for systems of nitrogen, oxygen, and carbon monoxide on Molecular Sieves 5A and 10X were presented by Danner et al. Curves for single-component adsorption isotherms, as shown in Fig. 3, indicate typical behavior of surface heterogeneity for nitrogen and carbon monoxide, lower slopes than that of oxygen though molecular sizes are not much different. For the sake of data reduction it is assumed that each gas molecule consists of unigroup and that the surface has two different sites, a and b; the latter site is labeled as more active. The site-fraction of the active site, \( f_b \), was assumed to be the ratio of the amount of cations to the amount of aluminium and silicon molecules, i.e.

\[ f_b = \frac{\text{amount of cations (Na}^+ \text{ and Ca}^{++})}{\text{amount of Al and Si}} \]

The values of 0.22 and 0.33 for \( f_b \) were estimated for Molecular Sieves 10X and 5A, respectively. Other parameters determined so as to fit the single-adsorption isotherms are listed Tables 1 and 2 where \( W^* \) is the amount of sites per gram of adsorbent. The
The difference of adsorption energies per site, $\Delta e = e_{\text{bl}} - e_{\text{a1}}$, is in the order of the quadrupole moments of adsorbate molecules. Figures 3 and 4 show the experimental and calculated isotherms for Molecular Sieves 10X and 5A, respectively, at $-200^\circ\text{F}$. Agreement between the experiments and the theory is excellent for nitrogen and oxygen and fairly good for carbon monoxide.

Figures 5 and 6 indicate the adsorptions of binary gas mixtures; the circles are experimental data points of Danner and Wenzel$^{1}$ and the solid lines are predictions calculated from the parameters listed in Tables 1 and 2. The broken lines show predictions of the ideal adsorbed solution theory$^{4}$ calculated by Danner and Wenzel.$^{1}$ Agreement between the experiments and the present theory is not satisfactory but they are better than the predictions of the ideal adsorbed solution theory.

**Concluding Remarks**

The equation of an adsorption isotherm for a heterogeneous surface has been developed on the basis of multi-site occupancy model followed by a group-contribution assumption. Though the equation neglects adsorbate-adsorbate interactions, an additional term for the lateral interactions may be the same as that for a homogeneous surface$^{5}$ when the heterogeneous surface is the so-called "random-surface" where sites of different energy are scattered completely at random.

Numerical calculations of the isotherm equation indicate the significance of the ratio of the site-fraction to the group-fraction in a molecule when a given group interacts with any specified sites.

The theory has been applied to systems of oxygen, nitrogen, and carbon monoxide on Molecular Sieves 5A and 10X. Though the values for the fraction of active sites assigned in the present work may be subject to change, the sets of parameters determined from the data of single-component adsorptions are compatible with the physical properties of each molecule and may support the speculation that the more active sites are cations of the adsorbent. The theory can predict adsorption equilibria of binary mixtures by using the parameters determined from single-component isotherms. It is noteworthy that the calculations do not include any extrapolation procedures for spreading pressures of each pure component, which are needed in other methods based on a thermodynamic framework such as the ideal adsorbed solution theory.

**Appendix 1**

**Derivation of thermodynamic properties in adsorbed phase**

Thermodynamic properties in an adsorbed phase are derived from partial differentiations of the partition function $Q$, Eq. (4), subject to Eqs. (5) and (6).

**Chemical potential**:

$$\mu_i = -\frac{\partial \ln Q}{\partial N_i} = -\frac{1}{kT} \frac{\partial N_i}{N}$$

$$=-\ln \left( \frac{N_i e_i}{N} \right) = -\ln \left( \frac{N_0 e_i}{N_0} \right) + \ln \left( \frac{N_0}{N} \right)$$

$$(A-1)$$

From the condition of maximum point with respect to $\{N_i\}$, the following relations are obtained.

$$\frac{\partial \ln Q}{\partial N_i} = \frac{\partial \ln Q}{\partial N_{eq}} = \beta_i \quad (i = 1, \cdots k)$$

where $\beta_i$ is a Lagrange multiplier relating to a group $i$. The differentials of constraint equations, (5) and (6), are given as

$$\sum_{a=a}^{m} dN_{ai} = n_i dN_i \quad (i = 1, \cdots k)$$

$$\sum_{j=0}^{m} dN_{aj} = dM_s \quad (a = a, \cdots m)$$

$$(A-2)$$

The condition that $dM = 0$ yields the following equations.

$$\sum_{a=a}^{m} \left( \frac{\partial N_{ai}}{\partial N} \right)_{M,T} = n_i \quad (i = 1, \cdots k)$$

$$\sum_{j=0}^{m} \left( \frac{\partial N_{aj}}{\partial N} \right)_{M,T} = 0 \quad (a = a, \cdots m)$$

$$(A-3)$$

By use of Eqs. (A-2), (A-5) and (A-6), the last term of Eq. (A-1) is simplified as follows.

$$-\sum_{a=a}^{m} \sum_{i=0}^{k} \left( \frac{\partial N_{ai}}{\partial N} \right)_{M,T}$$

$$=- \sum_{a=a}^{m} \left( \frac{\partial \ln Q}{\partial N_{ai}} \right)_{M,T} - \sum_{a=a}^{m} \sum_{i=0}^{k} \left( \frac{\partial \ln Q}{\partial N_{ai}} + \beta_i \frac{\partial N_{ai}}{\partial N} \right)_{M,T}$$

$$=- \sum_{i=0}^{k} \beta_n_i$$

Equation (7) in the text is used at the last transform.

The expressions of $N^*_s$ and $N^*_o$ are given from the random-distribution assumption as

$$N^*_s = \left( \frac{M_s}{M} \right) n_s N$$

$$N^*_o = \left( \frac{M_o}{M} \right) (M - n_s N)$$

$$(A-8)$$

Then the third term of Eq. (A-1) is

$$- \sum_{a=a}^{m} \sum_{i=0}^{k} \left( \frac{\partial \ln N^*_ai}{\partial N} \right)_{M,T} = - \sum_{i=1}^{k} n_i \ln \left( \frac{n_i N}{M - n_s N} \right)$$

$$(A-9)$$

Differentiation of $\ln g_0$ with respect to $N$ gives

$$-\left( \frac{\partial \ln g_0}{\partial N} \right)_{M,T} = -\ln \left( \frac{N}{M} \right) - \ln \left( \frac{M - n_s N}{M} \right) - \ln \zeta$$

$$(A-10)$$

The expression for $\mu/kT$, Eq. (8), is obtained from a combination of Eqs. (A-1), (A-7), (A-9) and (A-10).

Spreading pressure:
Combining Eqs. (A-3) and (A-4) with the condition that dN = 0, the last term is simplified as

\[ \phi = \frac{\partial \ln Q}{kT} \]

\[ = \frac{\partial \ln Q}{\partial M_{N,T}} + \sum_{a=1}^{N} \frac{\partial \ln N_a^*}{\partial M_{N,T}} \]

\[ + \sum_{a=1}^{N} \frac{\partial \ln Q}{\partial N_a} \left( \frac{\partial N_a}{\partial M_{N,T}} \right) \]

\[ = \sum_{a=1}^{N} \frac{\partial \ln Q}{\partial N_a} \left( \frac{\partial N_a}{\partial M_{N,T}} \right) + \sum_{a=1}^{N} \frac{\partial \ln Q}{\partial N_a} \left( \frac{\partial N_a^*}{\partial M_{N,T}} \right) \]

\[ = \sum_{a=1}^{N} \frac{\partial \ln Q}{\partial N_a} f_a - \sum_{a=1}^{N} f_a \ln N_a \]  

(A-12)

Differentiations in the first two terms of Eq. (A-11) are performed with ease; the expression of the spreading pressure is obtained as given in Eq. (9).

Internal energy:

\[ U = kT \sum_{a=1}^{N} \frac{\partial \ln Q}{\partial N_a} \]

\[ = NkT \sum_{i=1}^{N} \frac{\partial \ln Q}{\partial N} \left( \frac{\partial N_a}{\partial M_{N,T}} \right) \]

\[ + kT \sum_{i=1}^{N} \frac{\partial \ln Q}{\partial N} \left( \frac{\partial N_a^*}{\partial M_{N,T}} \right) \]

\[ (A-13) \]

The second term in the sum vanishes since the condition that dN = dM = 0 is applied to Eqs. (A-3) and (A-4); therefore, the expression of the internal energy is obtained as given in Eq. (10).

Appendix 2

Numerical method for determining a distribution \{ Y_i \}

Simultaneous equations to be solved, \( F_i (Y_1, \cdots, Y_k) = 0 \), are defined as follows.

\[ F_i = \sum_{a=1}^{N} \frac{f_a Y_a}{\theta f_a Y_a} = 1 \quad (i=1, \cdots, k) \]  

(B-1)

Iterative calculations are performed by the Newton-Raphson method in the domain of new variables \( \{ X_t \} \) which are transformed from \( \{ Y_t \} \) as \( X_t = Y_t \). The increments \( \{ h_{t+1} \} \), which determine \( (r+1)^{st} \) set of variables \( \{ X_t^{(r+1)} \} \) from \( r^{th} \) step as \( X_t^{(r+1)} = X_t^{(r)} + h_{t+1} \), are given by solving \( k \) simultaneous linear equations with respect to \( \{ h_{t+1} \} \).

\[ F_i^{(r+1)} + \sum_{a=1}^{N} \left( \frac{\partial F_i}{\partial X_a} \right) Y_a^{(r+1)} = 0 \quad (i=1, \cdots, k) \]  

(B-2)

where

\[ \frac{\partial F_i}{\partial X_a} = Y_i \frac{\partial F_i}{\partial Y_i} - \sum_{a=1}^{N} \frac{f_a \theta_{a} Y_a}{\theta_{a} Y_a} \]

\[ \frac{\partial F_i}{\partial X_a} = Y_i \frac{\partial F_i}{\partial Y_i} - 1 + F_i \sum_{a=1}^{N} \frac{f_a \theta_{a} Y_a}{\theta_{a} Y_a} \]

The Gauss-Jordan algorithm was useful in solving the above linear equations. Initial values for \( Y_i \)'s are set as \( Y_i^* \) (\( =1/(1-0) \)).

Nomenclature

\( E \) = molar desorption energy  
\( f \) = site-fraction of solid surface  
\( g \) = combinatorial factor  
\( H \) = Henry's constant  
\( J_b \) = internal partition function in gas phase  
\( J_s \) = internal and vibrational partition function of an adsorbed molecule  
\( K \) = adsorption equilibrium constant  
\( k \) = Boltzmann constant  
\( L \) = Avgadro constant  
\( N_a \) = number of group \( i \) in molecule \( A \)  
\( M \) = number of active sites of surface  
\( N \) = number of adsorbed molecules  
\( N_a \) = number of adsorption pairs of group \( i \) on site \( a \)  
\( n \) = number of sites occupied by a molecule or a group  
\( P \) = pressure  
\( p_l \) = partial pressure  
\( Q \) = partition function  
\( R \) = gas constant  
\( T \) = temperature  
\( U \) = internal energy  
\( W^* \) = amount of sites per gram of adsorbent  
\( Y_a \) = surface coverage coefficient defined by Eq. (15)  
\( y \) = mole fraction in gas phase  
\( z \) = mole fraction in adsorbed phase  
\( \beta \) = Lagrange multiplier  
\( e \) = pair desorption energy per site  
\( \gamma \) = a constant relating to flexibility and the symmetric number of a molecule  
\( \theta \) = surface coverage  
\( \lambda \) = thermal de Broglie wavelength  
\( \mu \) = chemical potential per molecule  
\( \phi \) = spreading pressure  

\( \text{(Subscripts)} \)

\( A, B, \cdots, C \) = component of \( A, B, \cdots \) or \( C \), respectively  
\( a \) = an arbitrarily specified site  
\( a, b, \ldots, m \) = site of \( a, b, \cdots \) or \( m \), respectively  
\( i, j, \ldots, k \) = group of \( i, j, \cdots \) or \( k \), respectively, in a molecule  
\( a_i \) = pair of group \( i \) on site \( a \)  
\( a_i \) = refers to site \( a \) being empty  
\( A \) = group \( i \) in molecule \( A \)

\( \text{(Superscripts)} \)

\( g \) = gas phase  
\( s \) = surface of adsorbed phase  
\( \star \) = refers to random distribution

Literature Cited


FUNDAMENTAL STUDY ON SOLAR POWERED ADSORPTION COOLING SYSTEM

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Fundamental experiments on the solar-powered adsorption cooling system were carried out with small-scale apparatus simulating ideally a practical unit by employing a combination of silica-gel and water vapor as an example of the adsorbent-adsorbate combinations. A simple model which takes into account both adsorption properties and apparatus characteristics was proposed to interpret our experimental results quantitatively. Then the transitional behavior of heat and mass transfer in continuous adsorption-regeneration experiments was successfully interpreted by the model. The model proposed here is not a complete one and is to be considered as a first-step model for estimating operation with practical equipment. Also, the contribution of the level of regeneration temperature of adsorbents to the cooling performance was quantitatively clarified on the basis of the adsorption equilibrium relation, which is considered useful in choosing a favorable combination of adsorbent and adsorbate for the system.

1. Introduction

The adsorption cooling system has drawn attention since a demonstration unit using natural zeolites as adsorbents and water vapor as adsorbate was constructed and its performance was qualitatively reported by Tchernev.5 Guilleminot et al.4 suggested the feasibility of this system in comparison with the absorption cooling system from the viewpoint of thermodynamics. The principle of operation of this system is shown as a sketch in Fig. 1. The system is composed of a packed bed of adsorbents, a condenser and an evaporator. A combination of adsorbent and adsorbate is confined in the closed system. In the adsorption cycle shown in Fig. 1(a), while adsorption is taking place in the adsorbent bed, evaporation of adsorbate occurs in the evaporator, absorbing heat from outside the system. Cooling is carried out by making use of this heat absorption. In the regeneration cycle shown in Fig. 1(b), since the temperature of the adsorbent bed rises by receiving solar heat, desorption and condensation of adsorbate takes place in the adsorbent bed and the condenser respectively. The most significant merit of this system is the absence of moving parts in principle, which is a point of difference from the absorption cooling system. As described above, the feasibility of the system is qualitatively suggested but quantitative studies for the design of practical equipment is not yet sufficient. In this work, from the standpoint of chemical engineering, a quantitative study of the system was made. Continuous adsorption-regeneration experiments were carried out with small-scale equipment simulating ideally a practical unit and the results obtained are interpreted by a simple model taking into account adsorption properties and apparatus characteristics.

2. Experimental

2.1 Apparatus

A schematic diagram of experimental apparatus is shown in Fig. 2. It consists of five T-type tubes used as packed beds of adsorbents, a condenser, an evaporator, an infrared lamp and a vacuum pumping system. T-type tubes are made of Pyrex and details of the one placed in the middle of the five are shown in Fig. 3. A copper-constantan thermocouple is inserted into a narrow glass tube which is inserted into the bed to reach the center of it. The condenser is also made of Pyrex and has a heat transfer area of about 0.06 m². The evaporator is a glass bottle of 0.025 m ID and 0.16 m height. To read from the outside the amount of adsorbate (working fluid) remaining in the evap-

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