Adsorption of Gas Mixtures: Effect of Energetic Heterogeneity

The ideal adsorbed solution (IAS) theory of adsorption of gas mixtures is extended to the case of energetic heterogeneity. A heterogeneous ideal adsorbed solution (HIAS) behaves ideally on a particular site, but energetic heterogeneity causes a segregation in the composition of the adsorbed phase. Equilibrium properties are obtained by integrating over a multivariate energy distribution based upon perfect positive correlation of site energies. The fact that predictions from HIAS are always an improvement over IAS indicates that heterogeneity is a factor that must be considered in theories of mixed-gas adsorption. Errors in HIAS predictions may be caused by steric exclusion of the larger molecules from micropores accessible to smaller molecules.

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Introduction

Langmuir (1918) was the first to recognize the importance of the spatial variation of the potential energy of adsorption, and Ross and Olivier (1964) established the methodology for studying heterogeneity of solid adsorbents in terms of an adsorption integral equation. Several recent reviews (House, 1983; Jaroniec and Bräuer, 1986) were devoted to surface heterogeneity and numerical techniques for solving the integral equation for the energy distribution.

Hoory and Prausnitz (1967) were the first to extend the adsorption integral equation to mixtures. They studied the bivariant Gaussian distribution, and Jaroniec and Borówko (1977) used the bivariant log normal distribution. In both cases the appropriate energy distribution is derived from experimental data for single-gas adsorption, and a correlation parameter ρ is used to fit data for binary gas adsorption. For adsorbates with similar chemical characteristics, such as CH_4 and C_2H_6, a strong correlation ($\rho \approx 1$) between the energy distributions was obtained. A value of $\rho = 0$ means no correlation between adsorptive energies and random matching of sites. In the random case the bivariant energy distribution is the product of the energy distributions of the individual gases (Jaroniec, 1975), but this is a "gross approximation" (House, 1983) and unrealistic from a physical point of view.

This paper is a continuation of the work cited above. The HIAS method developed in this paper is thermodynamic in nature, in the sense that it is not associated with a specific energy distribution or a particular equation for the pure-gas adsorption isotherm.

Adsorption Integral Equation

The specific amount N (mol/kg) of a pure gas adsorbed on a heterogeneous adsorbent at pressure P and temperature T is given by the integral (Ross and Olivier, 1964):

$$N = \int_0^\infty n(T, P, \epsilon) f(\epsilon)\, d\epsilon \tag{1}$$

where $f(\epsilon)$ is the probability density function for the distribution of adsorptive energies, and n is the specific adsorption if the surface were homogenous and characterized by energy ϵ.

The individual amount N_i of ith component adsorbed on a heterogeneous surface from a gas mixture containing r components is (Jaroniec and Rudzinski, 1975):

$$N_i = \int_{\epsilon_1} \int_{\epsilon_2} \cdots \int_{\epsilon_r} n_i (T, P, y, \epsilon_1, \epsilon_2, \ldots, \epsilon_r) \cdot g(\epsilon_1, \epsilon_2, \ldots, \epsilon_r)\, d\epsilon_1\, d\epsilon_2 \ldots d\epsilon_r \tag{2}$$

$g(\epsilon_1, \epsilon_2, \ldots, \epsilon_r)$ is the joint probability density function for the distribution of adsorption energies and y is the gas composition vector $\{y_1, y_2, \ldots, y_r\}$. The joint distribution reflects the fact that each site on the surface is characterized by r adsorption energies. n_i is the amount of ith component that would be adsorbed if the surface were homogeneous and characterized by the set of adsorption energies $\{\epsilon_1, \epsilon_2, \ldots, \epsilon_r\}$ for the r components.

Let component number 1 be the reference component. Then the joint distribution can be expressed as:

$$g(\epsilon_1, \epsilon_2, \ldots, \epsilon_r) = \prod_{k=2}^{r} h_{k1}(\epsilon_k|\epsilon_1) f(\epsilon_1) \tag{3}$$

where $h_{k1}(\epsilon_k|\epsilon_1)$ is the density function for the conditional probability that a particular site has the energy ϵ_k, given that it is characterized by the adsorption energy ϵ_1. If every site on the surface, irrespective of the component chosen as reference, has the same higher and lower energy neighbors, then the conditional probability can be written:

$$h_{k1}(\epsilon_k|\epsilon_1) = \delta|F_k(\epsilon_k) - F_1(\epsilon_1)| \tag{4}$$

where δ is the Dirac delta function and F is the cumulative energy distribution function:

$$F(\epsilon) = \int_0^{\epsilon} f(\epsilon)\, d(\epsilon) \tag{5}$$

Physically, Eq. 4 means that the ordering of the sites from low to high energy is the same for each adsorbate; this is called perfect positive correlation. Insertion of Eqs. 3 and 4 into Eq. 2 yields after integration:

$$N_i = \int_0^{\infty} n_i(T, P, y, \epsilon_1, \epsilon_2^*, \ldots, \epsilon_r^*) f_1(\epsilon_1)\, d\epsilon_1 \tag{6}$$

where the relation between ϵ_k^* and ϵ_1 is given by:

$$F_k(\epsilon_k^*) - F_1(\epsilon_1) = 0 \tag{7}$$

Thus a particular site is defined by its value in the cumulative energy distribution function F, independently of the component chosen to characterize the surface. Perfect positive correlation of sites is expected to be approximately valid for nonspecific energies of adsorption arising from dispersion forces (see Conclusions section). A site whose energy is above average for one adsorbate cannot be below average for another adsorbate unless chemical bonding or other specific effects such as steric occlusion govern gas-solid intermolecular forces.

In order to use Eq. 6, some information is needed on the function describing the behavior of the adsorbate solution on a homogeneous surface: $n_i(T, P, y, \epsilon_1, \epsilon_2^*, \ldots, \epsilon_r^*)$. The simplest approximation is to assume ideality, and we call this a heterogeneous ideal adsorbed solution (HIAS). Given T, P, and y, the composition $x = \{x_1, x_2, \ldots, x_r\}$ of the adsorbed phase is calculated from the equation:

$$Py_i = P_i^o x_i \tag{8}$$

$$\psi_1^o(P_1^o) = \psi_2^o(P_2^o) = \ldots = \psi_r^o(P_r^o) \tag{9}$$

$$\sum_{i=1}^{r} x_i = 1 \tag{10}$$

Given T, P, and y, Eqs. 8–10 provide a set of $2r$ equations that can be solved for the $2r$ unknowns $\{P_i^o, x_i\}$. The function $\psi_i^o(P_i^o)$ is the integral for the spreading pressure from the single-gas isotherm $n_i^o(P)$ for adsorption on a homogeneous surface characterized by energy ϵ_i:

$$\psi_i^o = \int_0^{P_i^o} \frac{n_i^o}{P}\, dP \tag{11}$$

Having determined the composition x of the adsorbed phase, the total amount adsorbed n is obtained from:

$$\frac{1}{n} = \sum_{i=1}^{r} \frac{x_i}{n_i^o(P_i^o)} \tag{12}$$

so that:

$$n_i = nx_i \tag{13}$$

Equations 8–13 can be reduced to the solution of one equation

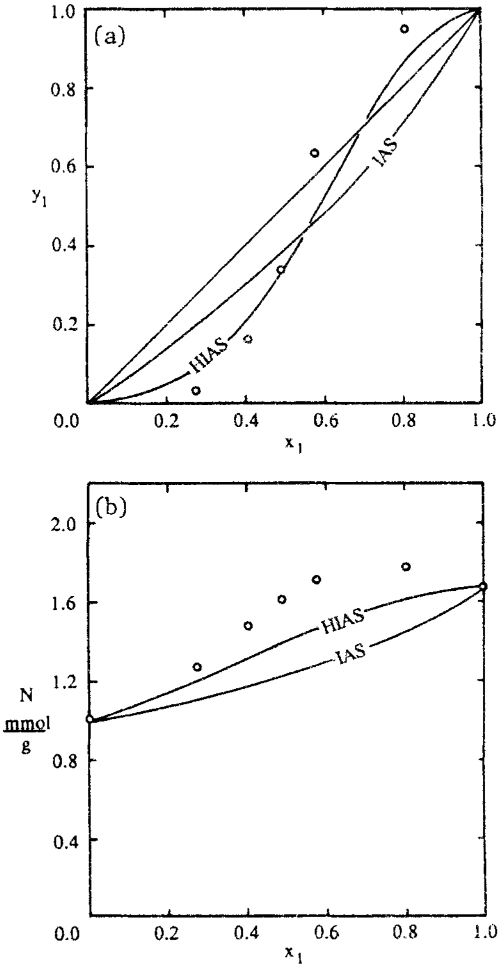

Figure 1. Prediction of mixed-gas adsorption of CO_2 (1) and C_3H_8 (2) on H-mordenite at 303.15 K and 40.93 kPa.

(a) Mole fraction in gas phase y_1 vs. mole fraction in adsorbed phase x_1

(b) Specific amount adsorbed N as a function of x_1

O Experimental data of Talu and Zwiebel (1986)

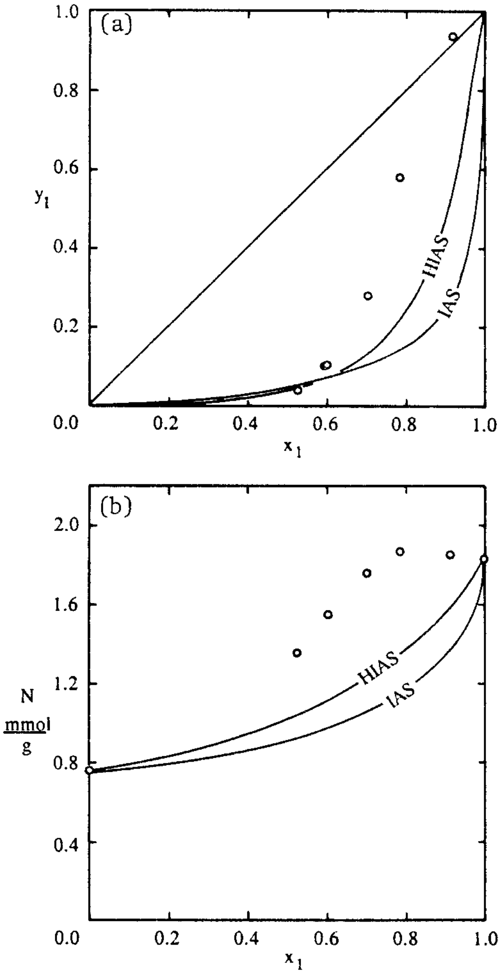

Figure 2. Prediction of mixed-gas adsorption of H_2S (1) and C_3H_8 (2) on H-mordenite at 303.15 K and 8.13 kPa.

(a) Mole fraction in gas phase y_1 vs. mole fraction in adsorbed phase x_1

(b) Specific amount adsorbed N as a function of x_1

O Experimental data of Talu and Zwiebel 1986

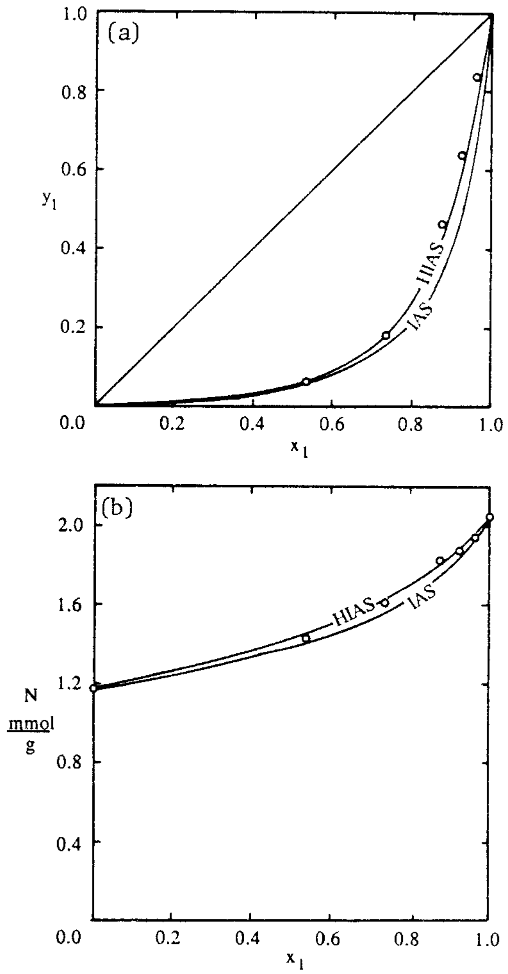

Figure 3. Prediction of mixed-gas adsorption of H_2S (1) and CO_2(2) on H-mordenite at 303.15 K and 15.55 kPa.

(a) Mole fraction in gas phase y_1 vs. mole fraction in adsorbed phase x_1

(b) Specific amount adsorbed N as a function of x_1

O Experimental data of Talu and Zwiebel 1986

for one unknown (Myers, 1987) so that the function $n_i(T, P, y, \epsilon_1, \epsilon_2, \ldots, \epsilon_r)$ inside the integral of Eq. 6 is easily programmable.

All of the equations in this paper are written for the case when the gas mixture and the single gases obey the perfect gas law. For a real gas, the proper integrand of Eq. 11 is $n_i^o d \ln f$, and this generates integrals that differ significantly from the approximate values of Eq. 11 if the pressure is several atmospheres or greater. Similarly, in Eq. 8 the pressure P_i^o and the partial pressure Py_i must be replaced by fugacity for a real gas. However, calculations of mixed-gas adsorption equilibria based upon Eqs. 8 and 11 are very nearly the same as the results obtained with the rigorous equations, because of a cancellation of errors. Therefore, although it is not necessary to do so, the effect of gas phase imperfections is usually neglected.

The details of implementing HIAS depend upon the equation chosen to represent adsorption of a single gas on a homogeneous surface: $n(T, P, \epsilon)$ in Eq. 1, as well as the type of probability distribution selected to represent $f(\epsilon)$. For the calculations described below, we used the Langmuir equation for $n(T, P, \epsilon)$ and the discrete binomial distribution for $f(\epsilon)$, as explained in the Appendix.

Comparison of HIAS with Experimental Data

In order to assess the effect of energetic heterogeneity upon mixed-gas adsorption equilibria, the theory of heterogeneous ideal adsorbed solutions (HIAS) was compared with experimental data for two systems that do not agree with IAS theory. First consider the system investigated by Talu and Zwiebel (1986) for adsorption on H-mordenite of the binary and ternary mixtures form with H_2S, CO_2, and C_3H_8 at 303.15 K. Figures 1 to 3 show the comparison between IAS and HIAS for the binary systems. IAS calculations show that $CO_2 + C_3H_8$ and $H_2S + C_3H_8$ form highly nonideal mixtures, as can also be inferred from the azeotropic behavior exhibited by these systems. For $CO_2 + C_3H_8$, HIAS correctly predicts an azeotrope but not the correct azeotropic composition. For $H_2S + C_3H_8$, HIAS does not predict the azeotrope but the prediction of HIAS is better than IAS. The mixture $H_2S + CO_2$ forms a nearly ideal solution; therefore IAS

Table 1. Performance of Theory, Adsorption of C_3H_8, CO_2, and H_2S on H-mordenite at 303.15 K

System	*D* Avg.,* %		No. Points
	IAS	HIAS	
$H_2S + C_3H_8$	39	30	8
$CO_2 + C_3H_8$	35	19	9
$H_2S + CO_2$	14	7	9
$CO_2 + H_2S + C_3H_8$	43	29	10

*Deviation from experimental data of Talu and Zwiebel (1986)

agrees fairly well with experiment and the HIAS calculation is in nearly exact agreement. Table 1 shows the average value of the percent deviation *D*, defined as:

$$D = \left| \frac{n_{\exp} - n_{\text{calc}}}{n_{\exp}} \right| \times 100 \qquad (14)$$

The statistics are for individual loadings. For example, for the first system in Table 1 there are eight experimental points and the average was taken over 16 values of amount adsorbed for both components.

According to Table 1, HIAS theory is an improvement over IAS because the average error is reduced by 35% for 82 values of amount adsorbed. Moreover, for every system, the improvement is in the right direction, as illustrated graphically in Figures 1–3.

Less impressive results for HIAS are shown in Table 2 for binary and ternary mixtures of CH_4, C_2H_4, and C_2H_6 adsorbed on activated carbon at 301.4 K.

The improvement of HIAS over IAS in Table 2 is hardly significant, but Tables 1 and 2 and other data (Valenzuela, 1987) confirm that HIAS generates predictions that are sometimes better but never worse than IAS.

Discussion

There is a special case when HIAS reduces to IAS theory (Jaroniec, 1977). If two adsorbates have energy distributions that differ only in their mean energies, then their cumulative distribution functions $F(\epsilon)$ can be superimposed by a lateral shift with respect to energy. Therefore the difference in energies of adsorption for the two adsorbates, as well as the selectivity, is the same on every site. The IAS calculation for each site in Eq. 6 is then the same as the IAS calculation for the surface as a whole.

If two energy distributions can be superimposed as described above, then their standard deviations σ must be equal: Appendix, Tables A1 and A2. Considering the adsorbates in Table 1, C_3H_8 is the most heterogeneous (largest value of σ) and CO_2 is the least heterogenous (relatively small value of σ). Therefore the HIAS prediction differs significantly from that of IAS, Figure 1, for $C_3H_8 + CO_2$. On the other hand, H_2S and CO_2 have nearly equal values of σ, and for this binary the predictions of HIAS and IAS are nearly the same, Figure 3.

Table 2. Performance of Theory, Adsorption of CH_4, C_2H_4, and C_2H_6 on Activated Carbon at 301.4 K

System	*D* Avg.,* %		No. Points
	IAS	HIAS	
$C_2H_6 + CH_4$	22	19	14
$C_2H_4 + CH_4$	19	15	14
$C_2H_6 + C_2H_4$	7	7	12
$C_2H_6 + C_2H_4 + CH_4$	21	20	13

*Deviation from experimental data of Reich et al. (1980)

The predictions from HIAS and IAS in Table 2 are similar because the energy distributions of the adsorbates (CH_4, C_2H_4, and C_3H_8) have relatively small values of σ. Therefore the differences $\Delta\sigma$ are also small and HIAS nearly reduces to IAS theory.

Figure 4 shows the difference in percent deviation for IAS and HIAS as a function of differences $|\sigma_1 - \sigma_2|$ in heterogeneity parameters. A significant advantage of HIAS over IAS can be expected if the difference $|\Delta\sigma/RT|$ is larger than unity.

Conclusions

The purpose of this study was to determine if the effect of energetic heterogeneity should be incorporated in predictive models of mixed-gas adsorption. Heterogeneity introduces an additional element of complexity into the single-gas adsorption equation (see Appendix), and the mixed-gas calculation contains an additional integration step expressed by Eq. 6. For the majority of systems, IAS theory provides predictions that are in good agreement with experiment (Valenzuela and Myers, 1984). Apparently these are systems for which either the surface coverage is low or the difference $|\Delta\sigma/RT| \leq 1$. However, there are several sets of data exemplified by Tables 1 and 2 for which the amounts adsorbed predicted by IAS disagree with experiment by 10 to 30%. HIAS theory always improves the predictions, but they are still not in quantitative agreement with experiment.

Heterogeneity is an important factor, but there are deviations from perfect positive correlation of adsorption energies. The deviations can be explained by specific interactions associated with both electrostatic and dispersion forces (Barrer, 1966), as well as steric effects. These factors are difficult to quantify and cannot be incorporated easily into predictive models. The recourse is to introduce a binary adsorption parameter whose

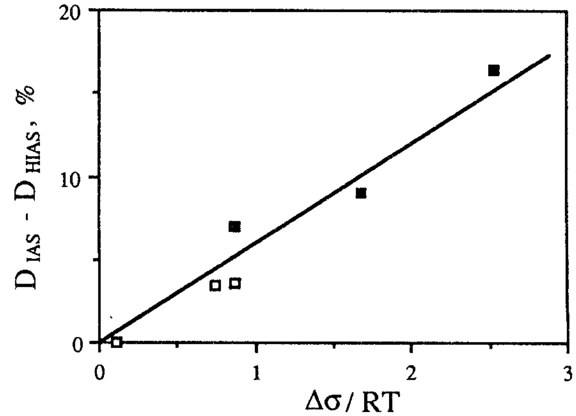

Figure 4. Difference between percent error of IAS and HIAS theories as a function of dimensionless heterogeneity $\Delta\sigma/RT$.

■ Binary data of Talu and Zwiebel (1986)

□ Binary data of Reich et al. (1980)

value is determined from experimental data (Hoory and Prausnitz, 1967). The Hoory-Prausnitz approach is limited by its dependence on the Gaussian distribution, which is insufficiently flexible for application to the systems considered in Table 1 and 2. What is needed is a one-parameter site-matching model for arbitrary energy distribution functions that provides quantitative agreement with binary adsorption data. The model should allow the prediction of multicomponent (ternary and higher) adsorption using parameters for the binary constituents.

The deviations of HIAS predictions from experiment in Figures 1 and 2 indicate that something is missing in the theory, such as steric exclusion of the larger molecules from micropores accessible to the smaller molecules.

Notation

A = specific surface area, m^2/kg
b = constant, Eq. A4
D = percent deviation, Eq. 14
f = energy density function, J^{-1}; fugacity, Pa
F = cumulative distribution function
g = joint energy density function, J^{-r}
h_{ij} = conditional probability of ϵ_i given ϵ_j
k = number of sites − 1
k^* = number of sites − 1 after truncation
k_o = constant, Eq. A5, J
m = amount adsorbed at saturation, mol/kg
n = specific amount adsorbed on particular site, mol/kg
N = total specific amount adsorbed, mol/kg
P_o = constant, Eq. A5, 1.0 kPa
P = pressure, Pa
r = number of adsorbates
R = gas constant
T = temperature, K
u = skewness, Eq. A1
x = mole fraction in adsorbed phase
y = mole fraction in gas phase

Greek letters

$\Delta\epsilon$ = constant, Eq. A2, J
ϵ = energy of adsorption, J
ϵ_o = constant, Eq. A2, J
Π = spreading pressure, N/m
σ = standard deviation, J
ψ = $\Pi A/RT$, mol/kg, Eq. 11

Superscript

o = standard state of single adsorbate

Subscripts

i = component i
j = site j

Appendix

The binomial distribution:

$$f(\epsilon_j) = \binom{k}{j} u^j (1 - u)^{k-j} \quad (0 \le j \le k) \tag{A1}$$

gives the "probability" of energy ϵ_j for $(k + 1)$ sites. u is a skewness parameter $(0 < u < 1)$, and for a symmetric distribution $u = 0.5$. In this work $k = 40$, which is large enough to represent any unimodal distribution but small enough not to be a computational burden. ϵ_j is given by:

$$\epsilon_j = \epsilon_0 + j\Delta\epsilon \tag{A2}$$

For a discrete distribution, the integral of Eq. 1 is replaced by summation:

$$N = \sum_{j=0}^{k} n(T, P, \epsilon_j) f(\epsilon_j) \tag{A3}$$

where $n(T, P, \epsilon)$ is approximated by the Langmuir equation:

$$n = m \frac{be^{\epsilon/RT}P}{1 + be^{\epsilon/RT}P} \tag{A4}$$

The constant b has the form:

$$b = (1/P_o) \exp{(k_o/RT)} \tag{A5}$$

$P_o \equiv 1.0$ kPa, and k_o is a constant with units of J/mol. From Eqs. 11 and A4:

$$\psi = m \ln{(1 + be^{\epsilon/RT}P)} \tag{A6}$$

In some cases it was necessary to truncate the binomial distribution to the k^* term $(0 < k^* < k)$ in order to obtain a quantitative fit of the single-gas adsorption isotherms, which required that the binomial distribution be renormalized:

$$f_{k^*}(\epsilon_j) = f(\epsilon_j)/F_{k^*} \tag{A7}$$

where

$$F_{k^*} = \sum_{j=0}^{k^*} f(\epsilon_j) \tag{A8}$$

For mixture calculations based on discrete energy distributions the integration of Eq. 6 becomes a summation:

$$N_i = \sum_{k} n_i(T, P, y, \epsilon_{1k}, \epsilon_{2k}, \ldots, \epsilon_{rk}) \Delta F_k \tag{A9}$$

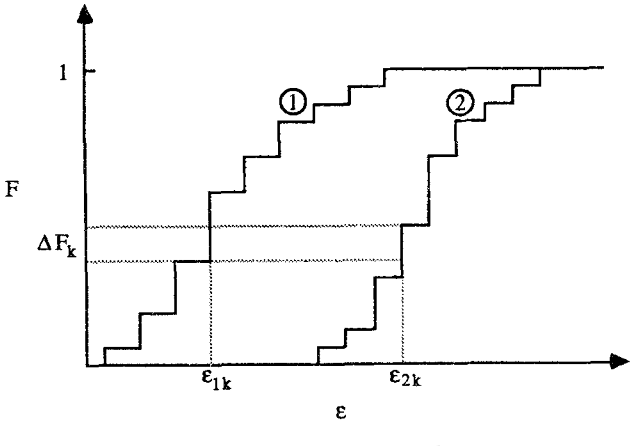

Figure 5. Site matching for binary mixture.
Curves are discrete, cumulative distribution functions $F(\epsilon)$

Table A1. Constants of Truncated Binomial Distribution for Adsorption of C_3H_8, CO_2, and H_2S on H-mordenite at 303.15 K

Comp.	k^*	u	$(\epsilon_o + k_o)/RT$	$\Delta\epsilon/RT$	m mol/kg	$(\bar{\epsilon} + k_o)/RT$	σ/RT
CO_2	19	0.3	−22.3959	1.3002	7.502	−6.864	3.673
C_3H_8	11	0.3	−43.3796	3.9968	2.225	−5.824	6.193
H_2S	16	0.3	−24.6950	1.7969	4.835	−3.848	4.535

Table A2. Constants of Truncated Binomial Distribution for Adsorption of CH_4, C_2H_4, and C_2H_6 on Activated Carbon at 301.4 K

Comp.	k^*	u	$(\epsilon_o + k_o)/RT$	$\Delta\epsilon/RT$	m mol/kg	$(\bar{\epsilon} + k_o)/RT$	σ/RT
CH_4	40	0.3	−10.5340	0.29098	5.7951	−7.042	0.843
C_2H_4	17	0.3	−13.0243	0.64107	6.6429	−5.474	1.705
C_2H_6	40	0.3	−11.3818	0.54937	5.9890	−4.789	1.592

where ΔF_k is the fraction of the distribution for which each adsorbate has a constant energy ϵ_{ik}. The meaning of ΔF_k is illustrated in Figure 5 for binary site matching; note that $\Sigma_k \Delta F_k = 1$.

In summary, the adsorption equation for a truncated binomial distribution has six parameters: k^*, u, ϵ_o, k_o, $\Delta\epsilon$, and m. For an isotherm the number of parameters is reduced to five: k^*, u, $(\epsilon_o + k_o)$, $\Delta\epsilon$, and m; these provide sufficient flexibility to fit the data for the single-gas isotherms within experimental error. The constants in Table A1 for the isotherms of Talu and Zwiebel (1986) were used to make the IAS and HIAS calculations in Table 1. Note that CO_2 is the most weakly adsorbed (smallest value of $\bar{\epsilon} + k_o$) and H_2S is the most strongly adsorbed species. Similarly, the constants in Table A2 for the single-gas isotherms of Reich et al. (1980) are the basis for the results in Table 2. Also reported in Tables A1 and A2 is the standard deviation of the energy distribution σ.

Literature Cited

Barrer, R. M., "Specificity in Physical Sorption," *J. Colloid Interf. Sci.*, **21**, 415 (1966).

Hoory, S. E., and J. M. Prausnitz, "Monolayer Adsorption of Gas Mixtures on Homogeneous and Heterogeneous Surfaces," *Chem. Eng. Sci.*, **22**, 1025 (1967).

House, W. A., "Adsorption on Heterogeneous Surfaces," *Colloid Science, Specialist Periodical Reports*, v. 4, Royal Society of Chemistry, London (1983).

Jaroniec, M., "Adsorption of Gas Mixtures on Heterogeneous Surfaces: Analytical Solution of Integral Equation for Jovanovic Adsorption Isotherm," *J. Colloid Interf. Sci.*, **53**, 422 (1975).

———, "Adsorption of Gas Mixtures on Heterogeneous Surfaces: Studies of Adsorption Equilibria at Constant Total Pressure," *J. Colloid Interf. Sci.*, **59**, 230 (1977).

Jaroniec, M., and M. Borówko, "Supplementary Note to the Paper: 'Adsorption of Gas Mixtures on Heterogeneous Surfaces," *Surf. Sci.*, **66**, 652 (1977).

Jaroniec, M., and P. Bräuer, "Recent Progress in Determination of Energetic Heterogeneity of Solids from Adsorption Data," *Surface Science Reports*, **6**, 65, North-Holland, Elsevier, Amsterdam (1986).

Jaroniec, M., and W. Rudzinski, "Adsorption of Binary Gas Mixtures on Heterogeneous Surfaces," *Phys. Lett.*, **53A**, 59 (1975).

Langmuir, I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum," *J. Am. Chem. Soc.*, **40**, 1361 (1918).

Myers, A. L., "Molecular Thermodynamics of Adsorption of Gas and Liquid Mixtures," *Proc. 2nd Int. Conf. Fundamentals of Adsorption*, Engineering Found., New York (1987).

Reich, R., W. T. Ziegler, and K. A. Rogers, "Adsorption of Methane, Ethane, and Ethylene Gases and Their Binary and Ternary Mixtures and Carbon Dioxide on Activated Carbon at 212–301 K and Pressures to 35 Atmospheres," *Ind. Eng. Chem. Process Des. Dev.*, **19**, 336 (1980).

Ross, S., and J. P. Olivier, "On Physical Adsorption," Interscience, New York (1964).

Talu, O., and I. Zwiebel, "Multicomponent Adsorption Equilibria of Nonideal Mixtures," *AIChE J.*, **32**, 1263 (1986).

Valenzuela, D. P., "Physical Adsorption on Energetically Heterogeneous Surfaces," Ph.D. Thesis, Univ. Pennsylvania (1987).

Valenzuela, D. P., and A. L. Myers, "Gas Adsorption Equilibria," *Separ. Purif. Methods*, **13**, 153 (1984).

Manuscript received June 22, 1987, and revision received Dec. 3, 1987.