ANNALES UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA LUBLIN – POLONIA

VOL. LVI, 7

SECTIO AA

2001

Effect of the form of adsorption energy distribution functions on the theoretical isosteric heats of mixed-gas adsorption

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A wide application of gas separation processes based on adsorption phenomena can be observed. This paper presents the possibilities of Integral Equation (IE) Approach to study the mixed-gas adsorption equilibria. As a result, the generalizations of Langmuir-Freundlich and Dubinin-Astakhov equation for the case of mixed-gas adsorption are presented. Also the corresponding expressions for isosteric heats of adsorption are obtained. To predict phase diagrams and isosteric heats of mixture components only the knowledge of single-gas isotherm adsorption and accompanying calorimetric effects are required. A special attention is given to possibilities of arriving at relatively simple analytical or combined analytical/numerical solutions.

1. INTRODUCTION

Recently growth of interest in gas separation by adsorption processes has been observed. At the same time there appears a need for relatively simple methods to predict theoretically mixed-gas adsorption equilibria. As follows from recently published literature [1-8] many methods are proposed. As the measurements of multicomponent systems are difficult and time consuming in comparison to the measurement of adsorption isotherm for pure components such theoretical predictions are important from a practical point of view.

Theoretical prediction of mixed-gas adsorption equilibria can be applied to control industrial processes of gas separation, for example Temperature Swing Adsorption (TSA) and Pressure Swing Adsorption (PSA) processes. They are controlled by computer programs because the precision of fast calculation of gas adsorption equilibria plays the substantial role in the industrial application.

PSA processes require reversible adsorption so that the preferentially adsorbed species can be removed readily during the regenerative portion of the cycle. As they are usually operated at ambient temperature, the adsorption and desorption steps in the cycle operate under approximately adiabatic conditions. The magnitude of the temperature change induced by adsorption or desorption is determined by the individual heats of adsorption of the mixture components through an energy balance. Since loading is highly sensitive to temperature, the selectivity is closely coupled to the magnitudes of the individual heats of adsorption. Also the heats of adsorption play the substantial role in the TSA processes where energy (major cost in TSA processes) is required to regenerate the column. Therefore accurate design calculations require values for heats of adsorption as well as selectivity. Surprisingly, although heats of adsorption have been measured extensively for pure gases, hardly anything is known about heats of adsorption from mixtures. Therefore, there is a need to present theoretical description of this phenomenon and to compare it with the experimental data.

Thermodynamic analyses of the isosteric principle and of the isosteric heats of multicomponent adsorption were performed previously by Sircar [9]. Molecular simulations supported on Ideal Adsorbed Solution Approach were performed by Karavias et al. [10]. Jaroniec [11] used the generalized integral equation and as a local adsorption isotherm the Jovanović equation to derive expressions for isosteric heats of simultaneously adsorbed components. Talu et al. [12] utilized the Vacancy Solution Theory to describe isosteric heats of adsorption of single gases. Theoretical description of heats effect of two and three component gas-mixture was performed by Sundaram and Yang [13]. The adsorption of binary liquid mixtures and accompanying heat effects at the solid/liquid interface was studied by Dekany et al. [14-18].

This paper presents the method for estimation of the theoretical equations describing the isosteric heats of adsorption of single gases and the components of a gas mixture. These equations can be obtained using the theories of mixed-gas adsorption. To predict isosteric heats of gas mixture components, only the knowledge of isotherms and isosteric heats of single gases is required.

The theory of gas adsorption, used by us, as one of the most common, is the Integral Equation Approach. The obtained results will be verified by comparison with the experimental data.

2. INTEGRAL REPRESENTATION FOR EQUILIBRIUM ADSORPTION ISOTHERMS

Let N_{ii} denote the total number of the molecules adsorbed at the pressure p_i and the temperature T on a heterogeneous solid surface, and M_i denote the total number of sites on that surface. Let further $\theta_i(\{\varepsilon\},\{p\},T)$ denote the "local" fractional coverage by the component i, of a certain class of adsorption sites, characterized by a set of the adsorption energies $\{\varepsilon\} = \{\varepsilon_1, \varepsilon_2, ..., \varepsilon_n\}$ for the single components. The experimentally monitored N_{ii} value is then expressed by the following integral equation,

$$\theta_{ii}(\{p\},T) = \frac{N_{ii}}{M_i} = \int_{\underset{\Omega_n}{\dots}} \int \theta_i(\{\varepsilon\},\{p\},T) \chi_n(\{\varepsilon\}) d\varepsilon_1 \dots d\varepsilon_n$$
(1)

where $\theta_i(\{p\},T)$ is the average fraction of surface coverage by the molecules of the component *i* at a set of the partial pressures $\{p\} = \{p_1, p_2, ...\}$. $\chi_n(\{\varepsilon\})$ is the n-dimensional differential distribution of the number of the adsorption sites among various sets $\{\varepsilon\}$, normalized to unity,

$$\int \dots \int \chi_n(\{\varepsilon\}) d\varepsilon_1 \dots d\varepsilon_n = 1$$
⁽²⁾

where Ω_n is the n-dimensional physical domain of $\{\varepsilon\}$. For the adsorption isotherms of single components,

$$\theta_{ii}(\{p\},T) = \int_{\Omega_i} \theta_i(\varepsilon_i,\{p\},T) \chi_i(\varepsilon_i) d\varepsilon_i$$
(3)

where

$$\chi_i(\varepsilon_i) = \int_{\Omega_{n-1}} \chi_n(\{\varepsilon\}) d\varepsilon_1 \cdots d\varepsilon_{i-1} \cdot d\varepsilon_n \qquad (4)$$

That equation is used either to calculate $\theta_{ii}(\{p\},T)$ when $\theta_i(\varepsilon_i,\{p\},T)$ and $\chi_i(\varepsilon_i)$ are known, or, to $\chi_i(\varepsilon_i)$ when $\theta_{ii}(\{p\},T)$ and $\theta_i(\varepsilon_i,\{p\},T)$ are known. The "local" adsorption isotherm may be the Langmuir isotherm or another one (BET, Bragg-Williams, Hill-de Boer, etc.).

The really existing adsorption energy distributions are expected to have a pretty complicated form, with a number of local maxima and minima. However, to a certain degree of accuracy, the really existing function $\chi_i(\varepsilon_i)$ can, for practical purposes, be approximated by some "smoothed" functions, the shape of which is described by a small number of parameters. The following functions have, most frequently, been used to represent the "smoothed" form of the actual adsorption energy distributions: 1. The rectangular function

$$\chi_i(\varepsilon_i) = \begin{cases} \frac{1}{\varepsilon_i^m - \varepsilon_i}, & \text{for } \varepsilon \in (\varepsilon_i^l, \varepsilon_i^m) \\ 0, & \text{elsewhere} \end{cases}$$

where $(\varepsilon_i^l, \varepsilon_i^m)$ is the physical domain of ε_i . 2. The Gaussian-like function

$$\chi_i(\varepsilon_i) = \frac{\frac{1}{c_i} \exp\left\{\frac{\varepsilon_i - \varepsilon_i^0}{c_i}\right\}}{\left[1 + \exp\left\{\frac{\varepsilon_i - \varepsilon_i^0}{c_i}\right\}\right]^2}$$

centered at $\varepsilon_i = \varepsilon_i^0$. For obvious physical reasons, there must be a certain minimum, and a maximum value of the adsorption energy ε_i , on a heterogeneous solid surface, ε_i' and ε_i^m . Thus, the Gaussian-like function (6) becomes a rectangular (constant) energy distribution when $c \to \infty$.

3. The Dubinin-Astakhov function

$$\chi_{i}(\varepsilon_{i}) = \frac{r_{i}(\varepsilon_{i} - \varepsilon_{i}^{\prime})^{r_{i}-1}}{(E_{i})^{r_{i}}} \exp\left\{-\left[\frac{\varepsilon_{i} - \varepsilon_{i}^{\prime}}{E_{i}}\right]^{r_{i}}\right\}$$
(7)

the variance of which is equal to E. The ε^{l} is the lowest value of the adsorption energy ε on a given heterogeneous surface. Depending on the shape parameter r, it is a pretty Gaussian-like function for r=3, right hand widened for r<3, and left hand widened for r>3. When r=1 DA function (7) changes to the exponential energy distribution function.

Single-gas adsorption isotherms. The most frequently used method to calculate the integral in eq. (3) is Condensation Approximation (CA). Application of the CA makes it possible to simplify the calculations. For example, if the local isotherm $\theta(\varepsilon_i, p_i, T)$ under the integral sign is the Langmuir isotherm:

$$\theta_{i}(\varepsilon_{i}, p_{i}, T) = \frac{K_{i} p_{i} \exp\left\{\frac{\varepsilon_{i}}{kT}\right\}}{1 + K_{i} p_{i} \exp\left\{\frac{\varepsilon_{i}}{kT}\right\}} = \frac{\exp\left\{\frac{\varepsilon_{i} - \varepsilon_{i}^{c}}{kT}\right\}}{1 + \exp\left\{\frac{\varepsilon_{i} - \varepsilon_{i}^{c}}{kT}\right\}}$$
(8)

where $\varepsilon_i^c = -kT \ln(K_i p_i)$. The Condensation Approximation is based on the assumption that adsorption on a heterogeneous surface proceeds in an ideally "stepwise" fashion in the sequence toward decreasing adsorption energies.

(5)

(6)

It means that the true kernel $\theta(\varepsilon_i, p_i, T)$ in eq. (3) is replaced by the following step function, $\theta_{ic}(\varepsilon_i, p_i, T)$

$$\theta_i(\varepsilon_i, p_i, T) \to \theta_{ic}(\varepsilon_i, p_i, T) = \begin{cases} 0, & \text{for } \varepsilon_i < \varepsilon_i^c \\ 1, & \text{for } \varepsilon_i \ge \varepsilon_i^c \end{cases}$$
(9)

Then,

$$\theta_{ii}(\{p\},T) = \int_{\varepsilon_i^c} \chi_i(\varepsilon_i) d\varepsilon_i = -\aleph(\varepsilon_i^c)$$
(10)

where $\aleph_i(\varepsilon_i)$ is the integral form of $\chi_i(\varepsilon_i)$.

While using symmetrical energy distribution function (6) we arrive at the Langmuir-Freundlich (LF) isotherm for the single-component adsorption isotherm θ_{μ} :

$$\theta_{ii}(\{p\},T) = \frac{\left[K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}\right]^{\frac{kT}{c_i}}}{1 + \left[K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}\right]^{\frac{kT}{c_i}}}$$
(11)

The experimentally measured adsorbed amount, $N_{ii}(\{p\},T)$, is equal to $M_i\theta_{ii}(\{p\},T)$, where M_i is the number of the adsorption sites on the solid surface, expressed in the same units as $N_{ii}(\{p\},T)$. A convenient way to analyze an experimental adsorption isotherm in terms of (11) is to use the following linear regression:

$$\ln \frac{N_{ii}/M}{1 - N_{ii}/M} = \frac{kT}{c_i} \left[\ln K_i + \frac{\varepsilon_i^0}{kT} \right] + \frac{kT}{c_i} \ln p_i$$
(12)

The only adjustable parameter is then the monolayer capacity M_i , which is chosen in such a way that the l.h.s. of (12) can possibly be the best linear function of $\ln p_i$ (the best linear regression). The heterogeneity parameter kT/c_i is then the tangent of that linear plot, and $K_i \exp\{\varepsilon^{0}_i/kT\}$ is found from the intercept multiplied by c_i/kT .

Now, we focus our attention on the case when the energy distribution function is described by the non-symmetrical Dubinin-Astakhov function (7). In this case the CA approximation leads to the following expression for the fractional coverage:

$$\theta_{ii}(p_i,T) = \exp\left\{-\left[\frac{kT_i}{E_i}\ln\frac{p_i'}{p_i}\right]^{r_i}\right\}$$
(13)

Eq. (13) is just the well-known Dubinin-Astakhov isotherm, or the Dubinin-Radushkevich isotherm for the particular case when r=2. When r=1 DA isotherm (13) becomes the Freundlich equation. Generally, r may vary from unity up to 5 or 6. It is established that 1 < r < 2 refers to carbons with large micropores. For molecular sieves the value is 2 while very fine pore carbons and zeolites may require values up to 5 or 6 [30,31]. Thus, it is clear that the heterogeneity parameter r is related in some way to the pore dimensions. It can be showed [29], that r also depends on the analyzed region of adsorptive pressures.

The parameter p' is commonly assumed to be the saturated vapour pressure of the adsorbate at a temperature T. But, the present computer simulations show that the state of the adsorbate molecules in the micropores is considerably different from that of the molecules in the bulk liquid. The critical temperature in the micropores is much lower, so the "micropore filling" cannot be identified with bulk condensation. Thus, p' cannot be identified generally with the saturated vapour pressure value.

The property of parameters r and kT/E was discussed earlier, they play a role of heterogeneity parameters.

Frequently to adjust the Dubinin-Astakhov equation (13) to the experimental data it is easier to use the following linear form:

$$\ln N_{ii} = \ln M_i - \left[\frac{kT}{E_i}\right]^{\eta} \left[\ln \frac{p_i^l}{p_i}\right]^{\eta}$$
(14)

When the parameters p'_i , r_i are correctly chosen, $\ln N_{ii}$ should be the linear function of $[\ln p'_i / p_i]'$ in the whole range of the surface coverages.

The mixed-gas adsorption equilibria. In order to obtain the theoretical expressions for the mixed-gas adsorption isotherms it is necessary to evaluate integral (1). A general strategy is to reduce this integral to a dimensional one, by using various physical arguments. Most commonly, it is done by taking into account the correlations between the adsorption energies ε_i and $\varepsilon_{j\neq i}$, $i \neq j = 1,2,3,...,n$ on different adsorption sites. Two physical situations have been considered so far:

1) The adsorption energies $\varepsilon_i, \varepsilon_{i\neq i}$ are not correlated at all;

2) A functional relationship exists:

$$\varepsilon_i = f_{ii}(\varepsilon_i) \quad , \quad i \neq j = 1, 2, 3, \dots, n.$$

$$(15)$$

In our theoretical model we use two adsorption energy distribution functions described by the Gaussian-like function (6) and the Dubinin-Astakhov function (7). Next, we assume that the local adsorption isotherm is described by the

Benton equation (Markham and Benton, 1931) which is simply the generalized Langmuir equation for the case of mixed-gas adsorption isotherm:

$$\theta_i(\varepsilon_i, p_i, T) = \frac{K_i p_i \exp\left\{\frac{\varepsilon_i}{kT}\right\}}{1 + \sum_j K_j p_j \exp\left\{\frac{\varepsilon_j}{kT}\right\}}$$
(16)

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$$\varepsilon_i^c = -kT \ln\left(\sum_j K_j p_j \exp\left\{\frac{\varepsilon_j}{kT}\right\}\right)$$
(17)

So, for a given adsorption energy distribution function we can obtain different equations corresponding to the accepted model of correlations between adsorption energies of various components. As the first step, we consider the model of lack of correlations. This is the case of coadsorption of components exhibiting much different character of interactions with the same solid surface. We use the idea proposed by Wojciechowski et al.[27]:

$$\theta_{it}(\{p\},T) = -\left(1 - \sum_{j \neq i}^{n} \theta_{jt}\right) \aleph_i(\varepsilon_i^c)$$
(18)

(16) is a kind of a master equation from which various expressions for the mixed-gas isotherm can be derived by assuming various adsorption energy distributions $\chi_i(\varepsilon_i)$.

For example, if $\chi_i(\varepsilon_i)$ is the Gaussian-like function (6) we arrive at the following isotherm equations for the case of mixed-gas adsorption:

$$\theta_{ii}^{LF}(\{p\},T) = \frac{\left[K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}\right]^{kT/c_i}}{1 + \sum_{j=1}^n \left[K_j p_j \exp\left\{\frac{\varepsilon_j^0}{kT}\right\}\right]^{kT/c_j}}$$
(19)

When $\chi_i(\varepsilon_i)$ is the function (7), eq. (18) leads to the generalized Dubinin-Astakhov equation:

$$\theta_{li}^{DA}(p,T) = \frac{\left[1 - \exp\left\{-\left[\frac{kT}{E_2}\ln\left(\frac{p_2'}{p_2}\right)\right]^{r_2}\right\}\right] \exp\left\{-\left[\frac{kT}{E_1}\ln\left(\frac{p_1'}{p_1}\right)\right]^{r_1}\right\}}{1 - \exp\left\{-\left[\frac{kT}{E_1}\ln\left(\frac{p_1'}{p_1}\right)\right]^{r_1} - \left[\frac{kT}{E_2}\ln\left(\frac{p_2'}{p_2}\right)\right]^{r_2}\right\}}$$
(20)

Let us consider the case of very high correlations between ε_i and ε_j represented by the following condition [28],

 $\varepsilon_j = \varepsilon_i + \Delta_{ji}$, i, j = 0, 1, 2...n on each adsorption site, (21) where Δ_{ji} 's are certain constants. This case can be used only when the components of the adsorbed mixture have a similar chemical character. Another obvious condition is that the molecules of different components should have similar sizes. Then, if $\theta_i(\varepsilon_i, p_i, T)$ is the Benton equation (16) and $\chi_i(\varepsilon_i)$ is the function (6), the CA approach leads to the following form of θ_{ii} [8]:

$$\theta_{ii}^{LF}(\{p\},T) = \frac{K_i p_i e^{\frac{\varepsilon_i^o}{kT}}}{\sum_j K_j p_j e^{\frac{\varepsilon_j^o}{kT}}} \frac{\left(\sum_j K_j p_j e^{\frac{\varepsilon_i^o}{kT}}\right)^{\frac{KI}{c_i}}}{1 + \left(\sum_j K_j p_j e^{\frac{\varepsilon_j^o}{kT}}\right)^{\frac{KT}{c_i}}}$$
(22)

When $\chi_i(\varepsilon_i)$ is DA function (7),

$$\theta_{ii}^{DA}(p,T) = \frac{p_i / p_i'}{\sum_{j=1}^n p_j / p_j'} \exp\left\{-\left[\frac{kT}{E_i} \ln\left(\frac{1}{\sum_{j=1}^n p_j / p_j'}\right)\right]^r\right\}$$
(23)

The conditions (22) and (23) assume implicitly that the functions $\chi_i(\varepsilon_i)$ have a similar shape. So, it is obvious, that when the shapes of energy distribution functions $\chi_i(\varepsilon_i)$ are not similar, (22) and (23) cannot be used, even if high correlations exist between the adsorption energies of various components. But this does not indicate the lack of correlations between adsorption energies of various components. Strong correlations also exist when, with the increasing surface coverage, various adsorption sites are covered by molecules *i* and *j*, in the same sequence [8]. Strong correlations also exist when, with increasing surface coverage, various adsorption sites are covered by molecules *i* and *j* in the same sequence. Then,

$$-\aleph_{i}(\varepsilon_{i}^{c}) = -\aleph_{j}(\varepsilon_{j}^{c})$$
⁽²⁴⁾

Thus, if we assume that the adsorption isotherms of both components i and j obey the Langmuir-Freundlich behaviour, originating from the Gaussian-like adsorption energy distribution (6) we arrive at the following relation:

$$\left[1 + \exp\left(\frac{\varepsilon_i^c - \varepsilon_i^0}{c_i}\right)\right]^{-1} = \left[1 + \exp\left(\frac{\varepsilon_j^c - \varepsilon_j^0}{c_j}\right)\right]^{-1}$$
(25)

and, consequently,

$$\varepsilon_{j} = \frac{c_{j}}{c_{i}}\varepsilon_{i} + \left(\varepsilon_{j}^{0} - \frac{c_{j}}{c_{i}}\varepsilon_{i}^{0}\right)$$
(26)

In the case of Dubinin-Astakhov adsorption energy distribution (7), eq. (24) leads to the following interrelation:

$$\varepsilon_{j} = \varepsilon_{j}^{\prime} + E_{j} \left(\frac{\varepsilon_{i} - \varepsilon_{i}^{\prime}}{E_{i}}\right)^{r_{i}/r_{j}}$$
(27)

Thus, the physical assumption that adsorption sites are covered in the same sequence is equivalent to assuming the above relationship between ε_i and $\varepsilon_{j\neq i}$. Then, for the Langmuir model of adsorption we have,

$$\theta_{ii}(\{p\},T) = \int_{0}^{\infty} \frac{K_{i}p_{i}\exp\left(\frac{\varepsilon_{i}}{kT}\right)}{1 + \sum_{j}K_{j}p_{j}\exp\left(\frac{\varepsilon_{j}}{kT}\right)}\chi(\varepsilon_{i})d\varepsilon_{i}$$
(28)

where $\varepsilon_j \neq \varepsilon_i$ in (28) have to be expressed by ε_i , using the relations (26) or (27).

Extension of the IE approach to regular adsorbed solutions. The term 'ideal solution' refers to the systems of interacting molecules, in which the *interchange energy* W_{ii} equals zero:

$$W_{ii} = \omega_{ii} + \omega_{ii} - 2\omega_{ii} = 0 \tag{29}$$

 ω_{ij} being the interaction energy between two molecules *i* and *j* adsorbed on two neighbouring adsorption sites. As it is well known, when the adsorption of interacting molecules (collective adsorption) on a heterogeneous surface is considered, one must also take into account the surface topography. So far two extreme models of surface topography, i.e. *patchwise* and *random* models have been commonly considered. To take into account the interactions between the adsorbed molecules, we will use here the Mean Field Approximation (MFA) approach.

So, when we assume that the heterogeneity of adsorption system is described by Gaussian-like function (6), application of the Condensation Approximation (CA) to develop corresponding expressions for θ_{ii} for single components, in the case of *patchwise* topography, leads to the following equation [8],

$$\theta_{ii}^{LF}(\{p\},T) = \frac{\left[K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}\right]^{kT/c_i} \exp\left\{\frac{\omega_{ii}}{2c_i}\right\}}{1 + \left[K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}\right]^{kT/c_i} \exp\left\{\frac{\omega_{ii}}{2c_i}\right\}}$$
(30)

whereas for random topography we obtain an additional sector and an additional sector and a sector additional sector add

$$\theta_{ii}^{LF}(\{p\},T) = \frac{\left[K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}\right]^{KT/c_i} \exp\left\{\frac{\omega_{ii}\theta_{ii}}{c_i}\right\}}{1 + \left[K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}\right]^{KT/c_i} \exp\left\{\frac{\omega_{ii}\theta_{ii}}{c_i}\right\}}$$
(31)

If we assume that energy distribution function is non-symmetrical (eq. (7)) CA leads to the following expression for θ_{ir} ,

$$\theta_{ii}^{DA}(p,T) = \exp\left\{-\left[\frac{kT}{E_i}\ln\frac{p_i^{I}}{p_i} - \frac{\omega_{ii}}{E_i}\theta_{ii}(p,T)\right]^{r_i}\right\}$$
(32)

A convenient way, frequently suggested in literature [8], to correlate the experimental data by eqs (31-32) is to use the logarithmic form of these equations like in the case when the interaction effects were neglected. But, due to a large number of best-fit parameters in the above equations that method is not as convenient as previously. Especially it concerns DA equation (32). To adjust LF or DA eqs (31-32) to the experimental isotherms another numerical method should be used.

Next, we arrive at the generalization of our mixed-gas isotherm equations for the case of interacting molecules. Unfortunately, for the case of *patchwise* topography it is difficult to obtain simple analytical expressions for mixed-gas isotherm adsorption. So, we consider only the case of *random* topography. Then, application of the Condensation Approximation to develop corresponding expressions for θ_{ii} in the adsorbed gas-mixture (the case of random surface topography) leads to the following form of ε_i^c :

$$\varepsilon_i^c = -kT \ln K_i p_i - \sum_j \omega_{ij} \theta_{ji}$$
(33)

While assuming lack of correlations between adsorption energies of mixture components, the use of eq. (18) leads to the following generalizations of eq. (19) [8]

$$\theta_{ii}^{LF}(\{p\},T) = \frac{\left[K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}\right]^{kT/c_i} \exp\left\{\sum_j \frac{\omega_{ij} \theta_{ji}}{c_i}\right\}}{1 + \sum_i \left[K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT}\right\}\right]^{kT/c_i} \exp\left\{\sum_j \frac{\omega_{ij} \theta_{ji}}{c_i}\right\}}$$
(34)

If we assume DA energy distribution function (7) [26] on a monotonic procession of an end of

$$\theta_{1i}^{DA}(p_1, p_2, T) = \frac{\exp\left\{-\left[\frac{kT}{E_1}\ln\frac{p_1^i}{p_1} - \sum_i \frac{\omega_{1i}\theta_{ii}}{E_1}\right]^{r_i}\right\} \left(1 - \exp\left\{-\left[\frac{kT}{E_2}\ln\frac{p_2^i}{p_2} - \sum_i \frac{\omega_{2i}\theta_{ii}}{E_2}\right]^{r_2}\right\}\right)}{1 - \exp\left\{-\left[\frac{kT}{E_1}\ln\frac{p_1^i}{p_1} - \sum_i \frac{\omega_{1i}\theta_{ii}}{E_1}\right]^{r_i} - \left[\frac{kT}{E_2}\ln\frac{p_2^i}{p_2} - \sum_i \frac{\omega_{2i}\theta_{ii}}{E_2}\right]^{r_2}\right\}\right\}$$

In the case of high correlations between adsorption energies of mixture components, we obtain the following expressions for θ_{i} , [8,26]

(35)

$$\theta_{it}^{LF}(\{p\},T) = \frac{K_i p_i \exp\left\{\frac{\varepsilon_i^0}{kT} + \sum_j \frac{\omega_{ij} \theta_{jt}}{kT}\right\}}{\sum_j p_j K_j \exp\left\{\frac{\varepsilon_j^0}{kT} + \sum_k \frac{\omega_{jk} \theta_{kt}}{kT}\right\}} \frac{\left(\sum_j K_j p_j \exp\left\{\frac{\varepsilon_j^0}{kT} + \sum_k \frac{\omega_{jk} \theta_{kt}}{kT}\right\}\right)^{\frac{kT}{c_i}}}{1 + \left(\sum_j K_j p_j \exp\left\{\frac{\varepsilon_j^0}{kT} + \sum_k \frac{\omega_{jk} \theta_{kt}}{kT}\right\}\right)^{\frac{kT}{c_i}}}$$
(36)

and

$$\theta_{ii}^{DA}(p,T) = \frac{(p_i / p_i') \exp\left\{\sum_j \frac{\omega_{ij} \theta_{ji}}{kT}\right\}}{\sum_{j=1}^{n} \left[(p_j / p_j') \exp\left\{\sum_k \frac{\omega_{ij} \theta_{ki}}{kT}\right\}\right]} \exp\left\{-\left\lfloor\frac{kT}{E_i} \ln\left(\frac{1}{\sum_{j=1}^{n} \left[(p_j / p_j') \exp\left\{\sum_k \frac{\omega_{ij} \theta_{ki}}{kT}\right\}\right]}\right)\right\rfloor^n\right\}$$
(37)

where eq. (36) corresponds to symmetrical energy distribution function (6), and (37) was obtained for the case of DA energy distribution function (7). It can be seen that when the interaction parameters ω_{ii} are equal to zero, the above equations (34-37) reduce for the case of non-interacting molecules (19), (20), (22) and (23).

It is important to remark that to calculate mixed-gas adsorption isotherms only the best-fit parameters obtained from adjustment of eqs (31-32) to the single-gas adsorption isotherms are required. So, assuming the ideal solution of the adsorbed phase, i.e. $W_{ij} = 0$ (see eq. (29)) to calculate theoretical phase diagrams no additional parameters are needed, except those obtained from adjustment by LF or DA eqs (31-32) to the single-gas adsorption isotherms. Reduction of the number of best-fit parameters simplifies our theoretical model and affects numerical calculations rate.

3. ISOSTERIC HEATS OF ADSORPTION

It is true to state that the calorimetric effects of adsorption give more valuable information about the adsorption system than the isotherm of adsorption. For example, the heat of adsorption profile reveals the degree of energetic heterogeneity of gas solid interactions. An increase in heat of adsorption with gas loading is characteristic for nonheterogeneous adsorbents with the constant gas-solid energies of interaction. The increase is due to cooperative interactions between the adsorbed molecules. A decrease in heat of adsorption with gas loading is characteristic for highly heterogeneous adsorbents with a wide distribution of gas-solid interaction energies. A constant heat of adsorption with gas loading indicates a balance between the strength of cooperative gas-gas interactions and the degree of heterogeneity of gas-solid interactions.

The isosteric heat of adsorption is defined as the difference of partial molar entalphy in the gas phase and the excess partial molar entalphy in the adsorbed phase:

$$q_i^{st} = H_i^b - H_i^e \text{ and } \text{ following output the second of th$$

Although q^{st} is traditionally called the isosteric heat of adsorption, the above eq. shows that it is actually the heat of desorption.

Another heat of adsorption in common use is the differential heat of adsorption, defined by:

$$q_i^d = U_i^b - U_i^e \tag{39}$$

since $H_i^e \approx U_i^e$, we obtain the relation between two types of heats of adsorption:

$$q_i^d = q_i^{st} - RT \tag{40}$$

The excess partial molar entalphy in the adsorbed phase is related to the chemical potential by the Gibbs-Helmholtz equation

$$H_{i}^{e} = -T^{2} \left(\frac{\partial(\mu_{i}/T)}{\partial T} \right)_{N_{e}^{e}}$$

$$\tag{41}$$

where N_{ii}^{ϵ} is the surface excess. Adopting the perfect-gas reference state μ^0 , the chemical potential is

$$\mu_i = \mu_i^0 + RT \ln(f_i / p^0)$$
(42)

and p^0 is the perfect-gas reference pressure (1 atm.).

Combination of eqs (38-42) yields the Clapeyron equation for mixtures:

$$q_i^{st} = RT^2 \left(\frac{\partial \ln f_i}{\partial T}\right)_{N_s^s} + \left(H_i^b - H_i^{b,0}\right)$$
(43)

where $(H_i^b - H_i^{b,0})$ is the enthalpy departure from the perfect-gas state. For the special case of adsorption from a pure perfect gas at the pressure p_i

$$q_i^{st} = RT^2 \left(\frac{\partial \ln p_i}{\partial T}\right)_{N_{\mu}^s} \text{ or, for one molecule } q_i^{st} = -k \left[\frac{\partial \ln p_i}{\partial (1/T)}\right]_{N_{\mu}^s}$$
(44)

In order to apply the above equations to calculate the isosteric heats of adsorption from the isotherm equation we can rewrite them in the following form:

$$q_i^{st} = -k \left[\frac{\partial \ln p_i}{\partial (1/T)} \right]_{\theta_a}$$

$$Q_i^{st} = -k \left[\frac{\partial \ln p_i}{\partial (1/T)} \right]_{\theta_a}, \quad j \neq i$$
(45)
(46)

where q_i^{st} and Q_i^{st} mean the isosteric heats for single and mixed-gas adsorption systems, respectively.

Based on the equations presented above it is easy to obtain the expression describing calorimetric effects of adsorption when one component is adsorbed. When we assume Gaussian-like adsorption energy distribution function (6), and use isotherm equation (11),

$$q_{i}^{st} = q_{i}^{st0} - c_{i} \ln\left(\frac{\theta_{it}}{1 - \theta_{it}}\right) = q_{i}^{st0} - kT \ln\left(K_{1} p_{1}\right)$$
(47)

where

$$q_i^{st0} = k \frac{d \ln K_i'}{d(1/T)}$$
and $K_i' = K_i \exp\left\{\varepsilon_i^0 / kT\right\}.$
(48)

Assuming non-symmetrical energy distribution function (7) we arrive at the following expression for isosteric heats:

$$q_{i}^{st} = q_{i}^{stl} + E_{i} \left[\ln \frac{1}{\theta_{it}} \right]^{\frac{1}{p_{i}}} = q_{i}^{stl} - kT \ln \left(\frac{p_{1}}{p_{1}^{l}} \right)$$
(49)

where

$$q_{i}^{sn} = -k \frac{d \ln p_{i}^{\prime}}{d(1/T)} = k \frac{d \ln K_{i}^{\prime}}{d(1/T)} + \varepsilon_{i}^{\prime}$$
(50)

Now, we show how to obtain theoretical expressions for isosteric heats of adsorption corresponding to the isotherm equations presented in this paper. Here we consider the simplest case when the interactions between adsorbed molecules are neglected. Theoretical description of calorimetric effects accompanying the mixed-gas adsorption equilibria for the case of Gaussian-like adsorption energy distributions (6) was precisely investigated in our recent paper [19,20]. Theoretical studies on calorimetric effects accompanying mixed-gas adsorption, when energy distribution function is represented by the Dubinin-Astakhov eq. (7) has not been made yet.

It can be stated that the simplest method, which can be used to obtain the expressions for isosteric heats of mixture components, is the transformation of the adequate isotherm expressions for $\ln p_i$. However, it is not easy in many cases. If transformation is not possible, the following general method can be used. Namely, the differentiation of isotherm equation function $\theta_{it}(p_1, p_2, C_1, C_2, T)$ of two components gives the following equation system:

$$\left(\frac{\partial \theta_{u}}{\partial \ln p_{1}}\right)\left(\frac{\partial \ln p_{1}}{\partial (1/T)}\right) + \left(\frac{\partial \theta_{u}}{\partial \ln p_{2}}\right)\left(\frac{\partial \ln p_{2}}{\partial (1/T)}\right) = -\left[\left(\frac{\partial \theta_{u}}{\partial C_{1}}\right)\left(\frac{\partial C_{1}}{\partial (1/T)}\right) + \left(\frac{\partial \theta_{u}}{\partial C_{2}}\right)\left(\frac{\partial C_{2}}{\partial (1/T)}\right) + \left(\frac{\partial \theta_{u}}{\partial (1/T)}\right)\right]$$
(51)

$$\left(\frac{\partial \theta_{2t}}{\partial \ln p_1}\right)\left(\frac{\partial \ln p_1}{\partial (1/T)}\right) + \left(\frac{\partial \theta_{2t}}{\partial \ln p_2}\right)\left(\frac{\partial \ln p_2}{\partial (1/T)}\right) = -\left[\left(\frac{\partial \theta_{2t}}{\partial C_1}\right)\left(\frac{\partial C_1}{\partial (1/T)}\right) + \left(\frac{\partial \theta_{2t}}{\partial C_2}\right)\left(\frac{\partial C_2}{\partial (1/T)}\right) + \left(\frac{\partial \theta_{2t}}{\partial (1/T)}\right)\right]$$
(52)

where all differentials are calculated when remain variables are constant. In the case of LF equations (34) and (36) $C_i = K'_i$ whereas in the case of DA eqs (35) and (37) $C_i = p_i^l$. The above equation system is simply linear with the two unknown: $(\partial \ln p_1 / \partial (1/T))_{\theta_{il},\theta_{2l}}$ and $(\partial \ln p_2 / \partial (1/T))_{\theta_{il},\theta_{2l}}$ which are the isosteric heats of adsorption divided by (-k).

In the above equation we assume that $(\partial C_i / \partial (1/T))$ will be the best-fit parameter which can be found from adjustment of theoretical isosteric heat of single component to the calorimetric data.

While considering the case of generalization of LF equation (19) (lack of correlations between adsorption energies) in order to obtain the expression for isosteric heats it is easier to use eq. (18). Of course, the use of eq. (18) leads to the same expression for isosteric heats of mixture components as the equation system (51-52). So, assuming that the expression for energy distribution function is represented by eq. (6) we arrive at the following equation:

$$Q_{1}^{st} = q_{1}^{st0} - c_{1} \ln \frac{\theta_{1t}}{1 - \theta_{1t} - \theta_{2t}} = q_{1}^{st0} - kT \ln(K_{1}p_{1})$$
(53)

If the Dubinin-Astakhov function (7) is used, eq. (18) leads to the following equation:

$$Q_{1}^{st} = q_{1}^{stl} + E_{1} \left[\ln \left(\frac{1 - \theta_{2t}}{\theta_{1t}} \right) \right]_{r_{1}}^{r_{1}} = q_{1}^{stl} - kT \ln \left(\frac{p_{1}}{p_{1}'} \right)$$
(54)

The above equations (53) and (54) can be used for the case of lack of correlations between adsorption energies of mixture components. If we assume that correlations between adsorption energies exist, and are described by relation (21) (adsorption energy distributions $\chi_i(\varepsilon_i)$ have a similar shape) the solution of equation system (51-52) leads to the following expressions for isosteric heats of adsorbed mixture components. In the case of Gaussian-like adsorption energy distributions (6) the use of eq. (22) leads to the following equation:

$$Q_1^{st} = q_1^{st0} - kT \ln(K_1 p_1 + K_2 p_2)$$
(55)

and when $\chi_i(\varepsilon_i)$ is DA function (7), i.e. we use isotherm equation (23)

$$Q_1^{st} = q_1^{stl} - kT \ln\left(\frac{p_1}{p_1'} + \frac{p_2}{p_2'}\right)$$
(56)

It is interesting to note that the existence of high correlations between adsorption energies of mixture components is reflected by difference under the logarithmic term of the corresponding expressions (53) and (55) or (54) and (56). While analyzing eqs (55) and (56) we can expect that theoretical isosteric heats of adsorption calculated for the case of high correlations between adsorption energies should be approximately linear in a wide range of surface coverages. Also another conclusion can be drawn: for high values of partial pressures p_i (and consequently high values of mole fractions Y_i and X_i in gas and adsorbed phases, respectively), the values of theoretical isosteric heats of mixture components should be similar (the second term under logarithm in eqs (55) and (56) can be neglected).

Another important fact is that theoretical isosteric heats calculated for the case of lack of correlations between adsorption energies of mixture components have the same form as in the case of single-gas adsorption. We can draw conclusion that if there are no correlations between adsorption energies, calorimetric effects accompanying adsorption of mixture components are similar to those accompanying single-gas adsorption isotherms. The existence of correlations causes differences in behaviour of the theoretical isosteric heats of adsorption of mixture components. Of course, such a conclusion can be drawn only in the case of non-interacting molecules, which is justified because if neither correlations nor interactions exist there are no reasons for existence of the differences in heat effects accompanying adsorption of single gases and those in the adsorbed mixture. The existence of molecules of the second component in the adsorbed phase exhibits only by blocking adsorption sites for molecules of the first component.

Such a conclusion can be extended: if experimentally measured isosteric heats of adsorption of single gases and those gases in mixture have a similar shape it indicates lack of correlations between energies of adsorption of mixture components and weak interactions between adsorbed molecules.

So, while recapitulating our theoretical study we can state that during the analysis of experimentally measured adsorption data we have two isotherm equations (11) and (13) obtained for the case of single-gas adsorption and four isotherm equations (19), (20), (22) and (23) useful during the investigation of phase diagrams. Likewise studying calorimetric effects we can also use two equations in the case of single gas adsorption (47) and (49), and four (53), (54), (55) and (56) in the case of isosteric heats of adsorption determined for mixture components.

4. CORRELATION OF EXPERIMENTAL DATA

To calculate theoretical phase diagrams and theoretical isosteric heats of adsorption for the adsorbed gas mixture we need specific experimental data. Namely, all experimentally measured data for the adsorption system i.e. singleand mixed-gas adsorption isotherms and isosteric heats of adsorption of pure and mixed gases must be measured at the same temperature. Unfortunately, it is not easy to find such data in literature. These requirements fulfil the experimental data reported by Dunne et al. [21-23] on silicalite: C_2H_6 at 23.31 °C, CH_4 at 23.07 °C, $C_2H_6+CH_4$ at 25.29 °C; for NaX: CO_2 at 31.4 °C, C_2H_6 at 32.4 °C, $CO_2+C_2H_6$ at the two temperatures: 29.4 °C and 28.94 °C (small differences between temperatures of measurements). While analyzing the isosteric heats of adsorption of these single gases adsorbed on silicalite and NaX it can be assumed that in all cases interactions between the adsorbed molecules exist. In particular, it concerns adsorption of CO_2 on NaX. For this reason we cannot use these adsorption data to examine our equations for isosteric heats of adsorption.

To elucidate the fundamental differences in the behaviour of the adsorption isosteric heats equations obtained by using the Integral Equation Approach, we use the adsorption data examined previously [19,25]. Namely, in our previous theoretical studies we considered the adsorption data for O_2 and N_2 and CO adsorbed on zeolite MS10X at the three temperatures: 172.04 K (-150 °F),

227.59 (-50 °F) and 273.15 (32 °F), reported by Nolan and coworkers [24]. Our previous research indicated that in the case of O_2 , N_2 adsorption and at the lowest experimental temperature of CO adsorption we have to do with lack of interactions between adsorbed molecules. Unfortunately, the authors [24] report only the adsorption data for single and mixed gases. From these experimental data we choose adsorption of N_2 and CO at 172.04 K. This choice is caused by similar values of the heterogeneity parameter c_i which makes it possible to use both equations obtained for the case of correlation or its lack between energies of adsorbed molecules.

Before calculating theoretical phase diagrams it is important to discuss the phenomenon of correlations between the adsorption energies of mixture components. Namely, the model of high correlations, eq. (21), assumes the same shape of adsorption energy distribution function. It means that when high correlations between the adsorption energies of various components exist, the adsorption energy distribution functions are just the same, only shifted on the energy axis.

The shape of $\chi_i(\varepsilon_i)$ functions is affected by the heterogeneity parameters: in the case of Gaussian-like adsorption energy distribution (6) it is kT/cwhereas the shape of Dubinin-Astakhov energy distribution function (7) is affected by the parameters r and kT/E. If we assume that high correlations between the adsorption energies of mixture components are described by relation (21), the correct use of the mixed-gas isotherm equations (22) and (23) requires the same values of heterogeneity parameters for both mixture components. In contrast, if kT/c, or r and kT/E for mixture components are notably different, only the model of lack of correlations should be used. Correlations between the adsorption energies of mixture components are shown graphically in Figures 1 and 2.

In our previous paper we applied the linear LF regression (12) to the pure N_2 and CO adsorption data. The results obtained in this way were presented in our previous paper [19,25]. Our investigations showed, that in the case of N_2 and CO adsorption on zeolite MS 10X it is sufficient to apply the model assuming lack of interactions between adsorbed molecules.

In the present paper we use another procedure, namely we adjust directly isotherm equations (11) and (13) to the experimental data. This procedure leads to better agreement of the theoretical isotherm equations (11) and (13) with single-gas adsorption data.



Fig. 1. The existence of correlations effect between the adsorption energies of mixture components (A) and (B) described by the Gaussian-like adsorption energy distribution (6). The figure shows also the influence of the values of parameters kT/c and ε^0 on the shape of the function $\gamma_i(\varepsilon_i)$



Fig. 2. The existence of correlation effects between the adsorption energies of mixture components (A) and (B) described by the Dubinin-Astakhov adsorption energy distribution (7). The figure also shows the influence of the values of parameters r, E and ε' on the shape of the function $\chi_i(\varepsilon_i)$

The obtained results are a little different from those obtained by applying linear regression (12) or (14). Figure 3 shows the adjustment of LF (11) and DA (13) equations to the experimental single-gas adsorption isotherms and we can see that both the Langmuir-Freundlich eq. (11) and the Dubinin-Astakhov eq. (13) reproduce very well the investigated adsorption systems. The best-fit parameters elucidated in this way are collected in Table 1.



Fig. 3. The single-gas adsorption isotherms of nitrogen and carbon oxide at the molecular sieve 10X reported by Nolan et al. [24] at the temperature 172.04 K. The solid lines are the theoretical isotherms calculated by using the LF (11) and the DA (13) isotherm equations with the parameter values given in Table 1

Tab. 1.	Values	of the	parameters	obtained	by a	pplying	the	Langmu	ir-Freu	indli	ch
equation	n (11) an	nd the	Dubinin-Asta	akhov eq.	(13)	to the	exper	imental	isother	rms	of
nitrogen	and car	bon oxi	de adsorbed	on the mo	lecula	r sieve	10X,	reported	by No	olan	et
al. [24]											

an Co Jo	La	ngmuir-Freu	undlich eq. (11)	and a	to the busic
néviolis př 20. – orpi	M (cm ³ STP/g)	K exp	$\left\{\frac{\varepsilon^0}{kT}\right\}$	$\frac{kT}{c}$	q ^{st0} (kJ/mol)
		(mmH	Ig ⁻¹)	transe of com	g. 2. The exist
N ₂	142.32	10-3	0.506	7.44	
CO	141.32	6.22.	0.443	8.87	
	deorption date. D	ubinin-Asta	khov eq. (13)		
	М	kT	p' (mmHg)	r	q^{stl}
	(cm ³ STP/g)	E			(kJ/mol)
N ₂	88.61	0.287	2227.85	1.33	6.01
CO	110.25	0.190	3938.98	1.60	4.00

The isosteric heat of adsorption can be easily determined from the adsorption data. Namely, it is necessary to construct graphically the dependence θ_{ii} vs. $\ln p$. It is important to use more than two experimental isotherms. Then, using the obtained data it is necessary to construct the graphical dependence $\ln p$ vs. 1/T for separate values of the fraction coverage. The slope of the obtained linear dependence is proportional to the isosteric heat of adsorption.

Fortunately, the experimental isotherms measured at three temperatures for both N_2 and CO adsorption are available. So, we used this method in our previous paper [19]. Figure 4 shows the obtained isosteric heats of adsorption for single gases.

The course of isosteric heats of adsorption presented in Figure 4 (the heats become small with the increasing coverage) suggests high heterogeneity and transient interactions between the adsorbed molecules. It justifies application of the equations neglecting the interaction effects in the adsorbed phase.



Fig. 4. The isosteric heats of adsorption of pure N_2 and CO adsorbed on the molecular sieve 10X determined by using the graphical method to the adsorption data reported by Nolan et al. [24]. The solid lines are the theoretical isosteric heats calculated from eqs (47) and (49) using the values of the parameters collected in Table 1

From Figure 4 we can obtain the configurational heats of adsorption q_i^{st0} and q_i^{stl} . Namely, in the case of eq. (47) it is the value of isosteric heats of adsorption when the fractional coverage is equal to 0.5. In the case of eq. (49), the value of configurational isosteric heats q_i^{stl} can be obtained for the fractional coverage equal to 1. These values are inserted in the last column of Table 1 because they will be helpful to calculate hypothetical isosteric heats of adsorption in the mixture (N₂+CO).

Figure 5 shows the comparison with experiment of the theoretically calculated phase diagrams for the case of (N_2+CO) adsorption. Lines are the

theoretically calculated phase diagrams: solid line – the case of lack of correlations between energies of adsorbed molecules and, broken line – the case of high correlations between adsorption energies described by eq. (8). Although as follows from the analysis of heterogeneity parameters collected in Table 1 in the case of Dubinin-Astakhov equation (13) only the model of lack of correlations, eq. (22) should be used, we also show the theoretical curve calculated from eq. (23) (high correlations between adsorption energies).

As can be seen in Figure 5 only in the case of Langmuir-Freundlich eq. (22) (high correlations) satisfactory agreement was obtained.

In Figure 6 we present the results of theoretical calculations of isosteric heats of simultaneous adsorption by using the Langmuir-Freundlich and the Dubinin-Astakhov eqs (47-50). This confirms the previous conclusions that differences in theoretical isosteric heats of adsorbed mixture components are explicit for the small values of mole fraction X_i in the adsorbed phase. With the increasing values of X_i the theoretical isosteric heats calculated for the cases of lack and high correlations between adsorption energies of components mixture become the same.



Fig. 5. Adsorption from the (N₂+CO) gaseous mixture on the molecular sieve 10X at the temperature 172.04 K, at the constant total pressure P=760 mmHg. Comparison with experiment (•) of the X-Y composition diagrams calculated by applying equations corresponding to given energy distribution functions: left figure: LF eq. (19) (solid line, lack of correlations) and eq. (22) (broken line, high correlations); right figure: DA eq. (20) (solid line, lack of correlations) and eq. (23) (broken line, high correlations). The theoretical curves were calculated by using the parameters collected in Table 1. X_1 means the mole fraction of the component 1 in the adsorbed phase and $Y_1 = p_1/(p_1 + p_2)$ in the gas phase

The above conclusions concerning isosteric heats of adsorption of mixture components are right only in the case when interactions between the adsorbed molecules are negligible. It is known that when the interactions between adsorption energies play a substantial role in adsorption phenomena, it is reflected in heat effects accompanying mixed-gas adsorption. The study taking into consideration interaction effects between adsorbed molecules for the case of the Gaussian-like adsorption energy distribution (6) has been carried out recently [19,20]. The case of the Dubinin-Astakhov energy distribution function (7) will be subject of our further publication.



Fig. 6. The hypothetical isosteric heats of simultaneous adsorption of N_2 and CO on the molecular sieve 10X (X_1 means the mole fraction of nitrogen in the adsorbed phase). The theoretical curves were calculated by applying the equations corresponding to given energy distribution functions: left figure: LF eq. (53) (solid line, lack of correlations) and eq. (55) (broken line, high correlations); right figure: DA eq. (54) (solid line, lack of correlations) and eq. (56) (broken line, high correlations)

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