

## Equilibrium adsorption of binary mixtures of gases by zeolites and the state of the adsorption phase

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A method for analyzing the state of the adsorption phase was developed on the basis of statistical thermodynamics for the case of equilibrium adsorption of binary gaseous mixtures. The procedure for treating experimental data to determine the Helmholtz energy and other thermodynamic functions of a mixture of molecules occluded within zeolite cavities was proposed. A measure of ideal behavior of a mixture of a small number of molecules in the micropore was formulated; in the asymptotic limit such a behavior leads to the Raoult law and to assumption of the validity of the Raoult law when moving along the line of constant value of the Gibbs integral in the ideal adsorption solution theory.

**Key words:** zeolite, equilibrium adsorption, multicomponent system.

Several major lines of theoretical investigations of equilibrium adsorption of gas and vapor mixtures can be distinguished. The ideal adsorption solution theory (IAST) proposed by Myers and Prausnitz<sup>1</sup> is based on the assumptions that (a) the adsorption phase occupies a constant volume (or surface area); (b) at fixed temperature, the partial molar volume (the unit surface area) is an unambiguous function of the pressure in the adsorption phase; and (c) the Raoult law is valid when moving along the line of constant pressure  $\Pi$  in the adsorption phase. Such assumptions made it possible to describe the adsorption in a multicomponent system in terms of individual adsorption. Actually, on moving along the line of constant pressure it is possible to arrive at a pure  $i$ th component with its pressure in the gas phase being  $p_i^0 = p_i/x_i$  ( $p_i$  is the partial pressure of the  $i$ th component, and  $x_i$  is its mole fraction in the adsorption phase). With the isotherms known, the pressure  $\Pi$  developed by any individual component can be found by integrating the Gibbs equation. Thus, in the case of a binary system the equality of  $\Pi$  values for both individual components is obtained; the root of this equality (with taking account of the Raoult law) is the mole fraction of any of the components. In such a manner the composition of the adsorption phase and then (using the first assumption) the adsorption values of the components of the system are determined. The wide use of this model is associated with the absence of limitations on the shape of individual isotherms.

The second line of investigations consists of various vacancy models. Treatment of the adsorption phase as a vacancy solution<sup>2,3</sup> implies that the vacancies penetrate through any obstacles and do not interact with the adsorption field.<sup>2,3</sup> The phenomenological thermodynamics of the equilibrium of two vacancy solutions, one of which is infinitely diluted (the gas phase), made it possible to derive specific equations describing individual and binary adsorption for different types of relations between the activity coefficients of the components of a vacancy solution and its composition. A binary system corresponds to a three-component vacancy solution. Previously,<sup>4,5</sup> it has been shown that the activity coefficients can be calculated from the Wilson equation.

In the third line of investigations,<sup>6,7</sup> the adsorbent that enters into a reversible addition or exchange reaction to form adsorbent-adsorbate complexes is considered as a component of the solution. In contrast to the vacancy model, the adsorbent is not regarded as thermodynamically inert. The volume of the adsorption solution remains constant upon varying its composition. The use of mathematical tools of chemical thermodynamics makes it possible to find intrinsic relations between the activity coefficients of the components of the adsorption solution and to relate these to the stoichiometric coefficients. For one of the activity coefficients, its value as a function of the composition of the adsorption solution is given empirically, just as in the vacancy model. This is a drawback of the last two lines of investigations. In the

case of ideal vacancy or adsorption solution, both theories lead to the Langmuir equation for individual adsorption and to the Markham—Benton equation for the adsorption of mixtures.<sup>8</sup>

The fourth investigation line of the adsorption of mixtures extends the Polanyi model and makes use of the heterogeneous distribution of the composition and pressure in the adsorption space.<sup>9–11</sup> It postulates that the progressive filling of wider micropores with higher adsorption potential occurs as the partial pressures increase. A solution that obeys the Raoult law in a narrow region between the filled and unfilled adsorption space, *i.e.*, in the micropores being filled at given partial pressures, is considered an ideal solution. In the micropores already filled, the composition of the adsorption phase varies depending on the adsorption potential and on the pressure  $\Pi$ . The micropore size distribution as a function of the adsorption potentials is determined from individual isotherms.

The above models are microscopic and no account of the limited size of micropores is taken in explicit form. In this connection fundamental problems arise, *e.g.*, those that are associated with physical interpretation of the pressure  $\Pi$ . By definition it is a microscopic quantity, which cannot be used in the case of individual micropores. For this reason, models in which the system of micropores is considered as the Gibbs grand canonical ensemble should be regarded as the most suitable. The subsystems (micropores) can exchange adsorbate molecules and energy. To exclude the surface effects at the boundaries, thus providing statistical independence, the Gibbs theory deals with macroscopic individual subsystems. However, if the condition for statistical independence of subsystems is satisfied, then the Gibbs method can also be applied to an ensemble of microsystems. Zeolites are the best object for the refinement of such an approach to adsorption.<sup>12</sup> Ruthven was successful in deriving the equation of the adsorption equilibrium both for individual adsorption and for adsorption of a binary mixture using mathematical tools of statistical thermodynamics and the simplest analogy between the state of groups of molecules held in a zeolite cavity and the van der Waals gas.<sup>13,14</sup>

All the approaches mentioned above are based on different definitions of ideal behavior of the adsorption phase. A system behaving ideally for one model can become strongly non-ideal for another model. Therefore, a more rigorous substantiation of the measure of the ideal behavior of the adsorption phase on the level of individual micropores is required. Solving this problem serves to establish the reasons for the deviations from the ideal behavior and to predict the properties of multi-component systems more accurately.

### Mathematical model

Let us consider the equilibrium adsorption of a binary mixture by zeolite assuming that individual cavities are statistically independent of one another. Ignoring

the distribution of cavities in the kinetic energy, we can write the equation of adsorption equilibrium as follows:<sup>12</sup>

$$a_1 = \frac{\lambda_1 \partial \log \Xi}{N_A \partial \lambda_1}, \quad a_2 = \frac{\lambda_2 \partial \log \Xi}{N_A \partial \lambda_2}, \quad (1)$$

where the grand canonical partition function

$$\Xi = \xi a_0 N_A, \quad \xi = \sum_i \sum_j \lambda_1^i \lambda_2^j Q_{i,j}. \quad (2)$$

Here  $a_1$  and  $a_2$ /mol kg<sup>-1</sup> are the amounts of the first and the second components adsorbed, respectively;  $a_0$ /mol kg<sup>-1</sup> is the number of cavities per unit mass of zeolite divided by the Avogadro constant  $N_A$ ;  $\Xi$  is the grand canonical partition function;  $\xi$  is the grand canonical partition function per cavity; and  $Q_{i,j}$  is the canonical partition function of a mixture containing  $i$  molecules of the first component and  $j$  molecules of the second component held in a zeolite cavity. The canonical partition function  $Q_{i,j}$  is related to the Helmholtz energy  $F_{i,j}$  for the cavity containing  $i$  molecules of the first component and  $j$  molecules of the second component:

$$F_{i,j} = -k_B T \log Q_{i,j}, \quad (3)$$

where  $k_B$  is the Boltzmann constant, and  $T/K$  is temperature. The parameters  $\lambda_1$  and  $\lambda_2$  are defined through the chemical potentials of the first and the second components ( $\mu_1$  and  $\mu_2$ , respectively) per one molecule:

$$\lambda_1 = \exp(\mu_1/k_B T), \quad \lambda_2 = \exp(\mu_2/k_B T). \quad (4)$$

The partition function for microcanonical ensemble  $\Omega$  is related to the grand canonical partition function by the following relationship:

$$\Omega = -W_0 \Pi = -k_B T \log \Xi. \quad (5)$$

Here  $W_0/m^3$  kg<sup>-1</sup> is the volume of the adsorption space, and  $\Pi$  is a macroscopic quantity defined from the Gibbs equation (its dimensionality coincides with that of pressure):

$$W_0 d\Pi = a_1 d\mu_1 + a_2 d\mu_2.$$

In the case of adsorption of an individual component, the value of pressure  $\Pi$  is equal to the integral of the sorption value over the chemical potential (the Gibbs integral) divided by the volume of the adsorption phase  $W_0$ , as defined in the IAST model. Therefore the assumption made by Myers and Prausnitz,<sup>1</sup> that the Raoult law is valid at a constant  $\Pi$  value, corresponds to a constant value of the grand canonical partition function  $\Xi$ . Designating the mole fractions of the components averaged over the entire adsorption phase as  $x_1$  and  $x_2$ , it is possible to write the following conditions of the ideal behavior of the adsorption phase:

$$\begin{aligned} \mu_1 &= \bar{\mu}_1 + k_B T \log x_1, & \mu_2 &= \bar{\mu}_2 + k_B T \log x_2, \\ \bar{\mu}_1 &= \mu_1^\circ + k_B T \log p_1^\circ, & \bar{\mu}_2 &= \mu_2^\circ + k_B T \log p_2^\circ \end{aligned} \quad (7)$$

Here  $\mu_1^\circ$  and  $\mu_2^\circ$  are the temperature-dependent standard chemical potentials of the first and the second components, respectively;  $p_1^\circ$  and  $p_2^\circ$  are the pressures of respectively the first and the second components in the bulk phase in the case of individual sorption at the same value of the Gibbs integral as in the case of adsorption of the mixture at partial pressures  $p_1$  and  $p_2$ ;  $\mu_k$  is the chemical potential of the  $k$ th component ( $k = 1, 2$ ) which in the case of its individual adsorption corresponds to the same value of the grand canonical partition function  $\Xi$  as in the case of adsorption of the mixture or to the same pressure  $\Pi$ . The condition (6) is another form of the Raoult law when moving along the line of the constant pressure for the ideal gas phase:

$$p_1 = p_1^\circ x_1, p_2 = p_2^\circ x_2. \quad (8)$$

The problem is to find such a pattern of dependence of the Helmholtz energy  $F_{i,j}$  of a mixture containing  $i$  molecules of the first component and  $j$  molecules of the second component held in an individual cavity on the  $i$  and  $j$  values such that conditions (6) and (7) would be met when moving along the line of the constant  $\Xi$  value. The analysis has shown that this is possible only if the adsorption capacities of the cavities are equal, *i.e.*, if the molecular volumes are fairly close. Otherwise, the model of ideal adsorption solution<sup>1</sup> is *a priori* inapplicable. (Of course, it is of no significance in the case of statistical approach.) Let  $N$  be the maximum number of guest molecules in the cavity for both components; then we can write for the grand canonical partition function per cavity:

$$\xi = \sum_{i=0}^N \sum_{j=0}^i \exp \left( \frac{(i-j)\mu_1 + j\mu_2 - F_{i-j,j}}{k_B T} \right). \quad (9)$$

At the same time, according to the condition mentioned above, the  $\xi$  value should be equal to the same quantity defined for any (*e.g.*, the first) component if its chemical potential is  $\mu$ :

$$\xi = \sum_{i=0}^N \exp((i\bar{\mu}_1 - F_{i,0})/k_B T). \quad (10)$$

Equating the right sides of Eqs. (8) and (9) at the same  $i$  to one another and expressing  $\mu_1$  and  $\mu_2$  through the mole fractions  $x_1$  and  $x_2$  using relationships (6), we obtain the following system of recursion relationships:

$$\sum_{j=0}^i x_1^{i-j} x_2^j \exp \left[ \frac{(i-j)\bar{\mu}_1 + j\bar{\mu}_2 - F_{i-j,j}}{k_B T} \right] = \exp \left( \frac{i\bar{\mu}_1 - F_{i,0}}{k_B T} \right). \quad (11)$$

The system is successively solved for  $i = 1, \dots, N$  by transforming each equation to a polynomial form of degrees in  $x_1$  (or  $x_2$ ) and equating corresponding coefficients to zero. As a result, the following system can be obtained:

$$F_{i,0} = F_{0,i} + i(\bar{\mu}_1 - \bar{\mu}_2). \quad (12)$$

$$F_{i,j} = \frac{i}{i+j} F_{i+j,0} + \frac{j}{i+j} F_{0,i+j} - k_B T \log \left[ \frac{(i+j)!}{i!j!} \right]. \quad (13)$$

It is convenient to pass to the specific Helmholtz energy  $\bar{F}_{i,j}$  per mole (rather than per molecule); then the last two expressions can be written as follows:

$$F_{i,0} - F_{0,i} = N_A(\mu_1 - \mu_2) = RT \log(p_1^\circ/p_2^\circ), \quad (14)$$

$$\bar{F}_{i,j} = \frac{i}{i+j} \bar{F}_{i+j,0} + \frac{j}{i+j} \bar{F}_{0,i+j} - \frac{RT}{i+j} \log \left[ \frac{(i+j)!}{i!j!} \right]. \quad (15)$$

By definition,  $p_1^\circ$  and  $p_2^\circ$  are the pressures of the individual components at the same  $\Xi$  (or  $\Pi$ ) value as that of the binary system with the partial pressures  $p_1$  and  $p_2$ . Therefore, in the general case  $p_1^\circ$  and  $p_2^\circ$  are functions of the total pressure and the composition of the gas phase. However, the Helmholtz energy  $F_{i,0}$  of  $i$  molecules of the first component occluded within a zeolite cavity and the Helmholtz energy  $F_{0,i}$  of  $i$  molecules of the second component in the left side of equality (13) cannot be dependent on the partial pressures in the gas phase. On the other hand, the right side of equality (13) cannot be dependent on the number of molecules  $i$  occluded within a cavity. Therefore, both the left side and the right side of Eq. (13) must have a constant value. Hence it follows that the individual isotherms plotted as the amount sorbed against the logarithm of the pressure should have the same pattern and match up when shifted along the pressure axis. This is a rare particular case for nonlinear isotherms and usually does not occur; however, this condition is necessary for the fulfillment of the major assumption of the IAST (the validity of the Raoult law when moving along the line of the constant pressure).

Equation (14) is similar to the equation for the specific Helmholtz energy of the ideal solution for which the Raoult law is valid. Actually, going to the approximate limit for very large  $i$  and  $j$  and using the Stirling formula, we get

$$\bar{F}_{i,j} = x_1 \bar{F}_{i+j,0} + x_2 \bar{F}_{0,i+j} + x_1 RT \log x_1 + x_2 RT \log x_2. \quad (16)$$

The last two terms in Eq. (16) are the products of temperature and the entropy of mixing upon the formation of ideal solution taken with the opposite sign. The importance of Eq. (14) lies in the fact that it can serve as the starting point when analyzing the deviations from ideal behavior of the adsorption phase. To this end, an additional term (*viz.*, the excess Helmholtz energy  $F^E_{i,j}$ ) can be introduced into Eq. (14) as in the classical theory of solutions

$$\bar{F}_{i,j} = \frac{i\bar{F}_{i+j,0} + j\bar{F}_{0,i+j}}{i+j} - \frac{RT}{i+j} \log \left[ \frac{(i+j)!}{i!j!} \right] + \bar{F}^E_{i,j}. \quad (17)$$

Using a particular fitting function and having determined the coefficients by the least squares method, it is

possible to analyze the state of the adsorbed substance in detail; in particular, the effect of the adsorption field inhomogeneity can be established.

### Results and Discussion

The major result of the analysis of the ideal adsorption solution theory, as applied to the adsorption of mixtures by zeolites, is the derivation of Eq. (12); this equation was implicitly included in the postulate that the Raoult law is valid when moving along the line of constant pressure in the adsorption phase. This equation is rather sufficient for calculating binary equilibrium adsorption from individual isotherms. Condition (11) implying the constant value of selectivity  $S = (p_1/a_1)/(p_2/a_2)$  can be considered as a "side effect" of inadequately rigorous definition of the measure of ideal behavior in the IAST model. If this condition is not met, then the Raoult law is also not valid. However, Eq. (12) or Eq. (14) may also serve well as a criterion for the ideal behavior of the adsorption phase instead of the outdated postulate used in the IAST. In this case the algorithm of calculations of the ideal binary mixtures can be conceived as follows. First, the dependences of the Helmholtz energies of each of the components on the number of guest molecules in a zeolite cavity are established from treating the individual isotherms. Then, the  $F_{ij}$  values for all possible combinations of  $i$  and  $j$  are calculated using Eq. (12) and the values of the adsorption of each of the components at given partial pressures are determined from Eqs. (1)–(4). If the system is non-ideal, then the problem is to establish the character of the deviations of experimental results from Eq. (12) based on treating the experimental data on the equilibrium adsorption of mixtures.

Experimental data on the adsorption of an oxygen–nitrogen mixture by NaX zeolite at 144 K<sup>15</sup> can be analyzed as an example. The adsorption of the mixture occurred at a constant total pressure equal to the atmospheric pressure. The following expanded form, which is a special case of the system (1)–(4), was used for treating the individual isotherms:

$$a_1 = a_0 \frac{\sum_{i=1}^{N_1} i \exp[\lambda \log p_1 - (F_{i,0} - i\mu_1^0)/(k_B T)]}{\sum_{i=0}^{N_1} \exp[\lambda \log p_1 - (F_{i,0} - i\mu_1^0)/(k_B T)]}, \quad (18)$$

$$a_2 = a_0 \frac{\sum_{j=1}^{N_2} j \exp[\lambda \log p_2 - (F_{0,j} - j\mu_2^0)/(k_B T)]}{\sum_{j=0}^{N_2} \exp[\lambda \log p_2 - (F_{0,j} - j\mu_2^0)/(k_B T)]}$$

The dependence of the Helmholtz energy on the number of molecules within the cavity was approximated by the following polynomials:

$$(F_{i,0} - i\mu_1^0)/(k_B T) = \sum_{k=1}^n b_k i^k,$$

$$(F_{0,j} - j\mu_2^0)/(k_B T) = \sum_{k=1}^n c_k j^k. \quad (19)$$

Polynomials of the fifth degree were used. The  $F_{ij}^E$  values were determined using the following regression equation:

$$F_{ij}^E = \sum_{k=1}^m \sum_{l=1}^{m+1-k} d_{k,l} i^k j^l. \quad (20)$$

The coefficients of the polynomials (18) and those of the regression equation (19) for  $m = 3$  (6 coefficients) were calculated by the least squares method; the sum of squared deviations of logarithms of the calculated partial pressures from experimental was minimized.

The individual adsorption isotherms of oxygen and nitrogen in semilogarithmic coordinates are shown in Fig. 1. The maximum numbers of the molecules per one cavity were taken to be  $N_1 = 16$  and  $N_2 = 13$ , respectively. The dependences of the specific Helmholtz energy on the cavity filling typical of most of the systems are presented in Fig. 2. The results of calculations of the dependence of selectivity on the composition of the adsorption phase at a constant total pressure in the gas phase are shown in Fig. 3. As can be seen in Fig. 3, the system under consideration is strongly non-ideal. The results of calculations according to the IAST model (curve 3) differ from those performed according to the model (1)–(4) for the case of ideal adsorption phase (curve 2) when Eq. (12) is valid. This distinction is due to the fact that in this case the condition (11) is not met, and the IAST model is inapplicable to the system under

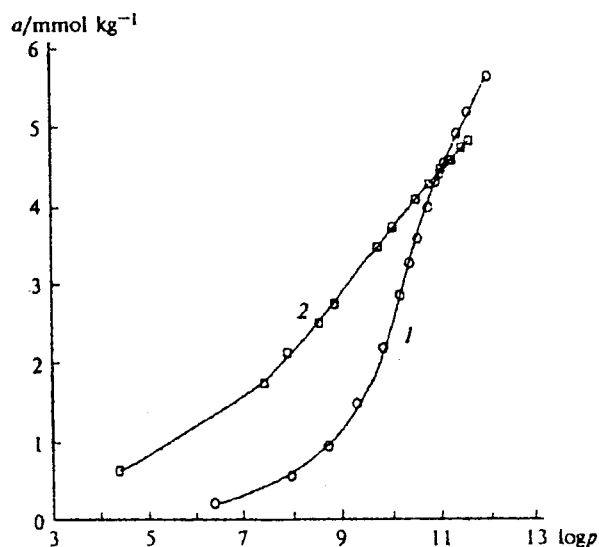


Fig. 1. Individual isotherms of oxygen (1) and nitrogen (2) adsorption by NaX zeolite at 144 K.<sup>15</sup>

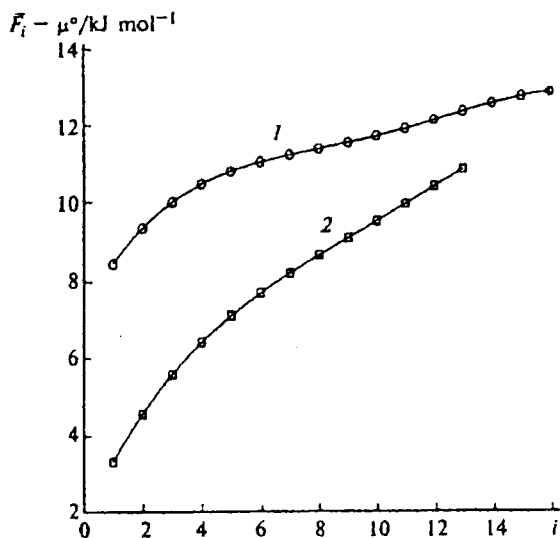


Fig. 2. Dependences of the specific Helmholtz energy ( $\bar{F}_i - \mu^0$ ) on the number of guest molecules ( $i$ ) in a zeolite cavity for individual adsorption of oxygen (1) and nitrogen (2).

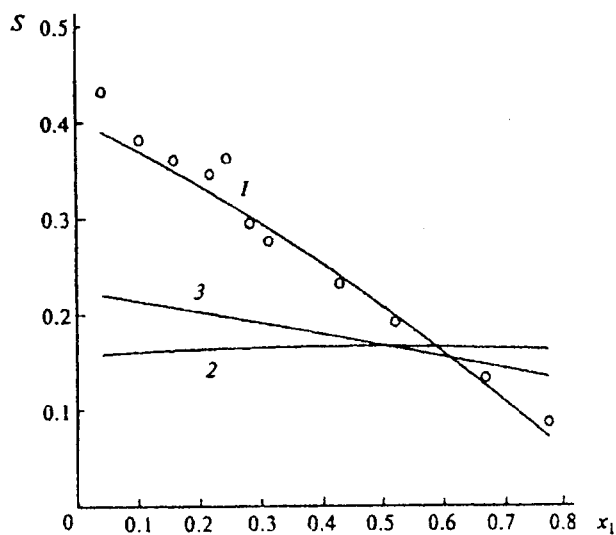


Fig. 3. Dependence of selectivity  $S = (a_1 p_2) / (a_2 p_1)$  on the molar fraction of oxygen ( $x_1$ ) in the adsorption phase at a constant total pressure in the gas phase of 101.3 kPa. The points are experimental data;<sup>15</sup> 1, calculations according to the statistical model; 2, calculations according to the statistical model for ideal solution ( $F_{ij}^E = 0$ ); and 3, calculations according to the IAST model.<sup>1</sup>

consideration. In Fig. 4, the calculated and experimental dependences of the composition of the gas phase on the composition of the adsorption phase at a constant total pressure are shown. It can be seen that the results of calculations performed according to the model presented agree well with the experimental data. The de-

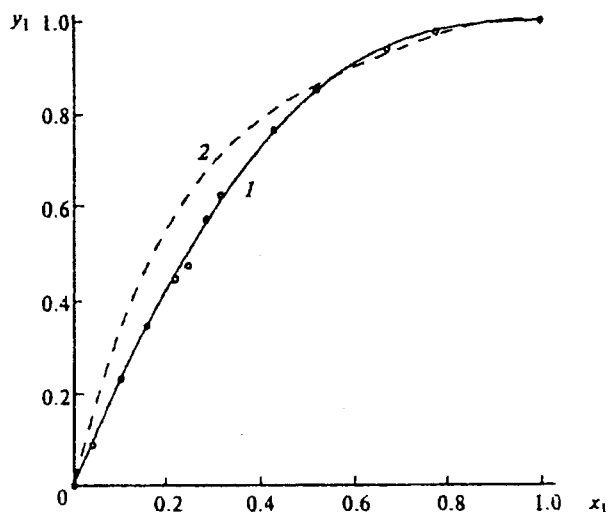


Fig. 4. Dependence of the composition of the gas phase on the adsorption phase composition when moving along the line of constant total pressure of 101.3 kPa;  $y_1$  and  $x_1$  are the mole fractions of oxygen in the gas phase and in the adsorption phase, respectively. The points are experimental data;<sup>15</sup> 1, calculations according to the statistical model; 2, calculations according to the IAST model.

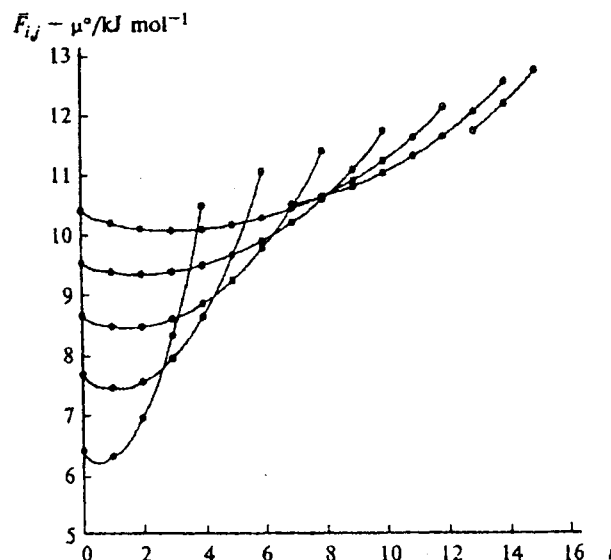


Fig. 5. Change in the Helmholtz energy ( $\bar{F}_{ij} - \mu^0$ ) of a mixture of  $i$  oxygen and  $j$  nitrogen guest molecules in a zeolite cavity on the number of oxygen molecules  $i$  when moving along the lines of constant total number of molecules  $i + j$  in an individual NaX zeolite cavity at 144 K. The total number of molecules for each curve is equal to the abscissa read from the last point.

pendences of the specific Helmholtz energy on the number of guest oxygen molecules in a zeolite cavity along the lines of a constant total number of molecules are shown in Fig. 5. The Helmholtz energy takes into

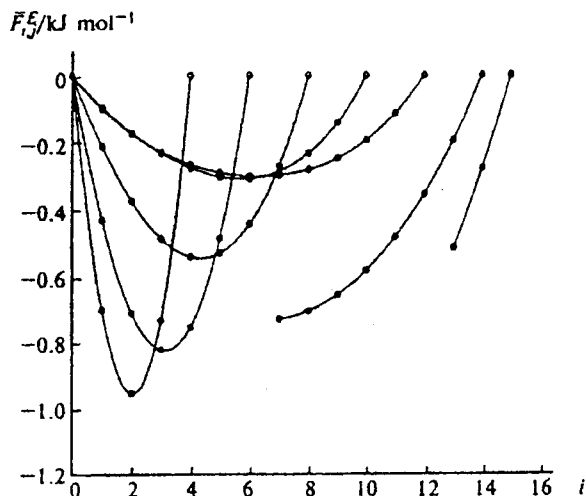


Fig. 6. Change in the excess Helmholtz energy of a mixture of  $i$  oxygen molecules and  $j$  nitrogen molecules within a zeolite cavity on the number of oxygen molecules  $i$  when moving along the lines of constant total number of molecules  $i + j$  in the cavity.

account both the interaction between the adsorbed molecules and their interaction with the adsorbent. The number of  $O_2$  molecules cannot exceed the total number of the molecules; therefore, the curves terminate at the right at an  $i$  value equal to the constant total number of the  $O_2$  and  $N_2$  molecules for each curve. On the other hand, the volume of the oxygen molecule is less than that of the nitrogen molecule. Hence, as oxygen is replaced by nitrogen, the volume of the molecular aggregate increases up to the maximum value that cannot exceed the cavity volume. Therefore two curves corresponding to large total numbers of molecules (14 and 15) terminate at the left. Analogous curves for the excess Helmholtz energy are shown in Fig. 6. As can be seen in this figure, the adsorption phase is non-ideal; in this case the excess Helmholtz energy is negative. Even at much lower temperature (78 K) the solution of oxygen and nitrogen is much like the ideal solution,<sup>16</sup> i.e., the excess Helmholtz energy is close to zero. Such a distinction in the behavior of the adsorption solution as compared to that of a liquid mixture can be explained by the effect of inhomogeneity of the adsorption field within individual zeolite cavities and by the different types of interaction between the molecules of the adsorbed components and the adsorption field. In contrast to oxygen molecules, the nitrogen molecules have a short-range quadrupole moment. Hence it is highly probable that nitrogen molecules occupy positions near cations. Therefore, the molecules are redistributed in the cavity volume so that their total internal energy decreases; this leads to a decrease in the Helmholtz energy.

Equation (12) for the Helmholtz energy of an aggregate consisting of mixture of molecules of different components may serve as a measure of ideal behavior of a non-macroscopic system (micropore). Such a measure

is convenient since it allows one to apply the Raoult law to the bulk solutions in the asymptotic limit (when the number of molecules increases without limit). For non-linear individual isotherms, the validity of the Raoult law when moving along the line of constant value of the Gibbs integral postulated in the LAST model can occur only in one special case, viz., when the adsorption capacities of micropores for both substances are equal and the isotherms can be matched up by shifting along the pressure axis in the gas phase.

Further development of the approach outlined above includes an analysis of experimental data on multicomponent equilibrium adsorption at different temperatures. This would make it possible to determine not only the excess Helmholtz energy but also the excess internal energy and the excess entropy; in turn, this will provide a way of establishing a quantitative relation between the deviation from ideal behavior of the adsorption phase, the inhomogeneity of the adsorption field, and different types of interaction between the adsorbed molecules and the adsorption field. The model considered can be applied to carbon molecular sieves and then to other active carbons taking into account the distribution function related to the micropore size distribution.

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