

## CALCULATION OF POTENTIAL RELIEF IN LARGE CAVITY OF NaX ZEOLITE FOR ADSORPTION OF METHANE AND CYCLOHEXANE

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The potential relief for adsorption of methane and cyclohexane molecules in a large cavity of NaX zeolite was calculated with the use of the potential function that takes into account the contributions of dispersion, repulsion, and polarization interactions to the total adsorption potential energy of the molecule. The calculations revealed that the deepest potential minimum for a methane molecule lies at the border of a large window, and for a cyclohexane molecule in the center of this window. A different character of the potential reliefs for each of these molecules is attributed to differences in their size and geometry. The energetic mapping was done so as to enable to determine the most probable routes for translation of the molecule in a crystal and at the same time also the potential barriers on these routes. This work is the first stage in numeric modelling of selfdiffusion of hydrocarbons in NaX zeolite.

To obtain molecular concepts about diffusion of an adsorbing substance in a zeolite crystal, it is necessary to determine the distribution of the potential energy of interaction of the molecule with the zeolite lattice in a large cavity. From the form of the potential relief it is possible to determine the position of the deepest potential minima where the molecule spends most of its time, further their distance, energetically most probable routes for the transition between neighbouring adsorption centers, and data about potential barriers on these routes. All these informations are necessary to obtain ideas about the motion of the molecule in the cavities and to calculate the corresponding selfdiffusion coefficient. The calculated selfdiffusion coefficients can then be compared with experimental data from the NMR method<sup>1,2</sup>, the discrepancies can be discussed and the physical model verified. Several microscopic models for diffusion in zeolites are known, especially for diffusion in A type zeolites<sup>3-7</sup>. A simplified model for X zeolites was given by Ruthven and Doetsch<sup>8</sup> and Kärger and coworkers<sup>9</sup>, who attempted to obtain detailed information about energetics of the translation motion of an adsorbate in an X zeolite.

Since an experimental determination of the potential map in zeolite cavities is practically impossible, the only possibility to solve this problem is a theoretical calculation of the interaction energy of a molecule with the zeolite lattice using known potential functions modified for the description of adsorption in zeolites. These potential functions involve hence not only the contribution of the potentials of dispersion and repulsion forces,  $\Phi_D$  and  $\Phi_R$ , but also the energy of interaction of the molecule with the electrostatic field in the zeolite cavity<sup>10-17</sup>. The necessity to consider the latter interaction together with the complicated zeolite structure complicates the calculations as compared with the similar calculations for a homogeneous nonspecific surface of graphite<sup>18</sup>. However, the problem can be simplified if we choose for the initial model

studies adsorbate molecules that have neither a dipole nor a quadrupole moment (in this case, only the polarization interaction of the molecules with the electrostatic field of the zeolite is important). It is also possible to propose a zeolite model such that the space distribution of the force centers and charges is highly symmetrical<sup>16,17</sup>.

The calculation of the potential energy in many points of a large cavity enables to make potential maps by projection on suitable planes and thus to obtain a schematic illustration of the potential relief at the surface of the cavity<sup>5,19,20</sup>. It is also of interest to determine how the potential relief changes in dependence on the structure and geometry of the adsorbed molecule.

We calculated the potential energy at zero filling and the potential maps were determined for adsorption of methane and cyclohexane on NaX zeolite crystals of various composition. These hydrocarbon molecules were chosen because they differ considerably from each other both by dimensions and geometry. It is interesting to compare the potential reliefs of mutual interaction of these molecules with the zeolite lattice, since it can be expected that the distribution of active centers in a large zeolite cavity should be different for adsorption of methane and cyclohexane. The obtained results give an information about the possibilities of motion of adsorbed molecules in zeolite crystals and form a basis for numerical modelling of the self-diffusion process.

#### *Model of NaX Zeolite*

The model of the lattice of NaX zeolite was constructed from cubo-octahedrons in such a way that eight cubo-octahedrons representing an elementary cell were shifted in three directions<sup>16</sup>. Each of them consisted of oxygen ions,  $O^{\delta-}$ , and  $Na^+$  cations. The contribution of Si and Al ions to the total lattice-molecule interaction was not considered because of their small polarizability<sup>21</sup> and their screening off with oxygen ions. We assume that the  $Na^+$  cations are localized in positions  $S_1$  (centers of hexagonal prisms),  $S_{II}$  (centers of six-membered rings) and further in the centers of four-membered rings in large cavities<sup>22</sup>.

An isolated cubo-octahedron contains sixty  $O^{\delta-}$  ions (24 ions  $O_1$  and 12 ions each of  $O_2$ ,  $O_3$  and  $O_4$ ) and 14  $Na^+$  cations (4 in positions  $S_1$ , 4 in  $S_{II}$  and 6 in  $S_{III}$ ). Since, however, the ions  $O_1$  and  $Na^+$  in positions  $S_1$  are always common for two neighbouring cubo-octahedrons, these ions are assigned to each of them half and half. Therefore, each cubo-octahedron in the lattice contains 48 oxygen ions and 12 sodium ions.

The coordinates of the ions  $O^{\delta-}$  and  $Na^+$  in positions  $S_1$  and  $S_{II}$  were determined from X-ray data<sup>23</sup>, the coordinates of  $Na^+$  ions in positions  $S_{III}$  were found from the van der Waals radii of oxygen atom and  $Na^+$  ion<sup>17</sup>. The assumption about the location of  $Na^+$  ions in the vicinity of  $S_{III}$  positions is supported by the results of other authors<sup>24,25</sup>.

We assumed that all positions  $S_1$  and  $S_{II}$  are fully occupied by  $Na^+$  cations with the charge +1. Other cations, whose number depends on the composition of the zeolite, are equally distributed among the positions  $S_{III}$ , *i.e.*, each of these positions bears a cation whose charge and polarizability are diminished in proportion to their occupancy factor. The charge of  $O^{\delta-}$  was determined by dividing the total positive

charge of cations in the elementary cell by the corresponding number of  $O^{\delta-}$  ions. Such a model ensures the electroneutrality of each cubo-octahedron and the whole lattice, spherical symmetry of the electrostatic field in the large zeolite cavity, and a high symmetry in the distribution of the lattice elements, which enables to reduce substantially the extent of calculations<sup>16,17</sup>. The characteristics of the NaX zeolites for which the calculations were done and the corresponding charges of  $Na^+$  ions in positions  $S_{III}$  and charges of oxygen ions are given in Table I. With methane and cyclohexane, the calculations were done for zeolites of various composition, for which experimental data are available, enabling later to compare the theory with experiments.

### Models of Methane and Cyclohexane Molecules

Two models of the methane molecule were studied. The first one assumes that the  $CH_4$  molecule is a sphere of effective radius  $0.2 \text{ nm}^{26}$ . According to the second one, the  $CH_4$  molecule is a tetrahedron with C atom in the center and with an interatomic distance of  $0.109 \text{ nm}^{27}$ . Each atom was characterized by an effective polarizability and magnetic susceptibility. The calculations for the tetrahedral model were carried out in the so-called atom-atom approximation<sup>18,28</sup>.

With cyclohexane, also two models were considered. In the first one, the six  $CH_2$  groups in *trans* configuration were considered as force centers (Fig. 1), whereas in the second one the same applied for the C and H atoms. The distance between the centers of the C atoms was set equal to  $0.153 \text{ nm}^{27}$  and the C—H distance to  $0.109 \text{ nm}$  as with methane. The second cyclohexane model enabled calculations in the atom-atom approximation.

TABLE I  
Characteristics of NaX Zeolite Samples and Charges of  $Na^+$  and  $O^{\delta-}$  Ions

Adsorbate Zeolite	$CH_4$	$C_6H_{12}$
	NaX-I	NaX-II
Si/Al ratio	1.480	1.285
Decationation deg.	0.3	0.2
No of cations per elem. cell and per large cavity	75.10 9.4	82.35 10.3
No of $S_{III}$ cat. per large cavity	3.4	4.3
Charge of $S_{III}$ cat.	+0.5667	+0.715
Charge of $O^{\delta-}$	-0.2	-0.214

### Scheme of Calculation of Potential Energy

Calculations of the potential energy,  $\phi$ , for the interaction of the force center of the adsorbate molecule with the zeolite lattice were done in every point of the large cavity according to the equation

$$\phi_k = -\sum_i C_{ik} \sum_j r_{ijk}^{-6} + \sum_i B_{ik} \sum_j r_{ijk}^{-12} - \frac{1}{2} \alpha_k |\mathbf{E}(\mathbf{r})|^2. \quad (1)$$

We denote  $k$  the index of the force center of the molecule,  $C_{ik}$  constant of dispersion interaction between the  $k$ -th force center and the lattice center of type  $i$ ,  $B_{ik}$  the corresponding repulsion constant,  $r_{ijk}$  distance between the  $k$ -th force center of the molecule and the  $j$ -th ion of the lattice of the type  $i$ ,  $\alpha_k$  is the polarizability of  $k$ -th force center of the molecule and  $\mathbf{E}(\mathbf{r})$  intensity of electrostatic field in the center of the  $k$ -th atom or molecule, whose position in the cavity is determined by the position vector  $\mathbf{r}$ . The summation in Eq. (1) is carried out over all oxygen and sodium ions of each cubo-octahedron. The calculations involved the  $O^{\delta-}$  and  $Na^+$  ions of ten cubo-octahedrons surrounding each large cavity<sup>17</sup>. In the case where the molecule consists of several force centers (atom or groups), their potential energy  $\phi$  is considered as the sum of the potential energies of these centers  $\phi_k$ .

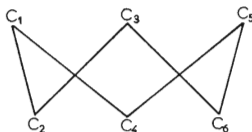
The constants  $C_{ik}$  in the term expressing the contribution of the attraction forces for a pair of force centers  $i, k$  were calculated from the Kirkwood-Müller equation. The repulsion constants  $B_{ik}$  were determined from the condition of potential energy minimum for pair interactions of the corresponding ions of the zeolite lattice of each kind with atoms or groups of the adsorbate molecule. The polarization contribution to the total interaction energy was also taken into the calculation of constants  $B$ . For every pair of interacting centers ( $i$ -th lattice center with  $k$ -th molecule center), the constant  $B_{ik}$  was calculated as<sup>10-12,14,16,17</sup>

$$B_{ik} = \frac{1}{2} r_0^6 (C_{ik} + \frac{1}{3} q_i^2 \alpha_k r_0^2), \quad (2)$$

where  $q_i$  denotes charge of  $i$ -th ions of the zeolite lattice,  $\alpha_k$  polarizability of  $k$ -th force center of the molecule,  $r_0$  equilibrium distance equal to the sum of the van der

FIG. 1  
Scheme of Cyclohexane Molecule in *trans* Conformation

Points  $C_1$  through  $C_6$  represent centers of  $CH_2$  groups.



Waals radius of the atom or atomic group and the ionic radius of the corresponding force center of the lattice.

The parameters necessary for the calculation of the constants  $C$  and  $B$  (the polarizability  $\alpha$ , magnetic susceptibility  $\chi$ , ionic and van der Waals radii  $r$ ) for atoms or groups in the adsorbate molecules as well as for the ions of the zeolite lattice are given in Table II. The van der Waals radii of atoms are in accord with ref.<sup>17</sup>; their selection is based on published data<sup>18,27-29</sup> with the intention to obtain a good agreement between the calculated and measured adsorption data for the  $\text{CH}_4$  molecule. The values of  $\alpha$  and  $\chi$  for the methylene groups in the cyclohexane molecule were calculated from those for the cyclohexane molecule<sup>30</sup> on the assumption of additivity. The values of  $\alpha$  and  $\chi$  for  $\text{O}^{\delta-}$  ions were determined from their graphical dependence on the ion charge<sup>13</sup>.

The constants,  $C$ , for interaction with  $\text{Na}^+$  ions in positions  $S_{\text{III}}$  to which fractional charges are assigned were determined by multiplying the corresponding constants  $C$  for  $\text{Na}^+$  ions by the corresponding charge number.

The components of the vector of electrostatic field intensity in Eq. (1) for every point where the force center of the  $k$ -th molecule of the adsorbate is located were calculated with the aid of lattice sums of the type

$$E_{qk} = \sum_i \rho_i \sum_j [(q_{ij} - q_k)/r_{ijk}^3], \quad (3)$$

where  $q_{ij}$  denotes coordinates ( $x, y, z$ ) of  $j$ -th ion of the type  $i$ ,  $q_k$  coordinates of the force center of the molecule.

TABLE II

Radii ( $r$ ), Polarizabilities ( $\alpha$ ), and Diamagnetic Susceptibilities ( $\chi$ ) for C and H Atoms,  $\text{CH}_4$  Molecules,  $\text{CH}_2$  Groups in Cyclohexane Molecule, and Lattice Ions of  $\text{NaX}$  Zeolite

Force center	$r$ , nm (ref.)	$\alpha \cdot 10^{24}$ , $\text{cm}^3$ (ref.)	$-\chi \cdot 10^6$ , $\text{cm}^3 \text{mol}^{-1}$ (ref.)
C	0.18 (17)	0.96 (30, 31)	7.4 (30)
H	0.135 (17)	0.43 (31)	2.0 (30)
$\text{CH}_2$	0.2 (26)	1.83 (30)	11.8 (30)
$\text{CH}_4$	0.2 (26)	2.6 (30, 31)	16.0 (30)
$\text{O}^{-0.2}$	0.152 (29)	1.4 (13)	10.0 (13)
$\text{O}^{-0.214}$	0.152 (29)	1.4 (13)	10.5 (13)
$\text{Na}^{+1}$	0.098 (32)	0.3 (30)	5.6 (30)

The calculations of the potential energy,  $\phi$ , in a large zeolite cavity were done as follows. An adsorbate molecule placed in the center of the large cavity was shifted by constant steps toward the wall of the cavity. The position vector of each its position was determined by spherical coordinates  $\varrho$ ,  $\theta$ , and  $\varphi$ ; after going through the whole radius of the cavity, the angles  $\theta$  and  $\varphi$  were changed by a predetermined step. The value of  $\phi$  was calculated for each of the points  $(\varrho, \theta, \varphi)$ ; of all these values the minimum,  $\phi_m$ , was found, which can be considered as the minimum of the potential curve,  $\phi(\varrho)$ , for this direction if the number of steps is sufficiently large. The set of  $\phi_m$  values for all the considered directions gives the potential relief in the large cavity.

Thanks to the high symmetry of the chosen model of the large cavity, it is possible to diminish the number of directions in which the function  $\phi(\varrho)$  is determined. This is seen from Fig. 2, where a large cavity of X zeolite is shown schematically as a sphere (its radius,  $R$ , is determined by the position of the most distant  $O^{2-}$  ion from the center of the cavity, *i.e.*,  $R = 0.868$  nm). Owing to an equal distribution of cations  $S_{II}$  and  $S_{III}$ , it is possible to divide the surface of this sphere by six large circles into 24 equal regions BDE, where the point D corresponds to the place  $S_{II}$ , E to  $S_{III}$ , and B to the center of a large window. Since the sphere is on four places intersected by the planes of large windows (one of these intersections is shown in Fig. 2 as circle), the point B' must be considered as the center of the large window, and the region AB'CDE as 1/24 of the surface area of the large cavity. To obtain a whole picture of the potential relief in the large cavity, it is sufficient to calculate the potentials  $\phi(\varrho)$  in the sector OB'CDEA.

For the molecules of methane and cyclohexane, several variants were calculated: 1) The  $CH_4$  molecule was considered effectively spherical (variant *S*). 2) The  $CH_4$  or  $C_6H_{12}$  molecule was in every point of the cavity oriented in the same manner with respect to cartesian coordinates (variant *F*). In the starting position in the center of the large cavity the  $CH_4$  molecule was oriented with respect to the coordinate system so that the base plane of the tetrahedron was oriented

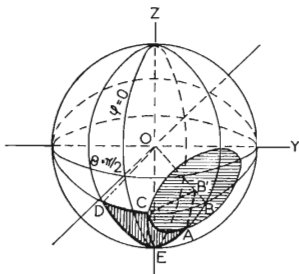


FIG. 2

Sphere Circumscribed to Large Cavity of NaX Zeolite

Point O corresponds to the center of the large cavity. The shaded circle with center in B' represents large window. The body OB'CDEA represents one of 24 equal units forming the space of the large cavity.

to the  $S_{II}$  cation and normal to the 3-fold axis. The  $C_6H_{12}$  molecule was in this variant oriented in the starting position in such a way that the planes of two triangles given by the centers of C atoms (planes  $C_1C_3C_5$  and  $C_2C_4C_6$  in Fig. 1) were normal to the three-fold axis. This orientation was preserved for all directions ( $\theta, \varphi$ ). 3) During changing the angles  $\theta$  and  $\varphi$  the orientation of the  $CH_4$  molecule changed so that the plane of the base of the tetrahedron remained perpendicular to the direction of motion of the molecules from the cavity center to the wall (variant  $V$ ). With the  $C_6H_{12}$  molecule in variant  $V$ , the planes  $C_1C_3C_5$  and  $C_2C_4C_6$  remained perpendicular to the direction of motion of the molecule.

In variants  $F$  and  $V$ , the second model was used for the methane and the first one for the cyclohexane molecule. 4) In every point of the large cavity the molecule of methane or cyclohexane was rotated in three directions with the use of Euler's angles (variant  $R$ ), while each Euler's angle changed with a given step. In this variant, the minimum value of  $\phi$  for all positions and orientations of the molecules in a given direction was denoted as  $\phi_m$ . This computational variant was applied to the second model of the methane molecule and for both models of the cyclohexane molecule. When the latter was considered as a system of six methylene groups, this variant was denoted as  $R-I$ , and for the same molecule in the atom-atom approximation as  $R-II$ .

The variant  $R$  would require a too large amount of the computer time if the lattice sums were calculated directly from Eq. (1). To shorten the calculation, the following simplification<sup>17</sup> was introduced: The region  $OB'CDEA$  was divided into a number of cells, which were delimited by the planes  $\varphi = \text{const.}$  and  $\theta = \text{const.}$  and by the surfaces parallel with  $AB'CDE$ . First the potentials  $\phi$  for the C and H atoms or for the  $CH_2$  groups were calculated in the center of each of these cells and these values were stored in the memory of the computer. During the motion of the molecule in the region  $OB'CDEA$ , the coordinates of its each atom or group were determined, which indicated the address of the cell in which this atom or group was placed. The potential corresponding to the center of the cell was then assigned to this atom or group. If the division of the region  $OB'CDEA$  into cells is sufficiently fine, this method gives a good agreement with direct calculations of the potential energy<sup>17</sup>. In the present work, we used the following numbers of steps for the coordinates: 21 for  $\varphi$ , 21 for  $\theta$ , and 31 for  $\rho$ . Hence, the region  $OB'CDEA$  was divided into 13 671 cells.

The potential relief of the large cavity was transformed in the form of a potential map as follows: Equipotential curves, obtained by linear interpolation of the function  $\phi_m = f(\theta)$  at constant  $\varphi$ , were projected onto the surface of spherical triangle  $BDE$  (Fig. 2). This is shown in the developed form in Fig. 3. The transformations in Figs 3

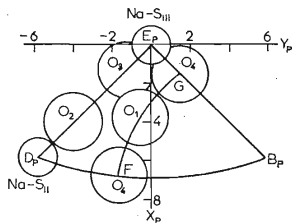


FIG. 3  
Projection of the Region  $BCDEA$  from Fig. 2  
in a Plane

and 2 are related as follows: The side  $E_pD_p$  corresponds to the arc ED, the side  $E_pB_p$  to the arc EB, and the arc  $D_pB_p$  to the arc DB. The development was done according to the relation  $d = R(\pi - \theta)$ , where  $d$  denotes length of an arbitrary arc joining the line DB with the point E (Fig. 3). The coordinates of the projection,  $x_p$  and  $y_p$ , on the potential map (Fig. 3) are given as  $x_p = d \cdot \cos \varphi$ ,  $y_p = d \sin \varphi$ . The projections of the positions of  $O^{\delta-}$  and  $Na^+$  ions contained in the studied region into the plane  $E_pD_pB_p$  are also shown in Fig. 3. The curve FG denotes the border and the point  $B_p$  the center of the large window.

## RESULTS AND DISCUSSION

The potential maps for adsorption of methane on NaX-I zeolite, obtained from different variants of calculations, are shown in Fig. 4 and for adsorption of cyclohexane on NaX-II zeolite in Fig. 5. The potentials of deepest minimums are summarized for all cases in Table III, where also the numbers of steps used in changing the coordinates and Euler angles are given.

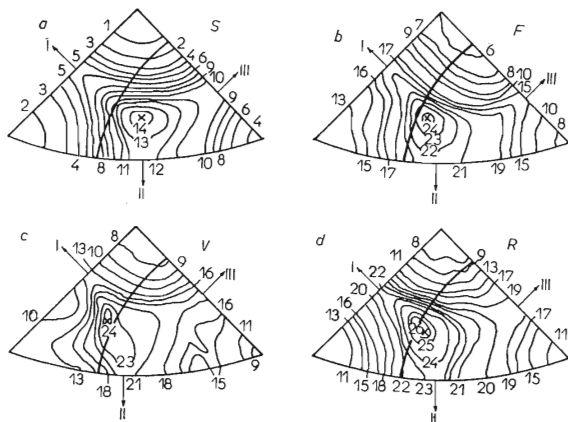


FIG. 4

### Potential Maps for Methane Molecule in Large Cavity of NaX-I Zeolite

Crosses denote the points of the deepest potential minimums. Numbers on the equipotential curves correspond to the following values of  $\phi_m$  in kJ/mol: 1 6-28; 2 6-70; 3 7-12; 4 7-54; 5 7-95; 6 8-37; 7 8-79; 8 9-21; 9 10-04; 10 10-89; 11 11-72; 12 12-14; 13 12-56; 14 12-98; 15 13-40; 16 14-23; 17 15-07; 18 15-91; 19 16-74; 20 17-58; 21 18-42; 22 19-26; 23 20-10; 24 20-93; 25 21-77; 26 22-19.



In Fig. 4a is shown the potential relief of the large cavity of NaX zeolite derived for the model  $\text{CH}_4\text{-S}$  (*i.e.*, for an effectively spherical methane molecule). The potential reliefs in Fig. 4b–d were obtained for a  $\text{CH}_4$  molecule in the atom-atom approximation based on the variants *F*, *V*, and *R*. In the case of variant *R*, the calculations were done for  $\text{CH}_4$  molecules with different numbers of steps in changing the coordinates and Euler angles (Table III). It follows from Fig. 4 that all variants yield for the adsorption of methane in the NaX zeolite cavity a potential relief of about the same character. On all potential maps for  $\text{CH}_4$ , the point of the deepest minimum lies close to the border of the large window. Proceeding from this point, the potential relief decreases in three directions: toward the both cations  $\text{S}_{\text{II}}$  and  $\text{S}_{\text{III}}$  and toward the center of the large window. Between these peaks there are valleys which represent possible exits of the molecule from the potential well during its shifting along the surface of the cavity. The potential barriers corresponding to these exits are given

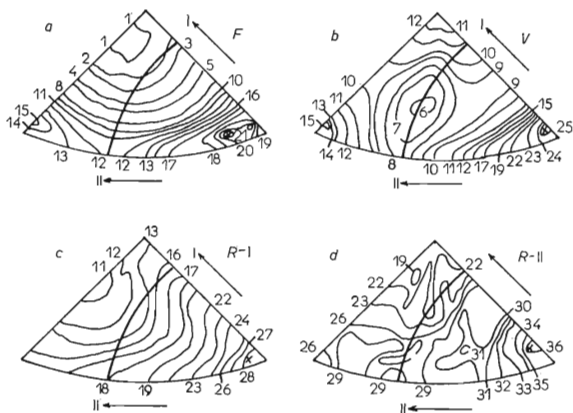


FIG. 5

#### Potential Maps for Cyclohexane Molecule in Large Cavity of NaX-II Zeolite

Crosses denote points of the deepest potential minimums. Numbers on the equipotential curves correspond to the following values of  $\phi_m$  in kJ/mol: 1 22·61; 2 23·03; 3 23·45; 4 24·28; 5 25·12; 6 25·54; 7 26·38; 8 27·21; 9 28·47; 10 29·31; 11 31·40; 12 33·49; 13 35·59; 14 36·42 15 36·84; 16 37·68; 17 38·77; 18 41·87; 19 43·96; 20 44·38; 21 45·21; 22 46·05; 23 48·14; 24 49·40; 25 49·82; 26 50·24; 27 50·66; 28 51·08; 29 52·33; 30 55·27; 31 56·52; 32 58·62; 33 60·71; 34 62·80; 35 64·90; 36 66·57.

in Table III. Since the calculations according to the variant *R* give at different numbers of steps in the coordinates and Euler angles approximately the same potential maps and values of the minimums, only one potential map is shown here (Fig. 4*d*), which corresponds to 11, 11 and 21 steps in the coordinates and 5, 5 and 5 steps in the Euler angles. The model CH<sub>4</sub>-S gives much too low potential values in the deepest minimum since it represents a too rough approximation (effective sphere) and does not reflect all fine details of the potential relief on the surface of the large cavity. This model leads also to much lower values of thermodynamic characteristics of adsorption as compared with experimental data<sup>17</sup>.

The potential maps for cyclohexane in the cavity of NaX zeolite are shown in Fig. 5. Variants *F*, *V*, and *R-I\** (Fig. 5*a-c*) were based on the first model of the cyclohexane

TABLE III

Potential Energies,  $\Phi_m$ , for Interaction of CH<sub>4</sub> and C<sub>6</sub>H<sub>12</sub> Molecules with NaX Zeolite in Points of Deepest Minima and Potential Barriers  $\Delta\Phi$  for Displacement of Molecules between these Points

Variant	Number of steps		$-\phi_m$ kJ mol <sup>-1</sup>	$\Delta\phi$ , kJ mol <sup>-1</sup>		
	in $\varphi, \theta, \varrho$	in Euler ang.		I	II	III
CH <sub>4</sub>						
<i>S</i>	31, 31, 51	—	13.16	5.0	0.8	6.1
<i>F</i>	21, 21, 31	—	21.26	6.1	2.1	6.7
<i>V</i>	21, 21, 31	—	21.16	8.6	1.5	5.2
<i>R</i>	11, 11, 21	5, 5, 5	22.49	3.4	2.5	5.4
<i>R</i>	21, 21, 21	5, 5, 5	22.82	2.7	1.9	5.7
<i>R</i>	11, 11, 21	7, 7, 7	22.94	2.9	2.1	5.4
C <sub>6</sub> H <sub>12</sub>						
<i>F</i>	21, 21, 31	—	46.08	23.5	12.6	—
<i>V</i>	21, 21, 31	—	50.12	21.8	22.6	—
<i>R-I</i>	21, 21, 21	5, 5, 5	51.16	16.3	15.5	—
<i>R-I</i>	15, 15, 21	7, 7, 7	51.13	16.7	15.1	—
<i>R-I</i>	11, 11, 21	9, 9, 9	51.28	16.7	15.1	—
<i>R-II</i>	11, 11, 21	5, 5, 5	66.65	22.6	16.3	—

\* In the latter case, the number of steps in coordinates was 11, 11 and 21, and in Euler angles 9, 9, and 9.

molecule (*i.e.*, with  $\text{CH}_2$  groups as force centers). The variant *R-II* (Fig. 5d) was based on the atom-atom approximation (second model). Fig. 5 shows that the character of the potential relief for the cyclohexane molecule is much different from that for methane. Different variants lead to somewhat different potential maps, however all of them (Fig. 5) enable to derive general relations. In all cases, the position of the deepest potential minimum is close to the center of the large window. From this point the potential relief elevates toward the oxygen bridge, *i.e.*, toward the border between two large windows. In the region of this bridge there are points that are energetically least suitable for the adsorption of the  $\text{C}_6\text{H}_{12}$  molecule (in contrast to adsorption of methane, for which there is the deepest potential minimum in this region). The potential barriers for displacement of the  $\text{C}_6\text{H}_{12}$  molecule from one window into the other in different directions (Fig. 5) are given in Table III.

The difference in the character of the potential relief in the large cavity of NaX for methane and cyclohexane can be within the framework of the given variant attributed to the difference in the geometry of the  $\text{CH}_4$  and  $\text{C}_6\text{H}_{12}$  molecules. The former, which is smaller, fits better into various irregularities on the wall of the large cavity than the latter, which is larger and has another symmetry. Therefore, for the methane molecule the most favourable position is near the border of the large window, where the concentration of oxygen ions on the wall is highest. In this region there are places with the highest potential of the dispersion forces due to the high polarizability of the oxygen ions. The methane molecule can, because of its shape and small dimensions, take such a position at the cavity wall which ensures an optimum contact between its atoms and oxygen ions and hence also the strongest interaction between the molecule and the zeolite lattice.

The points near  $\text{Na}^+$  cations and in the center of the large window turn out to be disadvantageous for the molecule since the cations protrude into the space of the large cavity and thus prevent a contact between the  $\text{CH}_4$  molecule and the oxygen ions on the wall; moreover the position of methane in the center of the large window is energetically unfavourable because of large distances between the atoms of the molecule and the force centers of the lattice. In contrast, the dimensions of the  $\text{C}_6\text{H}_{12}$  molecule are comparable with those of the large window of X zeolite, hence the position of this molecule in the center of the large window ensures an intimate contact between the molecule's force centers (atoms or  $\text{CH}_2$  groups) and the oxygen ions of the lattice.

As to the oxygen bridge between the large windows, *i.e.*, the cavity wall proper, its strong curvature and complicated potential shape do not allow the  $\text{C}_6\text{H}_{12}$  molecule to take the most favourable position with respect to oxygen ions. Therefore, in this region of the large cavity there are energetically least advantageous points.

The results of our calculations show that the geometry of the adsorbate molecules exerts a large influence on the distribution of the potential energy in the large cavity of X zeolite. This cavity contains 24 energetically equal active centers for the small

CH<sub>4</sub> molecule whereas only 4 such centers for the larger C<sub>6</sub>H<sub>12</sub>. The energetically favourable positions for cyclohexane are in the centers of the large windows, which are unsuitable for adsorption of methane.

It should be noted that even our simplified method of calculation requires a large amount of computer time. For this reason it is not possible to carry out more exact calculations (*e.g.*, by increasing the number of steps during shifting the molecule from the cavity center toward the wall and during its rotation, by involving a larger number of force centers of the lattice, or by calculating more exactly the polarization component of the potential). However, the calculations of this kind could be improved by using a better zeolite model, especially the positioning of cations on the surface of the large cavity, a better estimate of the charge attributed to these cations and oxygen ions, a better determination of the repulsion constant, and a better estimate of the parameters necessary for calculating the potential constants. Nevertheless, the approximate calculations are useful since they illustrate the distribution of the potential energy in the large zeolite cavity and hence the energetic picture of the equilibrium and transport processes, especially of intracrystalline diffusion.

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