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MODEL DESCRIPTION OF MOLECULAR ADSORPTION IN ZEOLITES

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INTRODUCTION

The study of molecular adsorption and diffusion in zeolites and other porous materials (molecular sieves) presents increasing interest because of their wide technical application /1-4/.

In zeolites we deal with a three-dimensional array of connected micropores with a size ranging from 10^{-9} to 10^{-10}m (1 to 10Å) where multilayer physical adsorption of not too large molecules from a liquid or gaseous phase can take place. These micropores are typical for the crystal structure of some alumino silicates of alcaline elements and in synthetic zeolites they form a periodic system of identical cavities, each with various adsorption centers. Usually, macropores of about 10^{-6} m size are also present but their contribution to adsorption can be deduced from the adsorbate mass density by estimating the total macropore volume. Micropore volume represents a considerable fraction (28% in the case of ref. /2/) of the sample volume and micropore adsorption is highly selective to the size and form of adsorbed molecules which gives it a great practical importance. It is also micropore adsorption which presents theoretical interest, since the dynamics and interactions of molecules inside the micropores are very different from those of gaseous or liquid phases.

The present paper contains an attempt to describe adsorption in zeolites from a quasi-microscopic point of view. Our model, presented in Sec.1, is a modification of the widely used gas lattice model.

The mathematical apparatus based on Green function methods is described in Sec.1 and the molecular energy levels inside the zeolite are obtained and discussed in Sec.2. The expressions for the coverage and the adsorption heat are obtained in 3 and the comparison with the experimental results of ref. /4/ is carried out in Sec.4.

1. THE MODEL

For the quantum statistical description of molecular adsorption in zeolites a model based on the following Hamiltonian is proposed:

$$\hat{H} = \hat{H}_0 + \hat{H}_I$$

$$\hat{H}_0 = -\epsilon \sum_{i,\alpha} \hat{n}_{i\alpha} - t \sum_{\substack{i \\ \alpha \neq \beta}} \hat{a}^+_{i\alpha} \hat{a}_{i\beta} - J \sum_{\substack{i \\ \alpha,\beta}} \sum_{j=1}^{z} \hat{a}^+_{i\alpha} \hat{a}_{j\beta}$$

$$\hat{H}_I = \frac{U}{2} \sum_{\substack{i \\ \alpha \neq \beta}} \hat{n}_{i\alpha} \hat{n}_{i\beta}; \quad \hat{n}_{i\alpha} = \hat{a}^+_{i\alpha} \hat{a}_{i\alpha}; \quad i = 1, \dots, N; \quad \alpha = 1, \dots, N_m. \tag{1}$$

The zeolite is considered (see fig.1) as a periodical three-dimensional array of N identical cavities "i" centered at $\vec{R}_i$ each containing N_m identical sites "α" where a molecule can be adsorbed with a bound energy "ϵ". The second and third terms in $\hat{H}_0$ describe transitions of molecules between sites in the same cavity and between near neighbouring cavities, respectively. Lateral (Van der Waals) interactions between molecules in the same cavity are included in $\hat{H}_I$.

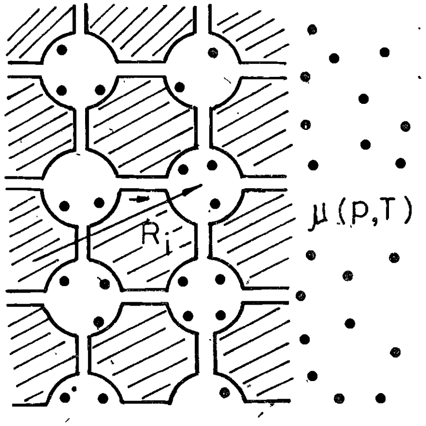

Fig. 1

The symbols $\hat{a}^+_{i\alpha}$, $\hat{a}_{i\alpha}$ represent respectively the Pauli creation and annihilation operators for adsorption or desorption of a molecule in the site "α" of cavity "i", while $\hat{n}_{i\alpha} = \hat{a}^+_{i\alpha} \hat{a}_{i\alpha}$ is the operator of the number of particles adsorbed in (i, α), whose eigenvalues are "0" and "1". Due to transitions between different sites, $\hat{n}_{i\alpha}$ is not conserved, but the operator of the total number of particles $\hat{N} = \sum_{i,\alpha} \hat{n}_{i\alpha}$ commutes with the Hamiltonian $\hat{H}$.

The Hamiltonian $\hat{H}_0$ describes the motion of molecules in the zeolite field in the absence of intermolecular interaction. Since the energy and wavefunction of a molecule bound to an adsorption center depend on its internal state, the parameters ϵ, t, J, U must be considered in principle as average quantities dependent on temperature and other external parameters (i.e., electric or magnetic fields) affecting the internal state of the molecule. The parameters "t" and "J" are related to the overlapping of the wavefunctions of molecules adsorbed at different centers. Depending on the sign of "U", intermolecular attraction $(U<0)$ or repulsion $(U>0)$ can be considered. The model contains six parameters: N_m, ϵ, t, J, U and (the number of near neighbours) allowing us to discuss very different physical situations. The values of these parameters must be determined by taking into account the concrete type of zeolite and adsorbed molecules under study and by comparison with experimental results.

One could also take into account that different centers inside the same cavity are not identical by replacing ϵ, t, J and U by ϵ_α, $t_{\alpha\beta}$, $J_{\alpha\beta}$ and $U_{\alpha\beta}$ in the corresponding terms of $\hat{H}$. This consideration is not necessary for the purpose of the present paper.

2. GREEN FUNCTION AND THERMODYNAMICAL CHARACTERISTICS OF THE SYSTEM

The main thermodynamical quantities of interest for the description of molecular adsorption are the coverage θ (proportional to the mass of adsorbed substance), the isoesteric adsorption heat Q and the heat capacity at constant pressure C_p:

$$\theta = \langle \hat{n}_{i\alpha} \rangle, \quad Q = -N_A \left(\frac{\partial \ln p}{\partial \beta}\right)_\theta, \quad C_p = \left(\frac{\partial E}{\partial I}\right)_p - \mu N N_m \left(\frac{\partial \theta}{\partial I}\right)_p,$$

where $\beta = 1/kI$, $\mu = \mu(p, I)$ is the chemical potential, $E = \langle \hat{H} \rangle$ the internal energy and $\langle \dots \rangle$ the grand canonical average:

$$\langle \dots \rangle = \frac{\mathrm{Tr}\{e^{-\beta(\hat{H}-\mu\hat{N})} \dots\}}{\mathrm{Tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}\}}.$$

To calculate these quantities it is enough to obtain the one-particle commutator Green function /5/ $\langle\langle \hat{a}_{i\alpha}; \hat{a}^+_{j\beta} \rangle\rangle_\omega$ or its Fourier transform

$$\langle\langle \hat{a}_\alpha; \hat{a}^+_\beta \rangle\rangle_{\vec{k},\omega} = \sum_{i=1}^{N} \langle\langle \hat{a}_{i\alpha}; \hat{a}^+_{j\beta} \rangle\rangle_\omega \, e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)},$$

where $\vec{k}$ takes N values in the first Brillouin zone. The spectral intensity $I_{\alpha\beta}(\vec{k}, \omega)$ is related to $\langle\langle \hat{a}_\alpha; \hat{a}^+_\beta \rangle\rangle_{\vec{k},\omega}$ by the formula /5/

$$I_{\alpha\beta}(\vec{k}, \omega) = \frac{\langle\langle \hat{a}_\alpha; \hat{a}^+_\beta \rangle\rangle_{\vec{k},\omega+i\eta} - \langle\langle \hat{a}_\alpha; \hat{a}^+_\beta \rangle\rangle_{\vec{k},\omega-i\eta}}{e^{\alpha\beta} - 1}; \quad \eta \to 0+. \tag{2}$$

Now, the coverage θ and the internal energy E are expressed by /5/

$$\theta = \frac{1}{N} \sum_{\vec{k}} \int_{-\infty}^{\infty} d\omega \, I_{\alpha\alpha}(\omega) \tag{3}$$

$$E = \frac{N N \mu\theta}{2} + \frac{1}{2} \sum_{\vec{k},\alpha,\beta} \int_{-\infty}^{\infty} d\omega \, \{(\omega - \epsilon + t)\Delta(\alpha - \beta) - t - J(\vec{k})\} I_{\alpha\beta}(\vec{k}, \omega), \tag{4}$$

where $J(\vec{k}) = J \sum_{j=1}^{z} e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)}$.

3. ENERGY SPECTRUM

The equation of motion for the Green function has the form/5/

$$[\omega + \epsilon + \mu] \langle\langle \hat{a}_{i\alpha} ; \hat{a}_{j\beta} \rangle\rangle_\omega = \frac{i}{2\pi}(1-2\theta)\Delta(\alpha-\beta) -$$

$$- t \sum_{\gamma \neq \alpha} [\langle\langle \hat{a}_{i\alpha} ; \hat{a}^+_{j\beta} \rangle\rangle_\omega - 2\langle\langle n_{i\alpha} \hat{a}_{i\gamma} ; \hat{a}^+_{j\beta} \rangle\rangle_\omega]$$

$$- J \sum_{\gamma} \sum_{k=1}^{z} [\langle\langle \hat{a}_{k\gamma} ; \hat{a}^+_{j\beta} \rangle\rangle_\omega - 2\langle\langle n_{i\alpha} \hat{a}_{k\gamma} ; \hat{a}^+_{j\beta} \rangle\rangle_\omega] + U \sum_{\gamma \neq \alpha} \langle\langle n_{i\gamma} \hat{a}_{i\alpha} ; \hat{a}^+_{j\beta} \rangle\rangle_\omega .$$

In mean field approximation

$$\langle\langle \hat{n}_{i\alpha} \hat{a}_{k\gamma} ; \hat{a}^+_{j\beta} \rangle\rangle_\omega \to \theta \langle\langle \hat{a}_{k\gamma} ; \hat{a}^+_{j\beta} \rangle\rangle_\omega$$

and for the Fourier transform we obtain

$$\left[\frac{\omega + \epsilon + \mu - U\theta(N_m - 1)}{1-2\theta}\right] \langle\langle \hat{a}_\alpha ; \hat{a}^+_\beta \rangle\rangle_{\vec{k},\omega} = \frac{i}{2\pi}\Delta(\alpha-\beta) -$$

$$- t \sum_{\gamma \neq \alpha} \langle\langle \hat{a}_\gamma ; \hat{a}^+_\beta \rangle\rangle_{\vec{k},\omega} - J(\vec{k}) \sum_{\gamma} \langle\langle \hat{a}_\gamma ; \hat{a}^+_\beta \rangle\rangle_{\vec{k},\omega} .$$

This equation can be solved by means of the orthogonal transformation

$$\langle\langle \hat{a}_\alpha ; \hat{a}_\beta \rangle\rangle_{\vec{k},\omega} = \sum_{n=1}^{N_m} A_{\alpha n} G_n(\vec{k},\omega) A_{\beta n} , \qquad (5)$$

where

$$\sum_{\alpha=1}^{N_m} A_{\alpha n} A_{\alpha m} = \Delta(n-m), \qquad \sum_{n=1}^{N_m} A_{\alpha n} A_{\beta n} = \Delta(\alpha-\beta) ,$$

$$A_{\alpha 1} = \frac{1}{\sqrt{N_m}}; \qquad \sum_{\alpha=1}^{N_m} A_{\alpha n} = 0 \qquad n \neq 1 .$$

As a result we obtain

$$G_n(\vec{k},\omega) = \frac{i}{2\pi} \frac{1-2\theta}{\omega + \mu - E_n(\vec{k})} ,$$

$$E_n(\vec{k}) = -\epsilon + U\theta(N_m - 1) + t(1-2\theta) - N_m(1-2\theta)[t + J(\vec{k})]\Delta(n-1) . \qquad (6)$$

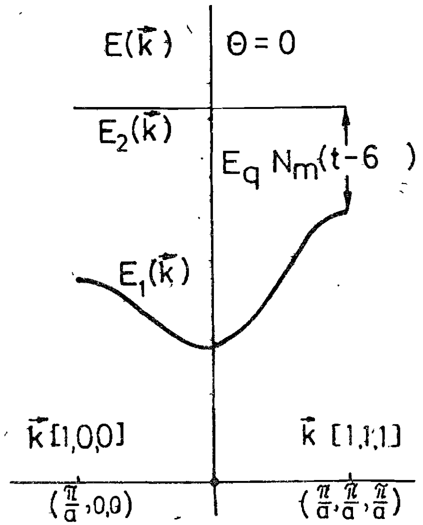

Fig. 2

In the framework of mean-field approximation, $E_n(\vec{k})$ are the energies of the possible states of a molecule in the zeolite field. The energy $-\epsilon + U\theta(N_m - 1) + t(1-2\theta)$ corresponds to $N(N_m - 1)$ -fold degenerated states in which the molecule is localized at some cavity. The energies $E_1(\vec{k})$ correspond to N delocalized states in which the molecule moves from one cavity to another with quasi-momentum $\hbar\vec{k}$. If phonon-assisted transitions from one cavity to another are not considered, only molecules in the states $E_1(\vec{k})$ take place in diffusion. The energy levels depend on θ and for $\theta = 1/2$ all levels coincide. If $t + J(\vec{k}) > 0$ there is an energy gap between localized and delocalized states $E_g = E_2 - \max E_1(\vec{k}) = N_m(1-2\theta)[t + \min J(k)]$.

Figure 2 schematically shows the energy levels in the case of a simple cubic lattice.

IV. COVERAGE AND ADSORPTION HEAT

Substituting (6), (5) and (2) into (3) we obtain for

$$\frac{\theta}{1-2\theta} = (1 - \frac{1}{N_m}) \frac{1}{e^{\beta[E_2 - \mu]} - 1} + \frac{1}{NN_m} \sum_{\vec{k}} \frac{1}{e^{\beta[E_1(\vec{k}) - \mu]} - 1} .$$

Let us suppose that the adsorbed molecules are in equilibrium with a gaseous phase which can be considered as an ideal gas. Then $\mu(p,T) = \frac{1}{\beta}\ln p + \mu_0(T)$, where $\beta\mu_0(T)$ depends weakly (logarithmically) on T. Let us introduce the notation

$$\ln p_0 = -\beta\mu_0 - \beta\epsilon_0 , \qquad \epsilon_0 = \epsilon - \frac{U(N_m - 1)}{2},$$

$$\epsilon_1 = t - \frac{U(N_m - 1)}{2}, \qquad \epsilon_{2,3} = \epsilon_1 - N_m[t \mp \sqrt{z} J]$$

and take the thermodynamical limit $\frac{1}{N}\sum_{\vec{k}} \ldots = \frac{1}{v} \int d^3\vec{k} \ldots$, where v is the volume of the first Brillouin zone over which the integration is performed. To second order in J the result is:

$$\frac{\theta}{1-2\theta} = \left(1-\frac{1}{N_m}\right)\frac{1}{\frac{p_o}{p}e^{\beta\epsilon_1(1-2\theta)}-1} + \frac{1}{2N_m}\left[\frac{1}{\frac{p_o}{p}e^{\beta\epsilon_2(1-2\theta)}-1} + \frac{1}{\frac{p_o}{p}e^{\beta\epsilon_3(1-2\theta)}-1}\right]. \qquad (7)$$

If $\epsilon_1 = \epsilon_2 = \epsilon_3 = 0$ expression (7) turns into the well-known Langmuir isotherms

$$\theta = \frac{1}{p_0/p + 1}. \qquad (8)$$

Equation (7) has three solutions in the general case. Thermodynamical equilibrium (minimum of the Gibbs energy at given T and p) corresponds to the solution for which: $\theta \to 0$ as $p \to 0$, $\theta \to 1$ as $p \to \infty$. Another universal feature of the isotherms (7) is that $\theta \to 1/2$ as $p \to p_0(T)$ (see Fig.3). The isoesteric adsorption heat Q can be written as

$$Q = N_A \frac{\partial}{\partial\beta}(\beta\mu_0) + N_A q, \quad q = \epsilon_0 + \Delta q, \quad \Delta q = -\left(\frac{\partial \ln p/p_0}{\partial\beta}\right)_\theta . \qquad (9)$$

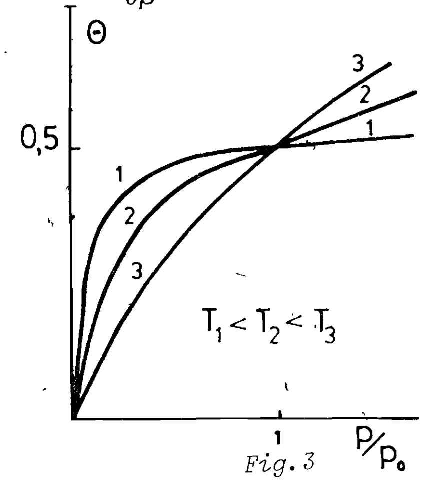

Fig. 3

Taking into account (7) we obtain for Δq

$$\Delta q = -\frac{\epsilon_1 S_1 + \epsilon_2 S_2 + \epsilon_3 S_3}{S_1 + S_2 + S_3}(1-2\theta), \qquad (10)$$

where

$$S_1 = \left(1-\frac{1}{N_m}\right)\frac{e^{\beta\epsilon_1(1-2\theta)}}{\left[\frac{p_0}{p}e^{\beta\epsilon_1(1-2\theta)}-1\right]^2},$$

$$S_{2,3} = \frac{1}{2N_m}\frac{e^{\beta\epsilon_{2,3}(1-2\theta)}}{\left[\frac{p_0}{p}e^{\beta\epsilon_{2,3}(1-2\theta)}-1\right]^2}.$$

5. NUMERICAL RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

In paper /4/ a detailed investigation of Nitrogen desorption isotherms in Molecular Sieves type 13X have been performed in a wide interval of temperatures and pressures:

$$0.02\cdot 10^5\ \mathrm{Nm}^{-2} < p < 20.68\cdot 10^5\ \mathrm{Nm}^{-2}, \quad 78.92\ \mathrm{K} < T < 374.2\ \mathrm{K}.$$

An important feature of the obtained data is that the mass fraction Δm/M (proportional to θ) tends to a constant limit 0.166778 gg^{-1} as the pressure tends to p_s, where

$$\log p_s = 8.9558 - \frac{306.30}{T}.$$

If, by comparison with (7), we take this limit as the value $\theta = 1/2$, then $p_s = p_0$ and ϵ_0 = 60 meV, a quite reasonable value. Unfortunately, we do not know the absolute value of μ for N_2 to compare 8.9558 with $-\beta\mu_0 \log e$ Rough estimates of the last quantity based on the expression of μ for an ideal diatomic gas and N_2 molecular constants /6/ show that it changes from 12 to 13 in the temperature interval from 148.7 to 372.04K.

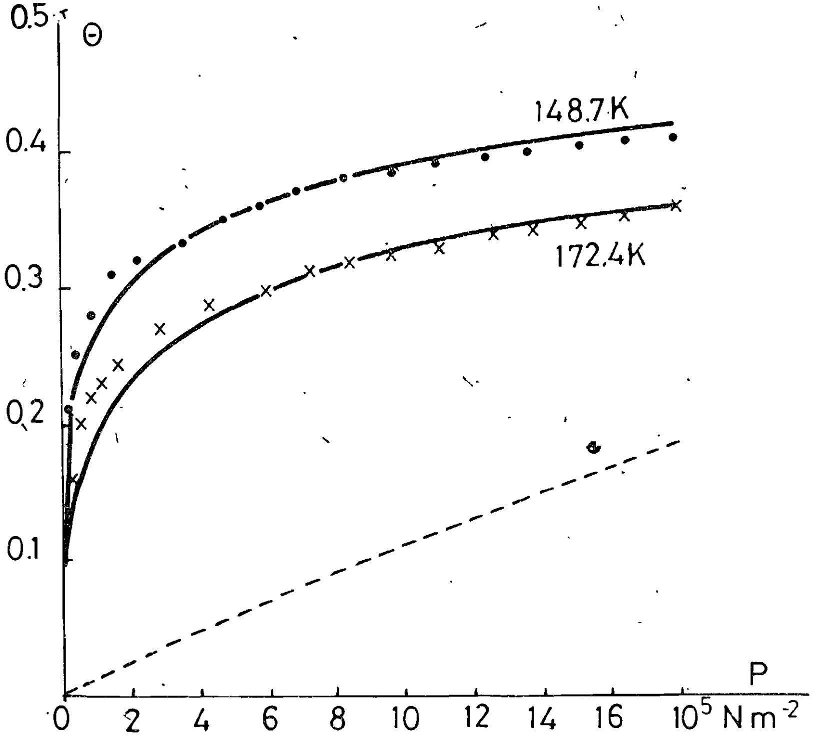

Fig. 4

Figure 4 shows a comparison of experimental data at 148.7K and 174.2K with theoretical curves taken for Nm = 5, ϵ = +0.05 eV, t = 0.016 eV, U = -0.05 eV, J = 0.005 eV. Experimental points have been scaled so that the value Δm/M = 0.16678 corresponds to θ = 1/2 and p_0 has been taken equal to p_S in formula (7). No optimal selection of the model parameters to fit the experimental data has been performed. The discontinuous line represents the Langmuir isotherm at T = 148.7K which is far from the experimental points.

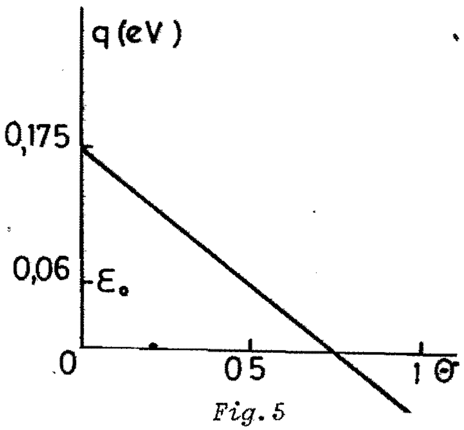

Fig. 5

Numerical results for the isoesteric adsorption heat q are presented in fig.5. Since for the given set of parameters $\epsilon_3 \ll \epsilon_2 < \epsilon_1$, $q(\theta)$ becomes temperature independent and can be approximated by the linear relation

$$q(\theta) = \epsilon_0 - \epsilon_3 (1 - 2\theta) ,$$

$$Q = 4{,}0 - 5{,}2\theta \left(\frac{\text{kcal}}{\text{mole}}\right) , \qquad (11)$$

where the temperature dependence of $\beta\mu_0$ has been neglected.

A rough estimate of the experimental value of Q can be done by comparing the values of p of near isotherms corresponding to approximately the same value of $\Delta m/M$ and using the formula

$$Q_e = -kN_A \frac{\ln p_2 - \ln p_1}{1/T_2 - 1/T_1} .$$

For example, comparing the values of p in the isotherms at 248.4K and 273.16K for which $\Delta m/M = 0.0505$ ($\theta = 0.15$) we obtain $Q_e = 3.2$ kcal/mole, coinciding with the value given by formula (11). The experimental and theoretical values of Q at low coverages are always far from the value 1.4 kcal/mole predicted from Langmuir isotherms ($q = \epsilon_0$).

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Де ла Крус Х., Родригес К., Роке Р. Е17-85-12
Модельное описание молекулярной адсорбции на цеолитах

Предлагается вариант модели решеточного газа для описания молекулярной адсорбции на цеолитах. Получен спектр энергетических состояний молекул внутри цеолита, а также выражения для покрытия и теплоты адсорбции. Проводится сравнение численных результатов с экспериментальными данными.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна 1985

De la Cruz J., Rodriguez C., Roque R. E17-85-12
Model Description of Molecular Adsorption in Zeolites

For the quasi-microscopic description of molecular adsorption in zeolites a modification of the gas lattice is proposed. The energy levels of the molecules inside the zeolite, the coverage and adsorption heat as functions of temperature and pressure are calculated. Numerical results and their comparison with experimental data are presented.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1985