SOLID-PHASE DEFORMATIONS OF DISPERSE SYSTEMS UNDER THE INFLUENCE OF ADSORBED WATER

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On the basis of diffractometric investigations, the expansion in volume of kaolinite in the course of hydration is established.

The experimental observation in [1, 2] that the density of adsorbed water changes as a function of its mass, the surface properties of the minerals, the composition, and the concentration of the exchange cations prompts the formulation of a new investigation of the structure of bound water — in particular, taking account of the deformation of the crystal lattice of clay minerals.

Note that, whereas many works have been published on the state of adsorbed molecules and the structure of adsorbed bonds, there is considerably less information on the perturbations in solids caused by adsorption.

In [3, 4] it was shown that the absorption of molecules of different types leads to measurable changes in the volume of the solid. It was found that even the low-temperature absorption of inert gases causes the expansion of porous glass. These changes in volume were attributed to the reduction in free surface energy on adsorption.

Considerably larger changes in volume were observed in the adsorption of polar molecules and molecules that are free to form hydrogen bonds (SO, NH_3, CH_3CH). For example, in the absorption of sulfur on the surface of porous glass [4] it was observed that at low levels of filling there is slight expansion at first, then a region of compression, and then further expansion. In the case of water, the region in which expansion is observed is considerably larger, and this is explained by the adsorption of water on coordinationally unsaturated centers of the surface.

In [5] the structure of the adsorbed layer of oxygen on the (001) face of an α-iron single crystal was investigated. The results of the calculation were compared with experimental data on the diffraction of slow electrons obtained on exposing a single crystal of iron in dry oxygen. It was shown that oxygen atoms are found at four-carbon vacancies at a distance of 0.53 ± 0.06 Å above the surface, and the distance between the first and second layers of iron rises on adsorption by 5-7% to 1.54 ± 0.06 Å.

The aim of the present investigations is not only to establish the existence of crystal-lattice deformations in clay minerals under the influence of a number of adsorbates (in particular, water) but also to introduce a correction in the calculation of the density of bound water. By means of such corrections, a more reliable basis may be obtained for the method proposed for the calculation of the adsorptional characteristics of complex disperse systems in [2], which involves determining the change in density of the disperse medium in the solid—adsorbed-water—liquid system and estimating the density of the adsorbed water.

The investigation is divided into two parts. In the first stage (the present work), the change in the parameters and the volume of the elementary cell for the natural form of kaolinite under the influence of adsorbed water is determined; in the second, the change in these elements of the crystal lattice will again be evaluated, but for the adsorption of organic compounds as well as water.

Experimental Techniques and Procedures

The method of x-ray diffractometry was employed with the use of a DRON-2 instrument.

The material investigated was the clay (less than 0.001 mm) kaolinite fraction separated from natural

Glukhovetskii kaolin. Powder (2 g) was pressed in a special cuvette, the reflecting plane of which was covered with beryllium foil almost transparent to x rays.

The sample moisture content was varied by drying in a vacuum dessicator and by wetting in a dessicator with water. Input or removal of water vapor was through a hole in the cuvette tightly closed by a threaded stopper. The moisture content was determined by a gravimetric method.

A reflection image of the sample was obtained in discrete conditions with Cu K_α radiation. The tube current was 16 A, the voltage 36 kW, and the slit size 0.5, 1, and 0.25 mm. The vertical divergence of the Soller slit was 1.5°. N_i filters were used. The limit of measurement was 1000 pulses/sec, RC = 5. The position of the angle 2Θ of kaolinite for specific moisture contents was fixed on a digital printer from the maximum of the reflection intensity with an error of $2\Theta = 0.005°$ (step length 0.01°).

The standards used were the (220), (222), and (400) reflections of cerium dioxide, which was mixed with kaolinite in a ratio of 1:20.

The crystal-lattice parameters and volume were determined from six reflections of kaolinite — (202), (11$\bar{4}$), (13$\bar{4}$), (060), (005), and (333) — according to the formula for triclinic syngony [6], using the X-RAY program written in Fortran IV. The time for a single calculation on an ES-1020 computer was about a minute. For moisture contents of 0–0.6% (air–dry moisture content of kaolinite), parallel measurements were made for the same amount of adsorbed water; the mean values of the measured quantities and their confidence limits calculated with a reliability of P = 0.95 are shown in Figs. 1 and 2.

Note that the parameter values obtained in the present experiments are somewhat different from those established for kaolinite, as a result of a systematic distortion of the angles of reflection 2Θ due to the presence of the beryllium barrier over the x-ray inlet. However, since it is the change in the parameters which is of interest here, the distortion is of no fundamental importance.
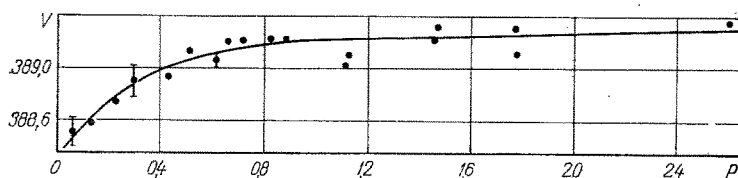

Fig. 1. Change in elementary–cell volume of the natural form of Glukhovitskii kaolinite as a function of the amount of adsorbed water. V, $\overset{\circ}{A}{}^3$; P, %.
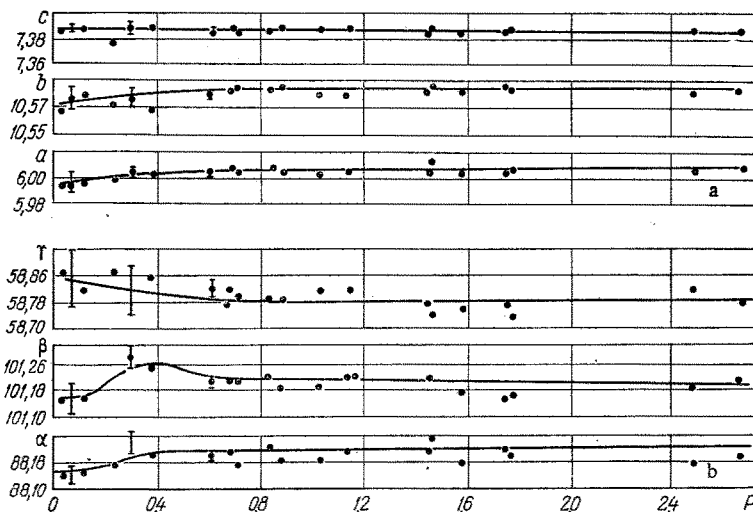

Fig. 2. Change in the linear (a) and angular (b) parameters of an elementary cell of the natural form of kaolinite as a function of the amount of adsorbed water. c, b, a, $\overset{\circ}{A}$.

As is evident from Fig. 1, the elementary cell of kaolinite is observed to expand in volume in the course of hydration, to a maximum extent of 0.2%. This expansion will not be discussed.

It is well known that the structural unit of kaolinite is a two-layer packet constructed from octahedral and tetrahedral layers. In the octahedral layer, only 2/3 of the vacancies are filled by Al^{3+}, while 1/3 remains free.

The tetrahedral layer is entirely occupied by Si^{4+}. Between the packets there are hydrogen bonds linking the oxygen of the silicon dioxide layer to the hydroxyl groups of the octahedral layer.

The adsorption centers on the kaolinite surface are oxygen atoms and hydroxyl groups on the side faces of the lattice, uncompensated by the charges of the cations Al^{3+} and Si^{4+} on the broken faces, and also by isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedral surface layers.

Evidently, however, a significant contribution to the adsorption energy of water is made by coordinationally unsaturated atoms (Si, Al) lying close to the side faces of the crystal lattice.

The change in the parameters of the kaolinite elementary cell are shown in Fig. 2 as a function of the moisture content; Table 1 shows their maximum and minimum values obtained experimentally, together with estimates of the contribution of different groups of parameters to the deformation in the volume of the triclinic elementary cell of kaolinite for two values of the moisture content (0.035 and 2%).

There is no change in the parameter c in the course of hydration because the water molecule cannot penetrate into the interlayer space of kaolinite.

The small change in elementary-cell volume (up to 0.015%) as a result of the change in the angles α and β is due to the small perturbations inside the OH-groups of the layer when water is adsorbed on the external faces of the crystal.

The main contribution to the deformation (0.216%) is that of the change in the parameters a, b, and γ due to perturbations in the OH groups of the side surfaces of the crystal lattice in other bonds involved in coordinationally unsaturated complexes of the cations Al^{3+} and Si^{4+} on the broken faces of the crystal.

In fact, as shown by the spectroscopic investigations, total dehydration is accompanied by displacement of the main bands in the region of OD-group valency oscillations toward higher frequencies, from 2680 to 2700 cm^{-1}. This displacement, due to the unloading of hydroxyl groups from the water molecules, is determined by the 1.5% increase in the OD-bond force constants and, according to [7], by a 0.005-Å linear deformation of the bonds.

It is easy to understand the finding that the maximum ratio $\Delta a/\Delta b = 0.13/0.07 \approx 2$, since, according to a number of works, including [8], the ratio of the number of oxygen atoms and hydroxyl groups lying close to the plane formed by the basic translations bc to the number of the same groups in the ac plane is also close to two.

Thus, experimental x-ray structural investigations confirm that the crystal lattice of clay minerals is deformed under the influence of adsorbed water, and the results obtained allow improvements to be made in the method of estimating the density of bound water; however, to the same end, it is necessary to perform a second stage of the investigation, taking account of the influence of organic compounds as well as water on the deformation.

TABLE 1. Change in Elementary-Cell Parameters and Volume for Kaolinite as a Function of the Moisture Content

Moisture content, %	Parameters						Volume
	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg	V, Å³
0,035	6,00	10,574	7,386	101,165	88,152	58,842	388,40
2,00	6,007	10,587	7,386	101,200	88,222	58,782	389,20

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INFLUENCE OF A CENTRIFUGAL FIELD ON THE
RESIDUAL PRESSURE IN THE VACUUM CAVITY
OF A ROTATING HELIUM CRYOSTAT

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The increase in the residual pressure in the vacuum cavity of a rotating helium cryostat subjected to centrifugal forces due to the redistribution of the molecule relative velocities as well as the stripping of molecules being condensed on the cold wall is theoretically computed.

In connection with the development of cryogenic electrical machine construction, it is of great practical interest to study the vacuum thermal insulation of liquid helium under strong centrifugal field conditions.

The vacuum cavity of a rotor cryostat in a typical cryogenic generator [1] is the volume formed by two coaxial cylinders. The outer cylinder is at room temperature, but the inner is at the liquid helium boiling point. It is known that the pressure in a vacuum system at helium temperatures is determined by the partial pressures of such residual gases as helium, hydrogen, and neon. However, in strong centrifugal fields a change occurs in the relative velocities of the molecules moving between the hot and cold walls, as does also the stripping of part of the molecules being condensed (adsorbed) on the cold wall. This can result in degradation of the vacuum in the dynamic mode of cryostat operation, and therefore, in an increase in the heat influx to the liquid helium.

For a quantitative estimate of the influence of the centrifugal field on the residual pressure, let us consider the flux of molecules escaping from the hot to the cold wall and conversely. The molecule thermal energy should evidently be higher than the centrifugal field energy for passage from the hot (outer) to the cold (inner) wall. This means that molecules whose mean thermal velocity $\overline{V}_t$ is greater than the average linear angular velocity of the cryostat V_l will overcome the potential barrier of the centrifugal field. The quantity of such molecules, i.e., the quantity of molecules making an impact per unit surface of the cold wall in unit time, is [2]

$$N_t = n_t V_t / 4. \tag{1}$$

We find the quantity n_t (the molecule concentration with thermal velocity greater than V_l) from the expression [3]

$$\frac{n_t}{n} = \frac{4}{\sqrt{\pi}} \int_{u_0}^{\infty} u^2 \exp(-u^2)\, du, \tag{2}$$