A method was developed earlier for determining the average density of water filling the pores, according to the curve of its temperature expansion in a limited temperature interval close to the melting point \[1\]. The ratio obtained between the temperature and the difference of the ordinates of the curves of the expansion of water in the pores and the volume can be written

\[ \eta = \frac{A (t - t_0)}{t + B}, \]

where \( \eta = \frac{\Delta V_1}{V_0 - \Delta V/V_0}; \Delta V = V - V_0; \Delta V_1 = V_1 - V_0; V_0 \) is the specific volume of the free liquid* at some selected reference temperature \( t_0; V_01 \) is the same for water in the pores; \( V \) and \( V_1 \) are the specific volumes of free water and water in the pores, respectively, at an arbitrary temperature \( t; B \) is an empirical constant; \( A = 1 - \frac{V_0}{V_01} \). At \( t_0 = 0 \), function (1) can be transformed into

\[ \frac{1}{\eta} = \alpha + \beta \frac{1}{t}, \]

where \( \alpha = \frac{1}{A} = \text{const}; \beta = \frac{B}{A} = \text{const}. \) Henceforth the Celsius temperature scale will be used.

If (2) is correct, the experimental data will fit on a straight line in a plot of \( 1/\eta \) versus \( 1/t \), which should intercept a segment with length \( 1/A = V_0/\Delta V_0 \) on the \( Y \) axis, where \( \Delta V_0 = V_0 - V_01 \).

Figure 1 gives the results of one of the experiments of [2] with water filling the pores of pressed quartz powder. The points fit well on a straight line, which is evidence of the correctness of the empirical function \( \eta(t) \) selected in [1]. The straight line intercepts a segment on the \( 1/\eta \) axis corresponding to \( \Delta V_0 = 3.3 \times 10^{-3} \text{ cm}^3/\text{g} \). This is almost three times as great as the value of \( \Delta V_0 \) cited in [1], which is explained by the gross approximation made in the estimation of \( \Delta V_0 \) in [1].

In the case of known \( \Delta V_0 \), the difference \( \Delta V_\ast \) of the specific volumes of free liquid and liquid in the pores at an arbitrary temperature \( t \) can be found according to the formula

\[ \Delta V_\ast = V - V_1 = \Delta V_0 - \eta V_0 \]

obtained from a determination of the value of \( \eta \).

Knowing the average density of the liquid in the pores, we can calculate the specific adsorption \( \Gamma \) of the liquid at the temperature \( t \) on the surface of a solid

\[ \Gamma = V_s \Delta \rho / S, \]

where \( \Delta \rho \) is the change in the average density \( \rho \) of liquid in the pores in comparison with the table \( \rho_0 \) (\( \Delta \rho = |\Delta \rho| = |\Delta V_\ast| \)); \( V_S \) is the total volume of pores; \( S \) is the total surface of the pores of the adsorbent. When

* Here free liquid denotes the volume liquid phase of water with the table value of the density.
† We have in mind the case \( \Delta \rho = \rho - \rho_0 \ll \rho_0; \rho_0 \approx 1. 
‡ Their complete filling with liquid is assumed.
Fig. 2. Adsorption of liquid water on the surface of quartz.

is used, it is assumed that the thickness of the boundary layer of liquid, in which its density is substantially changed, is small in comparison with the minimum pore dimensions.

Figure 2 presents the results of a calculation of the value of $\Gamma$ for the experiment under consideration according to Eq. (4). The dotted line corresponds to extrapolation of the experimental data, performed using (2). The specific surface of the powder of silica gel Y-333, according to the data on the adsorption of nitrogen, is 280 m$^2$/g [2]; the weights of the water and powder are 19 and 25 g, respectively. Values of 19 cm$^2$ and 7·10$^6$ cm$^2$ were assumed for $V_s$ and $S$.

Let us indicate three basic facts that follow from the function $\Gamma(t)$ found. In the first place, the adsorption of water on quartz is positive, i.e., there is a condensation of water close to the surface of quartz. In the second place, the value of the adsorption is very low (it corresponds to hundredths of a monolayer, converted to adsorption from the vapor phase). In the third place, within a relatively small temperature interval there is a pronounced temperature dependence of the adsorption, in contrast to adsorption from the vapor phase.

At the present time there are no theoretical estimates of the value of the adsorption of a monocomponent liquid on a solid surface. An exception is the case of dispersion forces discussed in [3], where an asymptotic formula was derived for the local change in the density of the liquid $\Delta \rho$ as a function of the distance $h$ from the surface of separation of the phases. This formula can be written as

$$\frac{\Delta \rho}{\rho_0} = \frac{\chi_0(A_{12} - A_{11})}{6\pi \frac{h^3}{h_{\text{min}}} \frac{1}{h^3}}. \quad (5)$$

Here $\rho_0$ is the density, while $\chi_0$ is the compressibility of the volume liquid; $A_{11}$ and $A_{12}$ are the Hamacher constants for the interaction of liquid—liquid and liquid—adjacent phase, respectively. The specific adsorption of the liquid on the surface of a solid is evidently equal to

$$\Gamma = \int_{h_{\text{min}}}^{\infty} \Delta \rho dh, \quad (6)$$

where $h$ is the distance from the exactly determined geometrical surface of the solid. If we use a dependence of the type of (5) for $\Delta \rho$, then as the lower limit of integration we should take $\log h = 0$, but $h = h_{\text{min}}$ is the minimum distance between the unit interacting volumes of the liquid and solid, for which the corresponding Hamacher constants have been calculated. In this case, the adsorption $\Gamma_d$ on account of the action of dispersion forces is

$$\Gamma_d = \rho_0 \chi_0 \frac{(A_{12} - A_{11})}{12\pi h_{\text{min}}}, \quad (7)$$

If we use the data cited in [4] for the water—quartz system: $A_{11} = 3.2·10^{-13}$ erg, $A_{12} = 6·10^{-13}$ erg; $h_{\text{min}} = 2.8$ Å, then $\Gamma_d = 4.5·10^{-10}$ g/cm$^2$. The value obtained for $\Gamma_d$ can be considered only as an estimate of the order of magnitude of this quantity, since in the first place, formula (5) is correct only for large $h$ in comparison with the dimensions of the molecule; in the second place, the values of $A_{11}$, $A_{12}$, and $h_{\text{min}}$ are not precisely known.

Our calculation gave a value of $\Gamma_d$ in agreement in order of magnitude with the value of the adsorption determined experimentally, however, from formulas (5) and (7) it follows that $\Gamma_d$ depends little on the temperature. The temperature dependence of $\Gamma(t)$ is already clearly evident from the experiment (see Fig. 2). This fact should be attributed to the action of the structural factor, i.e., the determining factor in the adsorption of water of temperatures close to 0° is the change in its structure in the boundary layer.

The role of the dispersion component in the adsorption of water on quartz at these temperatures is evidently small. This assertion is supported by the data of [4] on the relative value of the dispersion component ($E_d$) in the total value of the energy ($E$) of surface interaction in the water—quartz system: $E_d/E \simeq 0.2$, i.e., 80% of the total energy of the interaction is associated with dipole interaction and a hydrogen bond, leading directly to structural changes.