# PHYSICAL CHEMISTRY

1961

SovietRxiv

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## Abstract

## Full Text

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# ON THE THERMAL EXPANSION OF WATER IN MICROCAPILLARIES

*(Presented by Academician A. N. Frumkin, January 17, 1961)*

As has been shown in a number of works ([1–3]), a polar liquid at the boundary with a solid forms a special phase which, in its structure and, consequently, in its properties, differs from the bulk liquid. Therefore one should expect that in porous materials with pore sizes comparable with the thickness of the boundary phase, the properties of liquids must change. Study of the properties of water in porous materials—for example, in soils ([4,5])—suggests the existence of various liquid structures in pores; however, taking into account the inhomogeneity of the latter and the dissolution of various salts in the water, nothing can be said about the existence of a special structure in microcapillaries and about its properties.

One of the properties of liquids that depends strongly on structure is thermal expansion. It therefore seems advisable, for the study of the structure of boundary layers, to investigate the volume expansion of liquids in capillaries with radii on the order of the thickness of this layer, i.e., in the range 0.1–0.01 $\mu$ ([1–8]).

Since the main difficulty in such experiments is the measurement of capillary dimensions, we shall briefly discuss the method of these measurements. If a capillary whose diameter is less than the wavelength of light is placed under a microscope with a small magnification, of the order of 100–150 times, and a strong beam of light is directed from the side, then the unfilled channel will scatter light, and a shiny strip will be visible in the microscope. A channel filled with liquid will scatter light very weakly. In this way one can observe the displacement of the liquid meniscus.

Fig. 1. Cavity at the end of a capillary

To measure the diameter, a cavity was blown at one end of the capillary (Fig. 1), which was then filled with liquid. Knowing the volume $V$ of this cavity and the magnitude of the elongation of the liquid column $\Delta l$ in a certain part of the capillary when the cavity is heated by $\Delta t$ degrees, one can calculate the mean radius in this part from the formula:

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

$$r = \sqrt{\frac{V \Delta t \beta}{\pi \Delta l}},$$

where $\beta$ is the coefficient of volume expansion of the liquid in the cavity. Taking the cavity to be a body of revolution (and this can be verified by photographing it in two mutually perpendicular planes), its volume ⋯

is easily calculated from the projection, allowing, of course, for the magnification given by the walls of the capillary, which, as calculations and experiments show, is equal to 1.5 for glass. $\Delta t/\Delta l$ is found from the graph of the dependence of $\Delta l$ on $\Delta t$, which is constructed from the experimental data; from it one can also judge the uniformity of the channel in the given section.

By making such measurements in different parts, we select a section of the capillary with cylindrical walls, with which the further experiments are then carried out. The capillary thus obtained was partially filled with water and sealed at both ends, but in such a way that only one end was free of liquid.

**Fig. 2.** Dependence of $\Delta l/l_0$ on $t$. 1—$r = 0.022\,\mu$, 2—$r = 0.08\,\mu$, 3—$r = 0.19\,\mu$, 4— water

**Fig. 3.** Dependence of $\Delta l/l_0$ on $t$, referred to 23°. $A$—$r = 0.022\,\mu$; $B$— from tabular data for water

The apparatus for measuring the coefficient of volume expansion consisted of two cylindrical glass tubes, one inserted into the other, between which a thin nichrome heating coil was placed; a microscope with a horizontally positioned tube and a long-focus objective; and an illuminator, which from above directed a concentrated beam of light that had passed through a filter absorbing the infrared part of the spectrum.

The capillary was fixed in the inner tube; there a thermocouple was also installed so that its junction was at the middle of the capillary (it could, however, be moved to any position). Depending on the temperature range in which the measurements were made, alcohol or glycerin was poured into the tube. All this was mounted on a slide holder so that the tube was positioned horizontally, perpendicular to the microscope tube. The temperature of the liquid in the tube, and hence in the capillary, after equilibrium had been established, was measured by the thermocouple, and the elongation of the column by means of a

Fig. 4. Dependence of $\beta$ on r at 23°

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screw ocular micrometer. In this way the dependence of the elongation, referred to unit length, on temperature was constructed.

For a cylindrical capillary, the coefficient of volume expansion will be: $\beta = \Delta l / l_0 t$. The thermal expansion of the glass can be neglected in this case, since even at 100° it is two orders of magnitude smaller than that of water.

From Fig. 2 it is seen that the coefficient of volume expansion for capillaries with radii less than 0.1 $\mu$ depends only weakly on temperature and to a much greater extent depends on the radius of the capillary. Figure 3 gives experimental data on the expansion of water in a capillary with radius 0.022 $\mu$ in comparison with the expansion of water in bulk; the data are referred to 23°. The coefficient of volume expansion in this capillary, beginning at 10° and up to 120°, remains constant (above 120° no investigations were carried out).

It is clear from Fig. 4 that, as the capillary radius decreases, the coefficient of volume expansion increases in comparison with bulk water in the temperature interval 23-50°. Goldman and Polyani ([9]), measuring the expansion of adsorption films in porous materials in the temperature interval 0–5°, also found a deviation from volume expansion. A study of the structure of water by X-ray structural analysis ([10]) showed that water basically has three different structures, characteristic of different temperature intervals. Upon heating, a transition from one structure to another is observed. This explains the presence of anomalies in thermal expansion.

Fig. 4. Dependence of $\beta$ on $r$ at 23°

In capillaries with radii on the order of 0.02 $\mu$, as is seen from Figs. 2 and 3, there is no anomaly in the expansion; this indicates that the structure of the liquid here remains constant and, consequently, differs from the structure of bulk water.

From the results obtained it may also be concluded that the specific volume of water in narrow pores cannot be regarded as the same as that of the bulk liquid; it not only depends on temperature in a different way, but also depends on the pore size.

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Received
19 I 1961

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*Note: Figure translations are in progress. See original paper for figures.*