in a special report. Studies will also be continued. But it remains indisputable that the presence of a second component in an aqueous solution has a significant effect on the water structure, as reflected in the behavior of heat capacity.

NOTATION

c_σ, specific heat of liquid in equilibrium with its saturated vapor; m, mass; T, temperature; ΔT, temperature difference; T_m, mean temperature; τ, time; Q, amount of heat; c_{sp}, specific heat; m_c, mass of calorimeter; c_c, heat capacity of calorimeter.

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EXPERIMENTAL STUDY OF HIGH-TEMPERATURE LIQUID EVAPORATION FROM CAPILLARIES

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Experimental studies of liquid evaporation rates from capillaries in air at atmospheric pressure and temperatures near and above the boiling point are compared with the previously developed theory.

It is well known that an increase in the total pressure of a vapor–gas mixture within porous bodies may be a cause of their destruction [1].

To explain this increase in internal pressure with evaporation from capillaries a theory based on consideration of vapor and gas transfer with account taken of gas-kinetic slip [3] was developed [2]. Analysis of these solutions reveals that with a decrease in capillary radius r, the total pressure of the vapor–gas mixture above the meniscus P_e increases, exceeding both the saturated vapor pressure above the meniscus p_s and the pressure P_0 of the gas in the surrounding medium. Physically, this effect is explained by the fact that with decrease in r, hydrodynamic resistance increases, as a consequence of which ever-higher gradients in the total pressure of the vapor–gas mixture are necessary for compensation of the r-independent gas-diffusion counterflow. The solution obtained for small r has the form

$$M = \frac{P_0 D_0}{RTx} \ln \frac{(P_0 - p_{01}) P_e}{(P_e - p_s) P_0}. \qquad (1)$$

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As $r \to \infty$, $P_e \to P_0$, and the equation transforms to the well-known Stefan equation. The constancy of total pressure of the vapor–gas mixture which is postulated in deriving the Stefan equation is no longer maintained in thin capillaries where the vapor transfer resistance is high; this leads to a solution of the problem of [2] which differs from the Stefan solution. An analogous conclusion was also made in [4].

It is important to note that in Eq. (1), P_e is a function of both r and T. With decrease in r, the values of P_e increase, leading to a reduction in evaporation rate as compared to the Stefan value. The P_e values are found from the transcendental equation [2]

$$\ln\left[\frac{P_e^2}{(P_e - p_s)(P_e + Kp_s)}\right] = \frac{r^2(P_e^2 - P_0^2)}{8\eta P_0 D_0}, \tag{2}$$

where K is a coefficient which takes account of gas-kinetic slip [3].

In sufficiently large capillaries and for $T \geq T_b$, the P_e values practically coincide with p_s. Thus, for example, for water this occurs at T = 373°K for $r \geq 3$ μm and at T = 393°K for $r \geq 0.3$ μm. In this case one can use the viscous vapor flow equation for calculation of evaporation:

$$M = \frac{r^2(p_s^2 - P_0^2)}{8\eta RTx}. \tag{3}$$

For comparison of experimental and theoretical data, it is convenient to use values of the evaporation constant

$$C = Mv_m x,\ \text{cm}^2/\text{sec}. \tag{4}$$

To find the diffusion constants the relationship of [5] was used:

$$D_0 = 0.21\,(T/273)^2,\ \text{cm}^2/\text{sec}. \tag{5}$$

The viscosity of the vapor–gas mixture η was determined by averaging over the partial pressures of the vapor p_1 and of dry air p_2:

$$\eta = (\eta_1\bar{p}_1 + \eta_2\bar{p}_2)/(\bar{p}_1 + \bar{p}_2), \tag{6}$$

where the mean values $\bar{p}_1$ and $\bar{p}_2$ over capillary length were used. The viscosity of the vapor η_1 and gas η_2 were taken from [5].

To verify the theory which was developed, experimental studies were performed on the evaporation rate of water from the quartz capillaries with radii from 0.2 to 12 μm. The capillaries were drawn in an oxygen-burner flame from a fused-quartz tube with SiO_2 content greater than 99.99%. Before the experiments, pieces of the capillaries 8-10 cm long were filled with degassed liquid and sealed.

Evaporation observations were performed in a tube-type furnace. The furnace used was a metallic tube covered by fiberglass upon which a filament heater was mounted. Ceramic thermal insulation was installed externally. The capillaries were mounted within the furnace on a metallic substrate to eliminate temperature gradients. The furnace body contained two narrow longitudinal slits covered by sheet mica. The lateral horizontal slit was used to illuminate the capillary channel, while the upper vertical slit was used to observe the meniscus with a dark-field microscope. Meniscus displacement during evaporation was recorded with an IZA-2 comparator, on the movable table of which the tube furnace with capillary was mounted. Air temperature within the furnace was regulated by an autotransformer and measured by a thermocouple with working junction located near the capillary.

After the furnace was heated and the specified temperature stabilized, one end of the sealed capillary was cut off with a movable knife. The moment of opening the channel was taken as the zero point for measurement of evaporation time τ. Air pressure within the furnace was equal to atmospheric. Measurements were made at different temperatures varying from 359 to 414.5°K.

Figure 1 shows the results obtained for water evaporation from capillaries at $T < T_b$. The figure shows displacement of the meniscus x from the capillary mouth as a function of $\sqrt{\tau}$. The experimental points on curve 1 were obtained at T = 365°K for five capillaries with radii r = 10.6, 8.6, 5.7, 4.3, and 1.4 μm. Curve 2 contains points obtained at T = 359°K for four capillaries with r = 11.5, 6.1, 5.6, and 3.4 μm.

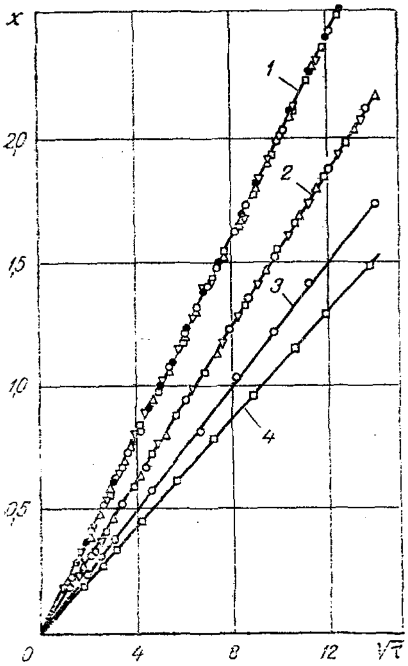

Fig. 1

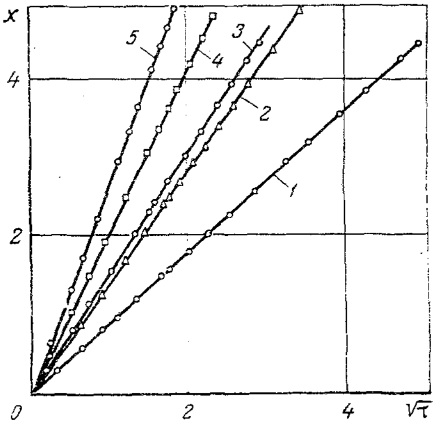

Fig. 2

Fig. 1. Water evaporation from capillaries at T = 365°K (1) and T = 359°K (2-4) in air at atmospheric pressure. x, cm; $\sqrt{\tau}$, $\min^{1/2}$.

Fig. 2. Water evaporation from capillaries at T = 380°K in air at atmospheric pressure: r = 1.65 μm (1), 3.7 μm (2), 4.6 μm (3), 6.3 μm (4), and 8.9 μm (5), x, cm; $\sqrt{\tau}$, $\min^{1/2}$.

Values of the evaporation constant C calculated from the slopes of the curves $x(\sqrt{\tau})$ agree well with those calculated from the Stefan equation:

$$C = \frac{v_m D_0 P_0}{RT} \ln \frac{(P_0 - p_{01})}{(P_0 - p_s)}. \qquad (7)$$

In the calculations, the values $D_0 = 0.364$ cm²/sec at T = 359°K and $D_0 = 0.377$ cm²/sec at T = 365°K were used. For T = 359°K, the experimental values was $C = 2.03 \cdot 10^{-4}$ cm²/sec, while the theoretical value was $C = 2 \cdot 10^{-4}$ cm²/sec. For T = 365°K, the corresponding values are $3.4 \cdot 10^{-4}$ and $3.31 \cdot 10^{-4}$ cm²/sec. Thus, for capillaries with radii greater than 1-3 μm, water evaporation at $T < T_b = 373$°K is described well by the conventional Stefan equation (7). In this case film flow cannot produce any noticeable contribution to the flow due to the small thickness of the water film on the quartz surface at such a temperature [6].

We begin to observe deviations from the Stefan eauation only in finer capillaries: r = 0.31 μm (curve 3, Fig. 1) and r = 0.21 μm (curve 2, Fig. 1).

Evaporation from fine capillaries obeys the more general equation (1). Thus, in fine-pored bodies with high internal vapor flow resistance, the pressure of the vapor—gas mixture at the meniscus P_0 may exceed the atmospheric pressure even at $T < T_b$.

Observations were then performed of water-evaporation rate from capillaries of various radii at T = 375, 380, 382, 395, and 414.5°K. As an example, Fig. 2 presents results of one such experiment. As is evident from the figure, the evaporation rate here depends on capillary radius, increasing with increase in r. Qualitatively analogous results were obtained at other temperatures.

Figure 3 shows C values calculated from the experimental evaporation curves $x(\sqrt{\tau})$ for capillaries of different radii. The experimental dependence of C on r is indicated by the solid lines. The dashed lines 1' and 2' depict the results of calculation by Eq. (3) inasmuch as capillaries of sufficiently large radius were used.

As is evident from Fig. 3, theory agrees with experiment only in the case of very small evaporation rates (corresponding to low C values). Deviation in the direction of reduced evaporation rate can be related to the phenomenon of meniscus cooling upon intense evapora-

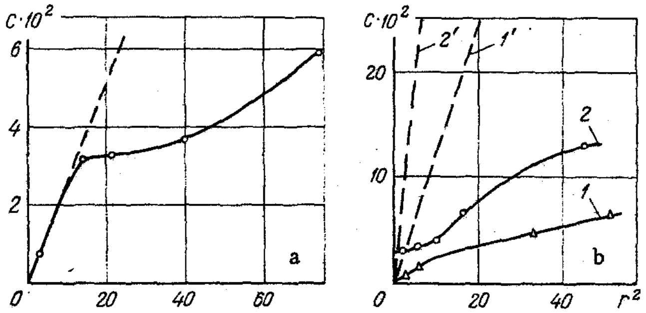

Fig. 3. Dependence $C(r^2)$ for water evaporation from quartz capillaries: a) $T = 380°K$; b) $T = 395°K$ (curve 1); $T = 414.5°K$ (curve 2). Dashed lines, calculation by Eq. (3). C, cm^2/sec; r^2, μm^2.

tion, which is not considered in the theory that uses the framework of an isothermal approximation [2].

Reduction in meniscus temperature leads to a reduction in vapor pressure above the meniscus, reducing the evaporation rate. This reduction would be all the stronger, the larger the capillary radius, i.e., the higher the evaporation rate from the meniscus surface.

It follows from observations of ethanol, hexane, and carbon tetrachloride evaporation that the effect of reduction of meniscus temperature T on phase transition manifests itself more markedly, the higher the temperature, the greater the heat of evaporation of the liquid, and the larger the capillary radius.

The experiments performed indicate that the pressure of the gas—vapor mixture above an evaporating meniscus may actually exceed atmospheric pressure. This excess is the greater, the greater the temperature and the smaller the radius of the capillaries, thus creating a danger of destruction in high-intensity drying (most of all, in fine-pored bodies).

Further development of the theory of high-intensity evaporation with consideration of the nonisothermal nature of the process is necessary in connection with temperature reduction of the evaporating meniscus. Conditions of heat exchange at the capillary walls or in the skeleton of the solid phase of the material being dried with the surrounding medium must be considered.

NOTATION

M, evaporation rate, $mole/cm^2 \cdot sec$; D_0, vapor-diffusion coefficient through gas at $P = P_0$, cm^2/sec; R, gas constant, ergs/mole•deg; x, distance from meniscus to capillary mouth, cm; p_{01}, partial vapor pressure in surrounding medium, dyn/cm^2; T, temperature, °K; η, viscosity of vapor—gas mixture, P; T_b, liquid boiling point, °K; v_m, molecular volume of liquid, $cm^3/mole$.

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