

an x-ray diffraction analysis, and thereby to refine the distribution obtained for the adsorbed water density.

#### NOTATION

$\rho/\rho_0$  and  $\rho_0/\rho$ , relative changes in the density of the dispersed medium;  $d_0'$ , density of the hydrated solid phase with a mass equal to the lower "critical" value;  $\rho_0$ , fluid density corresponding to this mass;  $d$ , density of the moist specimen;  $\rho$ , fluid density corresponding to the mass of solid phase greater than the lower "critical" value;  $d_w$ , density of adsorbed water;  $P$ , content of adsorbed water, %;  $d_0$ , density of dehydrated adsorbent;  $D_c$ , spacing between exchange cations;  $S$ , specific surface of solid phase particles;  $n$ , cation valency;  $c_x$ , quantity of adsorbed cations of a given valency;  $N$ , Avogadro number;  $P_{i,s}$ , quantity of adsorbed water corresponding to complete filling of interpacket space;  $d_{i,s}$ , density of this water;  $D_s$ , spacing between packet inner surfaces;  $P_{w,s}$ , quantity of adsorbed water corresponding to total covering of the whole surface;  $d_{w,s}$ , density of this water;  $D_H$ , projection of the length of the chemical bond on a plane perpendicular to the adsorbent surface from the active center (Ca ion) for the second adsorbed layer of water.

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#### WETTING ANGLES CLOSE TO CRITICAL TEMPERATURE

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Information available in the literature on the temperature dependence of the wetting angle in various systems is generalized for a wide range of temperatures. The dependence  $\theta = f(T)$  obtained experimentally is compared with theoretical results.

The wetting of solid surfaces by liquids is a process of considerable importance in engineering practice. The characteristics of wetting determine the operation of capillary evaporators, heat tubes, etc. Wetting is particularly important under conditions of weightlessness. Under these conditions, the Bond number is considerably less than unity ( $Bo \ll 1$ ), since the surface-tension forces predominate over the inertial forces and the form of the liquid surface depends exclusively on the equilibrium conditions at the solid-liquid-gas phase interfaces. This lends particular importance to information on wetting angles for various systems and their dependence on a number of factors, in particular, temperature.

The aim of the present paper is to generalize the known experimental results on the dependence of the wetting angle on the temperature and saturation pressure over a broad temperature range, extending to values close to the critical temperature  $T_{cr}$ , and to compare the experimental data with theoretical results.

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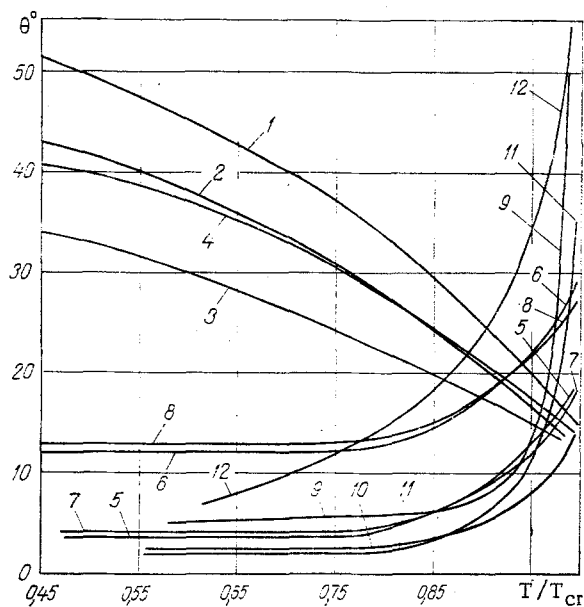


Fig. 1. Dependence of wetting angle  $\theta$  on reduced temperature  $T/T_{Cr}$  for various systems. 1-4) Wetting angle on metals [2]; 5-12) on dielectrics [1, 3, 4]: 1) water ( $H_2O$ )—niobium; 2) water ( $H_2O$ )—tantalum; 3) water ( $H_2O$ )—nickel; 4) water ( $H_2O$ )—stainless steel; 5) water ( $H_2O$ )—quartz; 6) water ( $H_2O$ )—sapphire; 7) water ( $D_2O$ )—quartz; 8) water ( $D_2O$ )—sapphire; 9) n-heptane—glass; 10) ethyl alcohol—quartz; 11) ethyl alcohol—glass; 12) ethyl ether—glass.

The large number of investigations of the wetting angle as a function of temperature relate predominantly to a narrow temperature range, and only a few cover a broad range of conditions approaching the critical temperature. The first investigation of this type was apparently the measurement of the wetting angle of ethyl ether on glass in [1]. The temperature dependence of the surface tension  $\sigma(T)$  for ethyl ether was investigated by the method of capillary uplift; in measuring the wetting angle  $\theta$ , account was taken of the effect of the curvature of the meniscus in determining  $\sigma$  up to the critical temperature. The measurement of  $\theta$  was accurate to  $\pm 5^\circ$ .

In [2-4] the dependence  $\theta = f(T)$  was obtained up to temperatures close to critical at the corresponding saturation pressure of the wetting liquid. These investigations were made for various systems; the solid surfaces were glass, fused quartz, sapphire, stainless steel, nickel, tantalum, and niobium; the wetting liquids were n-heptene, ethyl alcohol, and water ( $H_2O$  and  $D_2O$ ). The deviation of the measured values of  $\theta$  from the mean was within  $\pm 2^\circ$ .

Mathematical analysis of the experimental data of [2-4] gives empirical relations for the systems water ( $H_2O$ )—metals and water ( $H_2O$  and  $D_2O$ )—quartz.

For the systems water ( $H_2O$ )—metals (steel IKh18N9T, Ni, Ta, Nb), the temperature dependence of the wetting angle may be described by the universal relation

$$\theta^* = 0.97 + 0.65\tau - 1.3\tau^2, \quad (1)$$

where  $\theta^* = \theta/\theta_0$  and  $\tau = T/T_{Cr}$  are the reduced wetting angle and temperature, respectively;  $\theta$  is the wetting angle at  $T$ ,  $^\circ K$ ;  $\theta_0$  is the wetting angle at  $T = 293^\circ K$ ; and  $T_{Cr}$  is the critical temperature of water.

For the systems water ( $H_2O$ )—quartz and water ( $D_2O$ )—quartz, the temperature dependence cannot be described by a single equation. The relations recommended for water ( $H_2O$ )—quartz are

$$\cos \theta = 1 - 0.038\tau^5, \quad (2)$$

$$\theta = 3.5 + 5.9 \cdot 10^{-15} \tau^6, \quad (3)$$

and for water (D<sub>2</sub>O) - quartz

$$\cos \theta = 1 - 0.046\tau^5, \quad (4)$$

$$\theta = 3.9 + 5.6 \cdot 10^{-15} \tau^6, \quad (5)$$

where  $\tau$ , °C is the temperature at which the value of  $\theta$  is calculated.

Curves of the dependence of  $\theta$  on the reduced temperature  $\tau = T/T_{cr}$  are shown in Fig. 1. Curves 6, 8, 9, 10, 11, and 12 are drawn from the experimental data in [2, 3] and curves 1, 2, 3, 4, 5, and 7, from Eqs. (1), (3), and (5). The systems corresponding to the dependences  $\theta = f(T)$  shown in curves 5-12 have common characteristics. In these systems, the solid material is a dielectric, on which  $\theta$  rises with increase in temperature. The dependence of  $\theta$  on the reduced temperature is weak up to  $T/T_{cr} = 0.8$  and sharp increase in  $\theta$  only begins when  $T/T_{cr} > 0.8$ .

For curves 1-4, corresponding to water on metals, an inverse dependence ( $d\theta/dT < 0$ ) is first observed and then, as the critical temperature is approached, the wetting angles in the various systems tend to equalize, reaching a value  $\theta \approx 15^\circ$ . We have been able to draw certain qualitative conclusions from an analysis of theoretical [5-7] and experimental [1-4] results on the temperature dependence of  $\theta$ .

In [5] the change in equilibrium of the system solid-liquid-gas with variation in temperature was considered.

Assuming that the chemical composition and mass of the system are constant, and that no phase changes occur, the processes that occur as the temperature is changed are evaporation (condensation) of material in the system and change in form of the surface, i.e., change in the relations between the areas of the phase interfaces or else change in the wetting angle  $\theta$ . In [5], starting from the Le Chatelier-Brown thermodynamic principle, a relation obtained between the surface tension  $\sigma$ , the wetting angle  $\theta < \pi/2$ , and the temperature derivatives of  $\sigma$  and  $\theta$  as follows:

$$\frac{d\theta}{dT} > \frac{d\sigma}{dT} \cdot \frac{\text{ctg } \theta}{\sigma}. \quad (6)$$

Results calculated using Eq. (6) were found to be in good agreement with experimental data. In the case of a positive derivative ( $d\theta/dT > 0$ ), Eq. (6) cannot change sign, since the temperature coefficient of surface tension for pure liquids is always negative ( $d\sigma/dT < 0$ ) and  $\cot \theta > 0$  when  $\theta < \pi/2$ . If  $d\theta/dT < 0$ , however, Eq. (6) will retain the same sign only if

$$\left| \frac{d\theta}{dT} \right| < \left| \frac{d\sigma}{dT} \right| \cdot \frac{\text{ctg } \theta}{\sigma}. \quad (7)$$

Calculations showed that this condition is satisfied. Note that Eq. (6) provides only a qualitative idea of the degree of wetting.

In the theoretical investigation of the dependence  $\theta = f(T)$  in [7], the mechanism of the wetting of a solid by a liquid was regarded as a process directly related to the work of adhesion. On the basis of the macroscopic theory of van der Waals' forces [8], the equation

$$\frac{d\theta}{dT} = \left[ \frac{2}{3} (\beta_S + \beta_L) + \frac{d\sigma/dT}{\sigma} \right] \text{ctg } \frac{\theta}{2} \quad (8)$$

was obtained in [7] for a solid-liquid system (where both media are dielectrics);  $\beta_S$  and  $\beta_L$  are the thermal coefficients of bulk expansion of the solid and liquid. Calculation using Eq. (8) for the case when both the solid surface and the wetting liquid are dielectrics do not agree with the experimental data given above.

It follows from Eq. (8) that

$$\frac{d\theta}{dT} > 0 \text{ for } \frac{2}{3} (\beta_S + \beta_L) > \frac{|d\sigma/dT|}{\sigma}, \quad (9)$$

$$\frac{d\theta}{dT} < 0 \text{ for } \frac{2}{3} (\beta_S + \beta_L) < \frac{|d\sigma/dT|}{\sigma}, \quad (10)$$

$$\frac{d\theta}{dT} = 0 \quad \text{for} \quad \frac{2}{3} (\beta_S - \beta_L) = \frac{d\sigma/dT}{\sigma} . \quad (11)$$

Analysis shows that the expression in the square brackets in Eq. (8) is always negative and increases sharply with rise in temperature. This is because the surface tension  $\sigma$  falls more sharply with increase in temperature than the sum of volume-expansion coefficients of solid and liquid rises. Thus the temperature derivative of the wetting angle is always negative ( $d\theta/dT < 0$ ), which corresponds to Eq. (10), and the wetting angle should fall with rise in temperature, but this contradicts the experimental findings.

However, it is necessary to note the following. In [9, 10], it was shown that liquid forms the wetting angle not with the solid surface but with a polymolecular adsorption layer coating the surface; the thickness of this layer is on the order of  $10^{-6}$ - $10^{-5}$  cm. In polar liquids (water, for example), this layer is inhomogeneous and consists of several polymorphic modifications. This adsorption layer has significantly different physical properties from the bulk of the liquid: different density, viscosity, etc., and hence also different volume expansion coefficient  $\beta$ .

Strictly speaking, the value of  $\beta_L$  for the sorption layer should be used in Eq. (8), but this value is unknown. Therefore, the results obtained above in comparing Eq. (8) with experiment can only give a rough indication. Thus, it is not yet possible to make a reliable comparison of theoretical and experimental values of the derivative  $d\theta/dT$  and therefore it remains unclear why, in the wetting of a solid surface by a liquid, this derivative takes opposite sides for metals and dielectrics.

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