BOILING OF FLUID ON A METAL SURFACE

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An attempt is made to verify a hypothesis about the effect of a double electrical layer at a metal—polar-fluid boundary on the boiling process in the fluid.

The boiling point T* of a fluid was determined experimentally [6] by rapid heating of a platinum wire (0.02 mm in diameter) submerged in the fluid with a powerful current pulse.

The divergence between the theory of homogeneous nucleation [1-5] and experiment does not exceed 1-1.5° for n-pentane, n-hexane, diethyl ether, and n-heptane (about 20 test fluids in all), i.e., is within the limits of expected error and often is even a fraction of a degree. However, quite significant divergence between theory and experiment was observed for water (more than 10°) and also for methyl and ethyl alcohols (3-5°). If the entire divergence between experiment and theory is ascribed to surface tension σ alone, then σ must be reduced by $\Delta\sigma_{H_2O} = 0.0029$ N/m for water, by $\Delta\sigma_{CH_3OH} = 0.0008$ N/m for methyl alcohol, and by $\Delta\sigma_{C_2H_5OH} = 0.0006$ N/m for ethyl alcohol in order to match the theoretical and experimental boiling points, with the relative changes being

$$\left(\frac{\Delta\sigma}{\sigma}\right)_{H_2O} = 0.26, \quad \left(\frac{\Delta\sigma}{\sigma}\right)_{CH_3OH} = 0.17, \quad \left(\frac{\Delta\sigma}{\sigma}\right)_{C_2H_5OH} = 0.15 \text{ [6]}.$$

A common property of these fluids is the pronounced polarity of the molecules and the correspondingly high dielectric constant (an order of magnitude greater than for other fluids studied). The fact that a divergence between theory and experiment was only observed for polar fluids with the maximum divergence in fluids with the largest dielectric constant suggests that the cause of this divergence is not accidental.

Figure 1 shows a comparison between the correction $\Delta\sigma$ to the coefficient of surface tension for the fluids and the relative dielectric constant D. The points in the figure fall nicely on a straight line drawn from the origin.

It is well known that a so-called double electrical layer appears at a metal—polar-fluid boundary. Because of the difference in adsorptive forces acting on positive and negative ions, ions of a single sign are concentrated at the metal surface. The metal has a charge of the opposite sign. An ion cannot approach the boundary of the metal to a distance less than the radius $1/\varkappa$ of its ion atmosphere. Thermal motion of fluid molecules spreads out the charged layer at the metal surface and forms a diffuse portion of the double electrical layer. The pattern created resembles a condenser where the metal acts as one plate and the layer of solution with a high ion concentration acts as the other. The capacity C of such a condenser depends on the dielectric constant $\varepsilon_0 D$ of the fluid and on the radius $1/\varkappa$ of the ion atmosphere of an elementary charge [3]:

$$C = \varepsilon_0 D \varkappa. \tag{1}$$

Charge carriers in the fluid are attracted to the metal—fluid interface by electric interaction forces. Because the range of these forces exceeds molecular dimensions, the first layer of fluid molecules bordering on the surface of the metal experiences a separating action from the molecules of the second layer which leads to a reduction in the value of the surface tension by $\Delta\sigma$ in the double electrical layer.

Frenkel' [3] gives a formula for $\Delta\sigma$:

$$\Delta\sigma = \frac{1}{2} C\varphi^2$$

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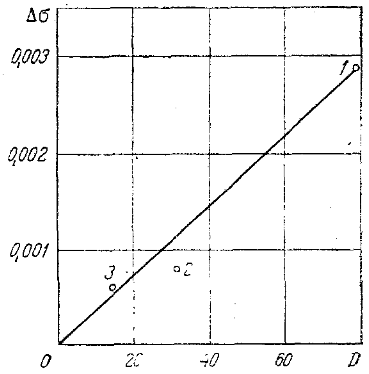

Fig. 1

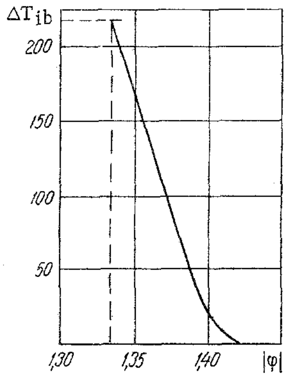

Fig. 2

Fig. 1. Corrections $\Delta\sigma$ (N/m) to the coefficient of surface tension for a fluid which matched the experimental boiling point to the theoretical value of Zeldovich—Kagan as a function of the relative dielectric constant D: 1) H_2O; 2) CH_3OH; 3) C_2H_5OH.

Fig. 2. Dependence of superheat ΔT_{ib} (°K) required for initiation of boiling on the absolute value of the potential drop $|\varphi|$ (V) in a copper—water boundary layer during a decrease in pressure (v_p = 10 bar/sec, zo = 2.2 mm, initial temperature $T_f = 443.17$°K).

or, considering Eq. (1),

$$\Delta\sigma = \frac{1}{2}\varepsilon_0 D \varkappa \varphi^2, \tag{2}$$

where φ is the potential drop between the metal and the fluid.

Methods have not yet been developed for the direct or indirect measurement of φ.

In physical chemistry, one makes extensive use of the concept of standard electrode potential, which is the potential difference between a test element and a normal hydrogen electrode submerged in the appropriate fluid.

The standard electrode potential includes two boundary-layer potential drops: at the test-metal—fluid boundary and at the boundary between the fluid and the hydrogen-saturated platinum electrode. Therefore, any sort of conclusions about the potential drop at a metal—liquid boundary from the value of the standard electrode potential can only be made under rather crude assumptions about the stability of the potential drop at the surface of a normal hydrogen electrode. Nevertheless, we note that Pleskov [7] gave standard electrode potentials for a number of metals in water, methyl alcohol, and ethyl alcohol which differ from one another by an amount of the order of 10%.

Several authors (including Frenkel') consider that the potential jump at a metal—fluid boundary is generally independent of the properties of the fluid and is determined by the nature of the metal. An order-of-magnitude estimate can be obtained from the formula given in [3]:

$$\varphi \approx \frac{9}{10^{-9}} \cdot \frac{z\varepsilon}{r_{\text{M}}}. \tag{3}$$

For monovalent copper z = 1, and the distance between atoms in a face-centered cubic lattice with an edge length of 3.597 Å is r_M = 2.544 Å; the potential φ = 5.67 V. If r_M is assumed equal to the edge length of the crystal lattice, r_M = 3.597 Å and φ = 4.02 V.

Thus if one assumes for water, methyl alcohol, and ethyl alcohol equality of contact potentials at a boundary with platinum and identical radii for the ion atmosphere, Eq. (2) gives a direct proportionality between the dielectric constant and the change in the coefficient of surface tension in the wall layer of a fluid.

Taking the material presented above into consideration, we solve the associated problem of the boiling of a thin layer (zo ≤ 2.2 mm) of water on a thick horizontal metal plate during a pressure drop (in the Zel'dovich—Kagan formulation [5]) and for nonstationary thermal conductivity in the wall including the temperature dependence of the thermophysical properties of the metal.

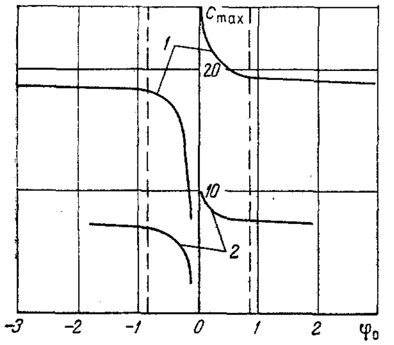

Fig. 3

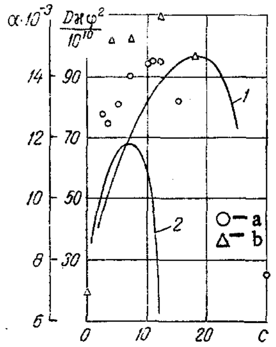

Fig. 4

Fig. 3. Dependence of the concentration c_{max} (%) corresponding to the minimum of the surface tension of the solution in a wall layer on the constant portion of the potential drop at the metal—solution boundary φ_0 (V): 1) NaCl; 2) NaOH.

Fig. 4. Dependence of heat-transfer coefficient α (W/m^2·deg) for quench cooling on solution concentration c (%): a) NaCl; b) NaOH. Dependence of the quantity $D\varkappa\varphi^2$ (V^2/m), which is proportional to the decrease in the coefficient of surface tension, on solution concentration c (%): 1) NaCl; 2) NaOH.

The number of ions of one sign per unit volume was assumed to be equal to the square root of the ion production in water at the corresponding temperature [9]. The initial thickness of the water layer was zo = 2.2 mm, the initial temperature was T_f = 443.17°K, and the rate of pressure drop was vp = 10 bar/sec.

The pressure range was the following: initial pressure, 7.92 bar; final pressure, 1.013 bar. (The thermodynamically possible superheat of water at a pressure of 1.013 bar is 212.5°K [6].) The wall material was copper. By assigning various values of $|\varphi|$, the superheat ΔT_{ib} required for initiation of boiling was calculated with Eq. (2) taken into consideration. It turned out that a rather narrow range of $|\varphi|$ — 1.422-1.335 V (Fig. 2) — corresponded to the range of possible superheat for the fluid (ΔT_{ib} = 0-212.5°K). It must be pointed out that the potential values obtained were determined under the assumption that the dielectric constant of the fluid in a layer next to the wall was equal to the dielectric constant within the volume. In fact, D is considerably less in the wall layer because of polarization of the water. Frumkin [10] sets the value at $D \approx 3$. Then, in order to obtain $\Delta\sigma$ for D = 3 the same as for D within the volume in accordance with Eq. (2), the range of $|\varphi|$ must be 5.188-4.869 V, which is close to the estimate from Eq. (3).

Weakening of surface tension in the wall layer of a fluid, which is significant in polar fluids (with large dielectric constants), may be one of the reasons for the spread in the experimental data for the magnitude of the heat-transfer coefficient as a function of the material comprising the heating surface. It should be noted that the greatest discrepancy is observed for those metals where the differences in electrode potentials are a maximum. On pure-metal surfaces [11], the maximum discrepancy of α was obtained for silver and chromium, where the difference of the standard electrode potentials was a maximum, $\Delta\varphi$ = + 0.799 — (—0.913) = 1.712 V.

We analyze the behavior of the quantity $\Delta\sigma$ determined from Eq. (2) as a function of the electrolyte concentration c in water. The inverse radius $\varkappa$ of the ion atmosphere is directly proportional to the square root of the number N of dissociating molecules, i.e., it increases with increase in concentration [15]:

$$\varkappa = \sqrt{\frac{4\pi\varepsilon^2\nu}{k\varepsilon_0}}\sqrt{\frac{N}{DT_f}}, \tag{4}$$

where

$$N = N_A c\left(\frac{\nu g - 1}{\nu - 1}\right) \tag{5}$$

in accordance with [12]. The change in potential between metal and solution is proportional to the logarithm of the ion activity. For a binary mono-monovalent electrolyte [15]

$$\varphi = \varphi_0 + \frac{RT_f}{F}\ln(\gamma m). \tag{6}$$

The activity coefficient γ and the Bjerrum osmotic coefficient g are monotonically increasing functions of m in the region of molar concentrations from one to the maximum for the majority of electrolytes studied.

The dielectric constant D of the solution decreases with increasing concentration [8]:

$$D = D_{H_2O} - 2\delta c. \tag{7}$$

Thus a maximum change in surface tension $\Delta\sigma_{max}$ is possible at some concentration c_{max}.

We analyze the effect of inaccuracy in the determination of the value of the potential drop φ at the metal—fluid boundary on the determination of the electrolyte concentration c_{max}. The molar concentration m and its monotonic function γ (within the limits m = 1-6) appear in the logarithm in Eq. (6) for the potential drop. Since the logarithm is a "slowly" increasing function, one should expect that the relative change in φ with change in concentration will be small when the value of φ_0 is sufficiently large. Figure 3 shows values of the (weight) concentration c_{max} corresponding to a maximum $\Delta\sigma$ as a function of various values of φ_0 for aqueous solutions of NaCl (curves 1) and NaOH (curves 2). If $|\varphi_0| > 0.8$ V, the error in c_{max}, outside the fact that φ is determined except for sign, does not exceed 1.5% for NaCl and 0.5% for NaOH. If one assumes that $|\varphi|$ for distilled water falls within the limits 1.422-1.335 V, that the activity of water is one, and that the concentration of ions of one sign is equal to the square root of the ion production in water at the corresponding temperature, the minimum absolute value of φ_0 will be 0.88 V.

Thus one can find the maximum of $\Delta\sigma$ as a function of the concentration c with comparatively small error by considering that the change in potential at the boundary has little effect on the position of the maximum.

The work involved in the formation of a viable vapor bubble in a superheated fluid is proportional to the cube of the coefficient of surface tension.

A decrease in the work, which is associated with a reduction in σ, leads to an exponential rise in the probability of fluctuational formation of vapor nuclei. In addition, the minimum radius of potentially possible vaporization sites on a heat-transfer surface also falls as σ decreases with a consequent increase in the density of active sites.

It is then clear that the heat-transfer coefficient for boiling of a solution after coming in contact with a heated metal surface must have an extremum corresponding to the extremum in $\Delta\sigma$.

Figure 4 shows experimental data for heat-transfer coefficients during quench cooling in NaOH (b) [13] and NaCl (a) [14] solutions. The maxima in curves for $\Delta\sigma$ calculated from Eq. (2) with Eqs. (4)-(7) taken into consideration agree satisfactorily with the maxima for the experimental values of α.

NOTATION

C, electrical capacitance; c, molar concentration; c_{max}, weight concentration corresponding to maximum $\Delta\sigma$; D, relative dielectric constant; F, Faraday number; g, osmotic Bjerrum coefficient; k, Boltzmann constant; m, solution molality; N, specific number of charges of one sign; N_A, Avogadro number; R, gas constant; r_M, distance between adjacent atoms in a crystal lattice; T*, boiling point of fluid; T_f, fluid temperature; ΔT_{ib} fluid superheat required for initiation of boiling; z, valence of atoms in metal wall; zo, initial thickness of fluid layer; α, heat-transfer coefficient; γ, activity coefficient; δ, coefficient for variation of dielectric constant with concentration; ε, electronic charge; ε_0, electric constant for a vacuum; $\varkappa$, inverse radius of ion atmosphere; φ, drop in electric potential; φ_0, drop in electric potential at metal—solution boundary when activity is 1; ν, number of monovalent ions formed by dissociation of electrolyte molecule; σ, $\Delta\sigma$, coefficient of surface tension and its variation; vp, rate of pressure drop.

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EXPERIMENTAL STUDY OF THE PROCESS OF FILM CONDENSATION OF NITROGEN VAPOR FROM A MIXTURE WITH HELIUM

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On the basis of an experimental study of the process of film condensation of nitrogen vapor from a mixture with helium and of the hydrodynamics of the film, data are obtained which make it possible to calculate counterflow condensers for cryogenic installations.

In apparatuses for the obtainment and enrichment of a neon—helium mixture through the fractionation of air, for the purification of helium from admixtures of neon, hydrogen, nitrogen, and oxygen, and for the low-temperature fractionation of hydrocarbons, the process of vapor condensation is complicated by the presence of a component with a small molecular mass, this presence having an important effect on the intensity of heat and mass exchange. The heat and mass exchanges in these apparatuses take place, as a rule, at increased pressures and low temperatures, which prevents the reliable use of experimental data on heat and mass exchange during the condensation of water vapor from mixtures with different gases [1-2]. Under the conditions of increased pressures, vapor—gas mixtures display the properties of physicochemical solutions, and their thermophysical properties do not obey laws of additivity.

The results of an experimental study of the process of condensation of nitrogen vapor from a nitrogen—helium mixture moving inside vertical pipes are presented in the report. The tests were performed on a stand which was created with allowance for the special features of the process of condensation of cryogenic substances. A shield cooled by liquid nitrogen was placed between the experimental model and the thermal chamber to reduce the heat influxes (Fig. 1). The thermal chamber had powder-vacuum insulation. A vacuum (1.33 Pa) was maintained in the space between the shield and the experimental model. The gas mixture of the required composition was made up in a gas holder; the pressure was produced with a membrane compressor. The preliminary cooling of the mixture was accomplished in a coil placed in a vessel containing boiling nitrogen. The pipeline from the heat exchanger to the experimental model had vacuum-shield insulation, which made it possible to obtain a vapor—gas mixture with a temperature exceeding the saturation temperature by 2-3°. Under these conditions the vapor—gas mixture was in the saturated state along almost the entire length of the zone of mass exchange.

The experimental model (Fig. 1) consisted of five copper pipes with an inner diameter of 8 mm, a wall thickness of 2 mm, and a length of 3000 mm, soldered to pipe grids. The height variation in the composition of the moving vapor—gas mixture was determined by sampling the mixture from the centers of the pipes through

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