

RISE OF LIQUID IN CAPILLARIES OF VARIABLE CROSS-SECTION AND CAPILLARY HYSTERESIS

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Abstract

Full Text

PHYSICAL CHEMISTRY

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RISE OF LIQUID IN CAPILLARIES OF VARIABLE CROSS-SECTION AND CAPILLARY HYSTERESIS

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For capillary tubes with a circular transverse cross-section, the height h of capillary rise of a nonviscous liquid can be found from the condition

$$\frac{\partial U}{\partial h} = 0, \tag{1}$$

where U is the potential energy of the wetting liquid in the capillary:

$$U = \pi \rho g \int_0^h r^2 h \, dh - 2\pi \sigma \int_0^h r \, dh, \tag{2}$$

where ρ is the density of the liquid, g is the acceleration due to gravity, r is the radius of the capillary, and σ is the surface tension of the liquid at the boundary with its saturated vapor. Expression (2) is valid under the assumption that the meniscus has a spherical form and that the liquid wets the walls of the capillary. In this expression the function $r = f(h)$ determines the form of the capillary (which is a surface of revolution about an axis coinciding with the axis of the capillary); for a cylindrical capillary $r = r_0$, where r_0 is the radius of the capillary; for conical capillaries $r = a + bh$, where a and b are constant quantities; for a periodically narrowing and widening (for example, according to a sinusoidal law) capillary $r = \alpha + \beta \sin \gamma h$, where α , β , and γ are constant quantities, etc. The real and positive roots $h_1, h_2, \dots, h_i, \dots$ of equation (1) for $(\partial^2 U / \partial h^2)_{h=h_i} > 0$ correspond to heights associated with stable equilibrium, and for $(\partial^2 U / \partial h^2)_{h=h_i} < 0$ —to heights associated with unstable equilibrium.* The rise of liquid in a capillary occurs in the interval of values of h from 0 to h_1 , or from h_i to h_{i+1} , if in this interval $\partial U / \partial h < 0$; for values corresponding to intervals for which $\partial U / \partial h > 0$, the rise of liquid in the capillary can be accomplished only at the expense of external work. For a cylindrical and a diverging conical capillary there exists one height of capillary rise; for a converging conical (open) capillary—two heights ⁽²⁾; for a periodically narrowing and widening capillary—several heights. In the latter case there is always obtained a finite number of heights, determined by the number of real and positive roots

Fig. 1

Figure 1: Fig. 1

of equation (1), i.e., by the form of the capillary, or by the type of the function $r = f(h)$.

The heights of capillary rise of a liquid in a capillary of variable cross-section can also be found from the simultaneous solution (for example, graphical) of the obvious system of equations

$$\begin{aligned} h\rho g &= \frac{2\sigma}{r} \\ r &= f(h) \end{aligned} \quad (3)$$

* Mention of the possible existence of several positions of equilibrium of a liquid in a capillary of variable cross-section is found in ⁽¹⁾.

It is interesting to note that for a capillary whose shape is determined by the equation $r = 2\sigma/h\rho g$ (the internal cavity of the capillary is obtained by rotating the hyperbola $rh = 2\sigma/\rho g$ about the vertical axis), any height will be an equilibrium height.

Apparently, the non-reproducibility of capillary-rise heights sometimes observed experimentally for certain liquids is connected with this circumstance. In many cases cylindrical capillaries in fact have a variable cross-section, and if the shape of the capillary and the values of σ and ρ for the liquid are such that the condition $rh = 2\sigma/\rho g$ is satisfied at least approximately, then non-reproducible heights of capillary rise are observed experimentally.

Fig. 1. *a*—Profile of the capillary: experimental (solid line) and calculated (dashed line); *b*—dependence of the potential energy of the gravitational and capillary forces acting on the liquid in the capillary on height; *v*—dependence of the hydrostatic and capillary pressure on height (graphical solution of the system of equations (3)).

The experimental verification of the considerations set forth above was carried out on the capillary rise of water in converging conical capillaries, as well as in specially made glass capillaries periodically narrowing and widening according to a sinusoidal law. Below, as an example, for a sinusoidal capillary, graphs are given of $U = f(h)$ *, $h\rho g = f(h)$, and $2\sigma/r = f(h)$. In Fig. 1a the solid curve shows the actual profile of one of the capillaries (obtained by measuring under a microscope the internal diameters of the capillary, half of which had been ground off), and the dashed curve shows the profile calculated according to the equation

* In the graph $U = f(h)$, the value $U = 0$ is conventionally made to coincide with the lowest value of the energy.

$r = \alpha + \beta \sin \gamma h$, whose constants α , β , and γ were found by averaging the results of measuring $2r$ at different h . It turned out that, for the capillary under consideration, $\alpha = 0.034$, $\beta = 0.022$, and $\gamma = 3.38$. As is seen from the plots $U = f(h)$ (Fig. 1b), $h\rho g = f(h)$ and $2\sigma/r = f(h)$ (Fig. 1c), for this capillary and water there must exist nine heights of capillary rise, of which five (h_1 , h_3 , h_5 , h_7 , and h_9) correspond to stable equilibrium and four (h_2 , h_4 , h_6 , and h_8) to unstable equilibrium. In the experiment (both when the liquid was raised and when it was lowered) all five heights were observed, practically coinciding with those calculated from (1) or (3). The most stable in the case considered proved to be the first of the stable heights, which agrees with the graph $U = f(h)$.

Thus, the conclusion that several heights of capillary rise exist for capillaries of variable cross-section, known as capillary hysteresis, can be obtained from consideration of the general conditions for the equilibrium of a liquid in capillaries.

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CITED LITERATURE

¹ A. Yu. Davidov, *Theory of Capillary Phenomena*, Moscow, 1851, p. 201. ² H. Bouasse, *Capillarité, phénomènes superficiels*, Paris, 1924, p. 189.

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

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