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THE DYNAMICS OF CAPILLARY FLOW.

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SYNOPSIS.

Penetration of Liquids into Cylindrical Capillaries.—The rate of penetration into a small capillary of radius r is shown to be: $dl/dt = P(r^2 + 4\epsilon r)/8\eta l$, where P is the driving pressure, ϵ the coefficient of slip and η the viscosity. By integrating this expression, the *distance penetrated by a liquid flowing under capillary pressure alone* into a horizontal capillary or one with small internal surface is found to be the square root of $(\gamma rt \cdot \cos \theta/2\eta)$, where γ is the surface tension and θ the angle of contact. The quantity $(\gamma \cos \theta/2\eta)$ is called the coefficient of penetrance or the penetrativity of the liquid.

Penetration of Liquids into a Porous Body.—(1) *Theory.* If a porous body behaves as an assemblage of very small cylindrical capillaries, the volume which penetrates in a time t would be proportional to the square root of $(\gamma t/\eta)$. (2) *Experiments with mercury, water and other liquids* completely verify the theoretical deductions.

Dynamic capillary method of measuring surface tension is described. It possesses certain advantages on the static method of capillary rise.

1. INTRODUCTION.

THE statical problems connected with the rise of liquids in capillary tubes have been investigated on both the theoretical and the experimental side, but the dynamical aspects of the subject do not appear to have received much attention. Aside from the theoretical interest attaching to the subject, the dynamics of capillary flow have certain practical aspects in connection with the movement of water or oil through soils, the impregnation of wood and other porous materials with liquids, and the determination of the porosity and true density of porous bodies, as well as offering a new method for measuring the surface tension or viscosity of a liquid. The present paper is a contribution to the theory of the subject.

2. THE VELOCITY OF CAPILLARY FLOW.

In the following development of the laws governing capillary flow we shall simplify our problem initially to the extent of assuming that we are dealing with a single capillary tube of uniform internal circular cross-section throughout, the radius being r. The tube may be of any length or shape otherwise. Such a tube may be represented by AB in Fig. 1.

The tube is so arranged that the end A may, at any desired moment, be placed in contact with a liquid having the depth h above the center of the opening at this end. The end B may either be open to the atmosphere or the tube may be closed at this end and completely evacuated previous to establishing connection with the liquid at A. In the former case the pressure of the atmosphere will be neutralized but the tube will offer a small though calculable resistance to the efflux of the air which is displaced by the entering liquid. The equation covering this case will therefore contain a small correction term for the resistance of the air.

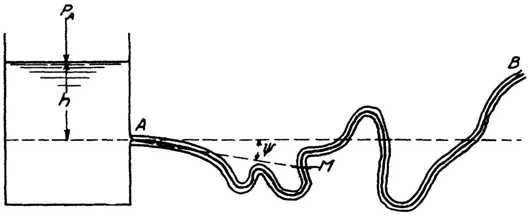

Fig. 1.

At the time 0 let connection be established with the liquid at the point A. At some time t_0 thereafter, the meniscus will have penetrated a distance l_0 at which point its velocity, which was initially very high owing to the small resistance encountered, will have dropped to such a value that the conditions of flow postulated in Poiseuille's law will have been established and these conditions will thereafter persist. Previous to the establishment of these conditions the velocity of flow will be governed by the laws of hydraulics, and an experimental investigation of this portion of the flow would perhaps disclose the two regions of turbulent flow and of slip flow, respectively, whose laws have been investigated by Reynolds, Sorkau[1] and others, and which are separated from each other and from the Poiseuille region by rather pronounced breaks. A theoretical and experimental study of the dynamics of capillary flow in these two regions offers much of interest but will not be entered into in this paper which will be confined to capillaries so small that the Poiseuille region covers practically the whole of the flow.

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[1] Sorkau, Phys. Z., 14, 739 (1913).

It has been found, by Osbourne Reynolds[1] that for a liquid of density D, the distance l_0 is determined by the relation

$$\frac{2rD}{\eta}\frac{dl}{dt} = k, \qquad (1)$$

where the constant k, a pure number, was found by experiment to have the value 2000. If we combine this relation with the expression for (dl/dt) to be developed below (see equation 9) we obtain the relation

$$l_0 = \frac{\left(P_A + g \cdot D \cdot h + \frac{2\gamma}{r}\cos\theta\right) r^3 \cdot D}{4\eta^2 \cdot 10^3}, \qquad (2)$$

from which the value of l_0 may be calculated. An extreme case will be represented by such a liquid as water in a capillary which it wets, the external driving pressure on the liquid being one atmosphere. For this case the above equation becomes

$$l_0 = \left(2.5 \cdot 10^6 + \frac{400}{r}\right) r^3 \text{ cms.} \qquad (3)$$

and the values of l_0 for various values of r are shown in the following table.

P_A = external driving pressure.

r, in mm.	1	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.
l_0 in mm. (P_A = 1 atmos.) . .	1.3×10^4	13	1.3×10^{-2}	1.5×10^{-5}	3.3×10^{-8}	1.1×10^{-10}
l_0 in mm. (P_A = 0).	2	4×10^{-2}	4×10^{-4}	4×10^{-6}	4×10^{-8}	4×10^{-10}

From this table it is evident that l_0 is entirely negligible for very small capillaries.

For such capillaries we may therefore assume Poiseuille's law which obviously takes the following form, if we neglect for the moment any air resistance,

$$dV = \frac{\pi \Sigma P}{8\eta l}(r^4 + 4\epsilon r^3)dt, \qquad (4)$$

where dV is the volume of the liquid which in the time dt flows through any cross-section of the capillary, l is the length of the column of liquid in the capillary at the time t, η is the viscosity of the liquid and ϵ its coefficient of slip, and ΣP is the total effective pressure which is acting to force the liquid along the capillary.

At the end of any time, t, the liquid will have gone a distance, l, along

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[1] Reynolds, Scientific Papers, Volume 2, pp. 563 and 535.

the capillary and the meniscus will have arrived at some point, M, where it is moving with the velocity (dl/dt). To calculate the magnitude of this velocity we proceed as follows: In equation 4 we can put

$$dV = \pi r^2 dl, \tag{5}$$

thus giving us the following expression for the velocity

$$\frac{dl}{dt} = \frac{\Sigma P}{8r^2 \cdot \eta \cdot l}(r^4 + 4\epsilon r^3). \tag{6}$$

We have now to find an expression for ΣP. The total driving pressure will be made up in general of three separate pressures, the unbalanced atmospheric pressure, P_A, the hydrostatic pressure P_h, and the capillary pressure P_s. P_A we shall take as constant. For P_h we can evidently write (see Fig. 1)

$$P_h = h \cdot g \cdot D - l_s \cdot g \cdot D \sin \psi, \tag{7}$$

where l_s is the linear distance from A to M, D is the density of the liquid and g is the acceleration due to gravity. Finally for P_s we have

$$P_s = \frac{2\gamma}{r}\cos\theta, \tag{8}$$

where γ is the surface tension of the liquid and θ is the angle of contact.

Summing up and substituting in equation 6 gives us the following law for the velocity of penetration,

$$\frac{dl}{dt} = \frac{\left[P_A + g \cdot D(h - l_s \sin\psi) + \frac{2\gamma}{r}\cos\theta\right](r^2 + 4\epsilon r)}{8\eta l}. \tag{9}$$

3. INTEGRATION OF THE EQUATION.

In equation 9, l_s, ψ, ϵ, and θ will be in general functions of t, and θ will perhaps also be a function of (dl/dt) and of the pressure gradient in the column of liquid. For *any* given known conditions, l_s and ψ could, of course, be determined and expressed as functions of l.

In the illustrations which follow we shall, however, assume ψ, θ, and ϵ, to be constants and on integrating equation 9 for these conditions we find the following integral:

$$\frac{(r^2 + 4\epsilon r)D \cdot g \sin}{8\eta}\psi t + l$$

$$= -\frac{P_A + D \cdot g \cdot h + \frac{2\gamma}{r}\cos\theta}{D \cdot g \cdot \sin\psi}\log_e \frac{P_A + Dg(h - l\sin\psi) + \frac{2\gamma}{r}\cos\theta}{P_A + D \cdot g \cdot h + \frac{2\gamma}{r}\cos\theta}. \tag{10}$$

The two limiting cases corresponding to $\psi = 90^\circ$ and $\psi = 0^\circ$ offer some special interest. For the former case the integral reduces to

$$\frac{(r^2 + 4\epsilon r)D\cdot g}{8\eta}t + l = \frac{-\left[P_A + D\cdot g\cdot h + \frac{2\gamma}{r}\cos\theta\right]}{D\cdot g}\log_e\left[1 - \frac{D\cdot g\cdot l}{P_A + D\cdot g\cdot h + \frac{2\gamma}{r}\cos\theta}\right]. \quad (11)$$

For the latter case the integral becomes indeterminate, but a second integration for this case gives us

$$l^2 = \frac{\left(P_A + D\cdot g\cdot h + \frac{2\gamma}{r}\cos\theta\right)(r^2 + 4\epsilon r)t}{4\eta}. \quad (12)$$

It may be noted here that with capillaries open at both ends, $P_A = 0$ and equations 11 and 12 assume the following forms:

$$\frac{(r^2 + 4\epsilon r)D\cdot g}{8(\eta - \eta_A)}t + l = \frac{-(\eta - \eta_A)\left(D\cdot g\cdot h + \frac{2\gamma}{r}\cos\theta\right) + D\cdot g\cdot\eta_A l_T}{D\cdot g\cdot(\eta - \eta_A)} \log_e\left(1 - \frac{D\cdot g\cdot l}{D\cdot g\cdot h + \frac{2\gamma}{r}\cos\theta}\right) \quad (11a)$$

and

$$l^2 + \frac{2\eta_A l_T}{\eta - \eta_A}l = \frac{\left(D\cdot g\cdot h + \frac{2\gamma}{r}\cos\theta\right)(r^2 + 4\epsilon r)}{4(\eta - \eta_A)}t, \quad (12a)$$

where η_A is the viscosity of air and l_T is the total length of the capillary.

4. VERTICAL CAPILLARIES; EXPERIMENTAL.

For a liquid which wets the capillary equation 11a becomes,

$$t = \frac{-8(\eta - \eta_A)l}{r^2\cdot D\cdot g} - \frac{8[(\eta - \eta_A)(h + \Delta h) + \eta_A l_T]}{r^2\cdot D\cdot g}\log_e\left(1 - \frac{l}{h + \Delta h}\right), \quad (13)$$

where Δh is written in place of $2\gamma/r\cdot D\cdot g$. In order to test this equation the experimental arrangement shown in Fig. 2 was employed. The bore of the glass capillary was not examined for uniformity but its average radius calculated from the weight of the mercury thread which filled it was 0.01454 cms. Lengths were measured with a cathetometer and were as follows: $h = 51.38$ cms.; $l = 58.23$ cms.; Δh (the capillary rise) $= 10.01$ and 9.90 cms., two direct measurements as determined by the *static* method at two different points in the tube; and $l_T = 96$ cms. The distilled water employed was from the laboratory supply system and the temperature was room temperature, $30° \pm 0.2°$. The time of rise through the distance l, as observed with a stop-watch in several successive experiments was 40.2 ± 0.2 seconds. Taking $\eta_A = 0.00018$, $\eta = 0.00800$, $g = 980.1$, $D_{30°} = 0.9956$, and calculating Δh and γ from equation (13) we find $\Delta h = 9.90$ and $\gamma = 70.2$ which agrees with the accepted value 71.03 (Landolt-Börnstein-Roth) within the accuracy of the above measurements. No great accuracy is claimed for these measurements which were made for illustrative purposes only.

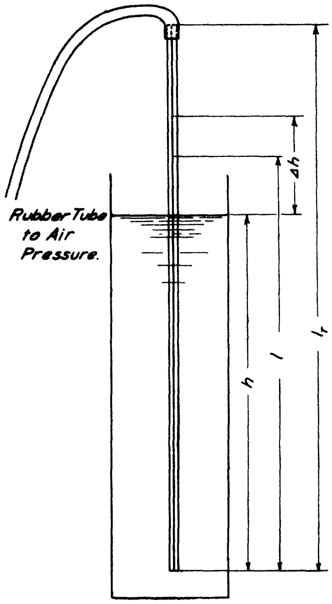

Fig. 2.

5. HORIZONTAL CAPILLARIES; EXPERIMENTAL.

An experimental study of equation 12*a* was made using mercury in open glass capillaries at room temperatures, and varying h, r and l. The results for $l = 95$ cms. are shown in Fig. 3 for two capillaries of different radii. The curves shown in this figure are graphs of the theoretical equation (12*a*) using values of $\eta\ (= 0.0152)$, $\gamma\ (= 440)$ and D given in the literature. The value of θ was computed by means of the observed points on the upper curve and found to be 112°. This value was used in plotting both curves.

The data obtained by experiment are indicated by small circles in the figure and it is evident that these experimental values are in good agreement with the theoretical curve. The apparent deviation of some of the points in the neighborhood of $h = 0$ is not significant, as under these conditions sticking friction developed and it was necessary to tap the capillary with the finger in order to keep the meniscus in motion. The observed times of flow for these points were therefore known to be somewhat too long. The measurements were not accurate enough to detect with certainty any variation of θ with h or dl/dt.

A number of experiments with different liquids (benzene, kerosene, alcohols, esters) for which values of η and γ were given in the literature demonstrated also the validity of equation 12*a* with respect to variations in these two variables.

The relation between l and t was also found to hold within the accuracy of the measurements in numerous experiments with horizontal capillaries wetted by the liquids.[1] In experiments with such liquids it is necessary after each run to elevate the capillary for drainage in order to insure the presence of a thin film of liquid on the wall. If too much liquid is left in the capillary, the observed times of flow will be too short while if the wall is not completely wet the value of θ will be greater than zero. The percentage differences between the observed times of flow with wet and dry tubes respectively, were found to be smaller the smaller the value of r, so that for sufficiently small capillaries the speed of wetting brought about by the diffusion of vapor ahead of the liquid might be sufficient to maintain the angle θ practically zero. Further evidence on this point is, however, needed.

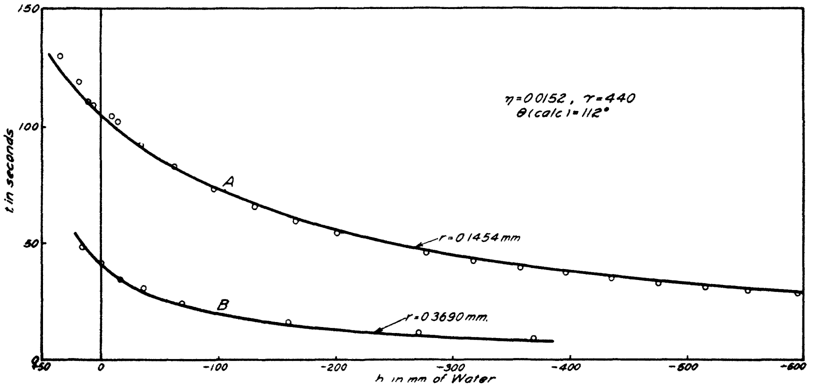

Fig. 3.

6. The Flow of Liquids under Capillary Pressure.

In discussing the rate of penetration of a capillary by a liquid moving under its own capillary pressure we shall consider only the two limiting cases of vertical capillaries and horizontal capillaries, respectively, the equation for the intermediate cases being obvious. The case under consideration is equivalent to assuming that $P_A + D \cdot g \cdot h$ may be neglected in comparison with $(2\gamma/r)\cos\theta$. In this discussion we shall

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[1] Bell and Cameron, Jour. Phys. Chem., **10**, 659 (1906), deduced the relation, $l^2/t = const.$ for a liquid moving through a horizontal capillary under a constant driving pressure and demonstrated its validity by experiments with water, alcohol, and benzene.

also write $\epsilon = 0$, which is the case for all liquids which wet the capillary and has been shown experimentally to be also true for mercury in glass.

Case 1. *Vertical Capillaries.*—For vertical capillaries with small internal surfaces the logarithmic term in equation 10 may be expanded and if we reject all the terms of the series beyond the term containing l^2, equation 10 becomes identical with equation (14) for horizontal capillaries and will be discussed under that head.

Case 2. *Horizontal Capillaries.*—Equation 12 for this case becomes

$$l^2 = \left(\frac{\gamma}{\eta}\frac{\cos\theta}{2}\right)rt, \tag{14}$$

air resistance being excluded or neglected. The corresponding equation for the rate is

$$\frac{dl}{dt} = \frac{r}{\eta}\frac{\gamma}{4l}\cos\theta, \tag{14a}$$

or in words, the rate at which a liquid penetrates any horizontal capillary (or any capillary with a small surface), under its own capillary pressure is directly proportional to the radius of the capillary, to the cosine of the angle of contact, to the ratio of the surface tension to the viscosity of the liquid and inversely proportional to the length already filled by the liquid.

The quantity $\gamma/\eta\,(\cos\theta)/2$ measures the penetrating power of a liquid and will be called the *coefficient of penetrance* or the *penetrativity* of the liquid. Its dimensions are obviously those of velocity. Stated in words, the penetrativity of a liquid is equal to the distance which the liquid will penetrate a capillary tube of unit radius in unit time, when flowing under its own capillary pressure. The presence of the factor $\cos\theta$ makes the penetrativity, in general, a function also of the nature of the material composing the capillary. Thus the penetrativity of mercury into a glass capillary is obviously a negative quantity. The penetrativity of a liquid which wets the capillary is otherwise independent of the material composing the capillary and is simply equal to $\frac{1}{2}$ the ratio of its own surface tension to its viscosity.

The relative penetrativities of two liquids are most easily compared with the aid of a coiled capillary which may be immersed in the liquid during the measurement. Time of flow is the only measurement required in using such a *penetratimeter*.

7. THE RATE OF PENETRATION OF A POROUS BODY BY A LIQUID.

For purposes of calculation we will assume that the penetration of the pores of a body by a liquid in which it is immersed may be taken as equivalent to the penetration of n cylindrical capillary tubes of radii $r_1, r_2, \cdots, r_n$ and we will ask ourselves the question; How much liquid will have entered the pores of the body at the end of the time t? For any one pore the volume which enters will obviously be

$$V = \pi r^2 l = \frac{\pi}{2\eta^{1/2}} t^{1/2} \left(P_E + \frac{2\gamma}{r} \right)^{1/2} r^3 \tag{15}$$

and hence the total volume which penetrates all the pores will be

$$V = \pi \Sigma r^2 l = \frac{\pi}{2\eta^{1/2}} t^{1/2} \Sigma \left(P_E + \frac{2\gamma}{r} \right)^{1/2} r^3, \tag{15a}$$

where P_E is the total external pressure behind the liquid.

For a given body under constant driving pressure this equation has the form

$$V = k \left(\frac{t}{\eta} \right)^{1/2} \tag{16}$$

and for capillaries so small that P_E is negligible in comparison with $2\gamma/r$ this can also be written

$$V = k' \left(\frac{\gamma}{\eta} \right)^{1/2} t^{1/2}, \tag{17}$$

where k' is independent of the nature of the liquid, that is, the degree of penetration is proportional to the square root of the time of soaking and to the square root of the ratio of the surface tension to the viscosity.

If the pores of the body cannot be taken as equivalent in their behavior to cylindrical pores, equations 16 and 17 would, of course, not be applicable. If the cross-section of a pore changes with its length and especially if the pore contains an enlargement or ends in a pocket, the above equations of course would not apply. Furthermore these equations would in all probability not apply to the filling of micro-pores, that is, pores with diameters approaching the molecular diameter of the liquid. Whether or not, therefore, equation 17 applies to the absorption of a liquid by a porous body in a given case could only be determined by experiment.

Some results obtained by Cude and Hulett[1] on the rate of penetration of charcoal by water give us an opportunity of making a comparison of the above relation. The comparison is shown in Fig. 4. It is evident from this figure that the linear relation holds good within the experimental error for the initial period of penetration. Whether the later deviation corresponds to the complete filling of all except the micropores, or whether it is due to the slower filling of enlarged pores or pockets

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[1] Cude and Hulett, Jour. Amer. Chem. Soc., **42**, 391 (1920).

cannot, of course, be determined although the former supposition seems the more probable in this instance.

It is of some interest to note that if a porous body consists of n capillaries of radius r and length l, each of these quantities may be calculated, if one of them is known.

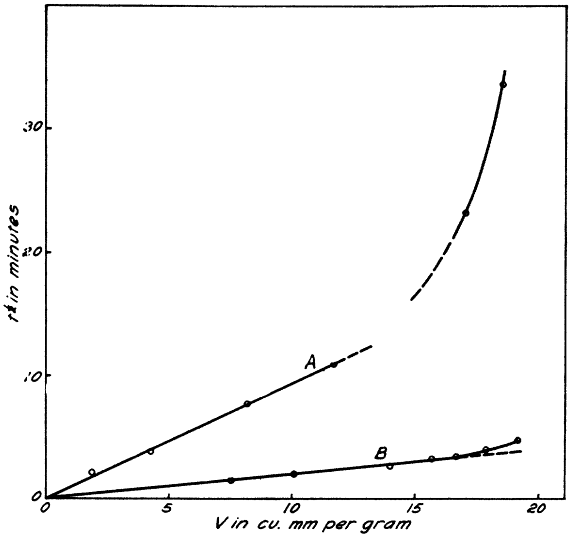

Fig. 4.

The velocity of penetration of charcoal by water. Data by Cude and Hulett. Curve A from their Table I., curve B from their Fig. 8.

8. THE MEASUREMENT OF SURFACE TENSION BY THE DYNAMIC METHOD.

Horizontal capillaries are perhaps the most convenient to use for this purpose, although, by using a vertical capillary immersed some distance in the liquid and allowing the liquid to drop from a point some distance *beyond* its equilibrium position, it should be possible to obtain very good results. With horizontal capillaries under practically zero head, equation 12a shows that the accuracy with which r can be measured is practically determined by the accuracy with which η is known. The factors l and t can be made as large as desired and the value of r called for is the average value for the whole tube. In this respect the dynamic method is superior to the static where the height of the capillary rise for a given tube is not under the control of the operator, and where the value of r involved is the particular value at the position occupied by the meniscus when equilibrium is reached, a value rather difficult to determine accurately.

The writer is indebted to Dr. E. N. Bunting of this department for valued assistance in the experiments reported in this paper. The writer also recalls with much pleasure his discussions of the subject of capillary flow with his colleague, Dr. Eric K. Rideal.

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