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### CVIII. On the flow of liquids under capillary pressure

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a constant orientation of the elementary wave are defined by the same criterion, viz. zero phase-difference between two adjacent wave-lengths. Thus it becomes obvious that one implies the other.

To Prof. Lorentz and Prof. Ehrenfest the author is very grateful for the discussion of the subject.

CVIII. *On the Flow of Liquids under Capillary Pressure.*

By ERIC KEIGHTLEY RIDEAL\*.

THE rate of penetration of liquids into capillary porous materials, of importance not only in biochemical problems but also in the study of the phenomena of adsorption by materials such as charcoal and substances constituting the membranes of semi-permeable osmometers, has attracted but little attention. Bell and Cameron (*Journ. Phys. Chem.* x. p. 659 (1906)) showed that in the case of a few liquids the rate of movement of a liquid moving through a horizontal capillary was such that the relationship  $x^2 = kt$  (where  $x$  was the distance traversed in time  $t$ ) held within the limits of accuracy of the experimental method. Cude and Hulett (*J. A. C. S.* xlii. p. 391 (1920)), in their study of the rate of penetration of charcoal by water, obtained for the initial period of penetration a similar relationship. Washburn (*Phys. Rev.* xiii. p. 273 (1921)) has examined the problem in more detail, and deduced for the conditions of horizontal

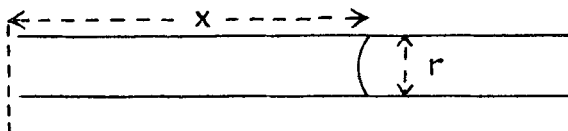
flow the equation  $x^2 = \frac{\gamma \cos \theta}{2\eta} rt$ , where  $\gamma$  is the surface

tension,  $\eta$  the viscosity,  $r$  the capillary tube radius, and  $\theta$  the angle of wetting. The validity of a similar expression was tested experimentally for liquids moving through capillaries under the influence of their own capillary force as well as a constant large external pressure. For all liquids which wet the tube wall of the material,  $\cos \theta$  is evidently equal to unity. The same value obtains for liquids which do not wet the tube, since the angles of wetting noted in the literature are probably fictitious, and are due to observations on the alteration in the radius of curvature at some point distant from the point of contact with the tube wall, and not at the contact point itself. Washburn has assumed that Poiseuille's law holds true during the flow after the initial period of turbulence has ceased, and has calculated with the aid of this

\* Communicated by the Author.

expression the rate of flow from the driving pressure made up of three separate pressures, the unbalanced atmospheric pressure, the hydrostatic pressure, and the capillary pressure. In the case of horizontal tubes the first two pressures are eliminated. The effective total driving pressure, however, varies with the length of the column, since the frictional resistance to the flow increases with the length of the column in the capillary tube. With this correction a somewhat different expression from that of Washburn is obtained for the rate of penetration, which, however, reduces to the form obtained by him on the neglect of terms which are insignificant except for very small and very large values of  $x$  the distance of penetration. A simple derivation of the relationship may be obtained in the following manner:—

Fig. 1.



The forces acting on a column of liquid  $x$  cm. long in a capillary tube  $r$  cm. radius are :

- (1) The surface tension forward, in magnitude  $2\pi r\gamma$ .
- (2) A retarding force due to the viscosity of the liquid in the tube.

According to Poiseuille's law, neglecting the slip factors, this retarding force may be expressed in the following form,

$$\frac{dv}{dt} = P \frac{\pi r^4}{8\eta x},$$

where  $\frac{dv}{dt}$  is the rate of flow; hence, solving for P the pressure, we obtain

$$P = \frac{8\eta x}{\pi r^4} \frac{dv}{dt} = \frac{8\eta x}{\pi r^4} (\pi r^2 \dot{x}) = \frac{8\eta x \dot{x}}{r^2}.$$

The retarding force acting on the column is consequently

$$F = \pi r^2 P = 8\eta x \pi \dot{x}.$$

The net force acting on the column thus varies not only with the length of tube wetted, but also with the velocity of flow, and is equal to

$$2\pi r\gamma - 8\eta x \pi \dot{x}.$$

The mass of the column in motion is  $\pi r^2 x \delta$ , where  $\delta$  is the density of the liquid ; hence

$$\pi r^2 x \delta \ddot{x} = 2\pi r \gamma - 8\eta v \pi \dot{x},$$

$$\text{or} \quad \ddot{x} = \frac{2\gamma}{\delta r x} - \frac{8\eta \dot{x}}{r^2 \delta},$$

$$\text{or} \quad \ddot{x} + a\dot{x} = \frac{b}{x}.$$

On integrating this expression, we obtain

$$c + t = \frac{1}{2} \frac{a}{b} x^2 - \frac{1}{a} \log x + \frac{1}{2} \frac{b}{a^3 x^2} + \frac{11}{4} \frac{b^2}{a^5 x^4} - \frac{17b^3}{a^7 x^6},$$

$$\text{or} \quad t = \frac{2\eta}{\gamma r} x^2 - \frac{\delta r^2}{8\eta} \log x + \frac{\delta^2 r^5}{512\eta^3 x^2} + \dots$$

For small values of  $r$  this equation reduces to the form given by Washburn for a liquid wetting the tube wall or

$$x^2 = \frac{\gamma r}{2\eta} t.$$

Experiments on the rate of penetration of liquids moving through horizontal glass capillaries under their own capillary pressure alone without any external force, indicated that when the liquid wets the tube the angle of wetting is zero, and that the penetration coefficient is given by the expression

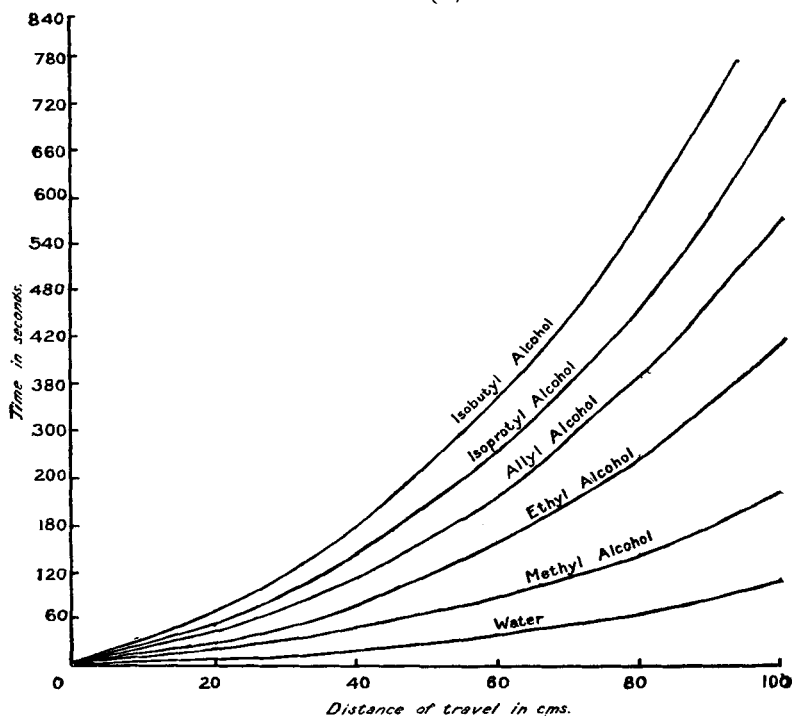
$$\sqrt{\frac{\gamma r}{2\eta}}.$$

#### *Experimental.*

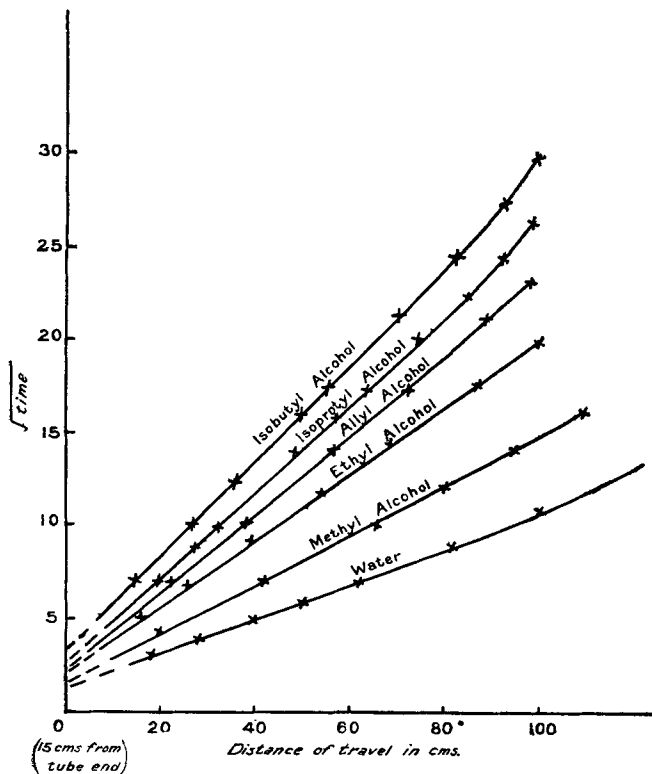
A piece of capillary tube 1.2 metres long, of average internal diameter 0.708 mm., chosen for uniformity of bore, was mounted horizontally in a condenser tube maintained at 20° C. One end of the tube was fused into the side of a wide boiling-tube containing the liquid to be tested. In each experiment the boiling-tube was filled until the surface of the liquid just covered the mouth of the capillary. The liquid was drawn through the capillary by suction, and forced back to within 15 cm. of the end by compressed air so as to thoroughly wet the tube. This operation was performed several times, the final removal of the liquid being accomplished very slowly to ensure removal of all excess

liquid from the tube wall. The rate of flow was determined by means of a stop-watch at increments of 10 cm. along the tube. In the following curves (I.) are shown the distance traversed in various times for a series of aliphatic alcohols; and from these data the derived curves (II.) were obtained, indicating the relationship between  $x$  and  $\sqrt{t}$ , which, according to the theory outlined above, should be linear for values of  $x$  within a relatively wide range.

Curves (I.).



The values of the penetration coefficients obtained from the slope of these derived curves are given, together with those calculated from the data on the viscosity and surface tension given in the tables of Landolt-Börnstein according to the expression  $K = \sqrt{\frac{\gamma r}{2\eta}}$ , where  $r = 0.0354$  cm.



Substance.	K calc.	K. obs.
Isobutyl alcohol .....	3.75	3.70
Isopropyl ,, .....	4.10	4.20
Allyl ,, .....	5.43	4.82
Ethyl ,, .....	5.52	5.65
Methyl ,, .....	8.16	7.90
Chloroform .....	8.73	8.60
Benzene .....	8.90	9.90
Ether .....	11.38	10.95
Water .....	11.31	11.40
Acetone .....	11.70	12.70
Ethyl acetate .....	9.60	10.20

It will be noted that the agreement is remarkably close in those cases for which the values for the surface tensions and

viscosities at 20° C. have been determined with accuracy, *e g.* water and chloroform. In the other cases, with the possible exception of benzene, the variations in the values of the determinations by various investigators for these quantities is sufficiently large to account for the discrepancies.

A few experiments were made on the rate of penetration of ethyl alcohol water mixtures, when the following values for the penetration coefficients were obtained:—

Per cent. Ethyl alcohol.	K obs.	K calc. static.
0 .....	11.40	11.31
20 .....	5.6	6.2
40 .....	5.1	4.9
60 .....	5.0	4.6
80 .....	5.4	5.07
100 .....	5.65	5.52

It will be noted that a minimum is obtained at ca. 50 per cent. in agreement with the calculated\* values; but the discrepancy between the calculated and the observed values is considerably greater than the experimental error. Data are lacking on the dynamic values of the surface tensions of alcohol-water mixtures; but these figures, including some experiments on the rate of flow of dilute soap solutions, indicate that the surface film in the capillary tube is being continually renewed during its progress through the tube. The method is consequently applicable to the determination of dynamic surface tensions of mixtures which frequently differ considerably from the stated values.

The penetration coefficient of a liquid is a physical constant of importance in that it is related to similar constants for gases and solids. Determination of the Maxwellian period of molecular relaxation in gases (Jeans, 'Dynamical Theory of Gases,' p. 261; Boltzmann, *Vorlesung über Gas Theorie*, pt. I, p. 167) or the "sensibilité" of Perrin (*Ann. de Phys.* xi, p. 21 (1919)) indicates that the molecules, even when acted upon by the mutually relatively feeble forces of adhesion in the gaseous state, are highly damped, the relaxation period for nitrogen at 0° C. and 760 mm. being  $1.66 \cdot 10^{-12}$  sec. In the case of solids, the force fields or adhesion forces are naturally much greater, causing the molecular vibration to be even more highly damped. For

\* Dunstan, J. C. S. lxxxv. p. 824 (1904); Firth, J. C. S. xxxiii. p. 268 (1920).



metals, the period of relaxation (Langmuir, *Phys. Rev.* viii. p. 171 (1916)) is in many cases identical with the period of electronic vibration as determined by the ultra-violet radiation frequency ( $10^{-14}$  sec.), whilst for non-metals a close approximation to the relaxation period is to be found in the vibration frequency of the residual rays or natural infra-red vibration frequency ( $10^{-12}$  sec.) (Rideal, *Phil. Mag.* xl. p. 462 (1920)). For liquids, it is to be anticipated that the period of molecular relaxation should lie between these values, *i. e.* ca.  $10^{-12}$  sec., the more polar the medium the shorter being its time of molecular relaxation. This period is given by the expression  $\tau = \frac{\eta}{P}$ , where  $\eta$  is the viscosity of the fluid and P the pressure.

In the case of liquids, P is identical with the internal adhesional pressure  $P_2 = \frac{\rho^2}{m} \int f(r) dr$ . Although  $f(r)$  cannot be evaluated without a knowledge of the nature of the intra-molecular forces, yet it is possible to obtain values for P from various sources, such as the  $\frac{a}{v^2}$  term of van der Waals' equation, from the latent heat of evaporation (Stefan, *Wied. Ann.* xxix. p. 655 (1886)), from the coefficients of expansion and compressibility, or from the surface tension of the liquid. In this latter case

$$\frac{1}{\tau} = K \frac{\gamma}{\eta} = K' (\text{penetration coefficient})^2.$$

In the following tables are given the approximate values of P, being the mean values of the determinations by the various methods, and the values of  $\tau$  calculated therefrom, compared with the values obtained from the penetration coefficient. [ $K_0$  being evaluated from the data for ether.]

Substance.	P atmospheres.	$\tau$ $10^{12}$ .	Penetration coefficient K.	$\tau$ $10^{12}$ from K.
Ether .....	1,590	1.31	11.38	(1.31)
Chloroform .....	2,200	2.13	8.93	2.10
Isobutyl alcohol .....	1,900	14.7	3.76	12.2
Isopropyl „ .....	2,370	9.4	4.10	10.1
Acetone .....	2,520	1.32	11.03	1.41
Water .....	18,050	0.54	11.26	1.35

Better agreement is scarcely to be anticipated, since the values of  $P$  for any liquid are not known to any degree of accuracy;  $P$  for benzene, for example, varying from 1300 to 3810 atmospheres, according to the method employed for its evaluation (Hildebrand, J. A. C. S. xli. p. 1072 (1919)). The parallelism between the two sets of determinations and the decrease in the molecular relaxation period or increase in molecular "sensibilité" with increasing polarity is, however, clearly marked.

#### Summary.

The rate of penetration of a liquid into a fine capillary under its own forces is shown to be expressed by the relationship  $t = \frac{2\eta}{\gamma r} x^2 - \frac{\delta r^2}{8\eta} \log x$ . For relatively large capillaries the penetration coefficient is  $\sqrt{\frac{\gamma r}{2\eta}}$ .

The experimental determination of the coefficient is shown to agree with the calculated values. In the case of mixed solvents the dynamic surface tensions and not the static values are probably the governing factors.

The reciprocal of the penetration coefficient is proportional to the square root of the period of molecular relaxation as defined by Maxwell, and on analogy with reactions in the solid state is probably important in reactions taking place in liquid media.

The writer is indebted to Mr. R. L. Huntingdon for assistance in the experiments detailed in this paper.

Chemical Department,  
Cambridge University,  
June 5th, 1922.

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CIX. *On a Balance Method of measuring X-Rays.* By Professor S. RUSS, D.Sc., and L. H. CLARK, M.Sc., Physics Department, Middlesex Hospital\*.

THE frequent and prolonged running of X-ray tubes calls for some convenient method of recording continuously the intensity of the X-radiation emitted during the period of excitation. The balance method described below indicates at any instant this intensity and is capable of giving a continuous record of it. It is suitable for the measurement of the ionization produced by a powerful beam of X-rays.

\* Communicated by the Authors.