

Displacement of Liquids in Capillaries.

THE phenomenon to which this communication refers is so striking, and its probability of occurrence in any chemical laboratory so great, that the absence of mention of it in the literature was very surprising to me.

If one places in a glass tubing, 5 mm. in diameter or less, drops of two immiscible liquids, end to end, so as to form a liquid-liquid interface, the continuous bubble these two liquids make will begin to move in the direction of the liquid of greater surface tension, and continue so indefinitely depending on the length of the tube. By raising the end of the tube toward which the bubble is moving to a certain height from the horizontal, the motion of the bubble is stopped; when it is raised still higher it slides back, and when lowered below the stationary height it

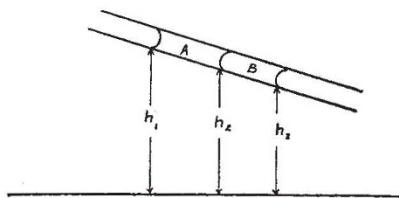


FIG. 1.

will move up again. It is evident from Fig. 1 that at equilibrium

$$(1) \quad P = [(h_1 - h_2)\rho_A + (h_2 - h_3)\rho_B]g$$

where P is the pressure, ρ_A and ρ_B the densities of the liquids, and g the acceleration constant. The force $\pi r^2 P$ exerting this pressure is the resultant of the forces acting at the three interfaces, and therefore

$$(2) \quad \pi r^2 P = -2\pi r \sigma_A \cos \theta_A + 2\pi r \sigma_{AB} \cos \theta_{AB} + 2\pi r \sigma_B \cos \theta_B$$

where r is the radius of the capillary, σ is the surface tension, and θ the angle of contact.

The resultant pressures become quite measurable when we make use of small capillaries, as is shown in equation (2), written in the form

$$(3) \quad P = \frac{2}{r} (-\sigma_A \cos \theta_A + \sigma_{AB} \cos \theta_{AB} + \sigma_B \cos \theta_B).$$

By modifying the conditions the liquid column can be made to move in the opposite direction; that is, if we construct a capillary as illustrated in Fig. 2,

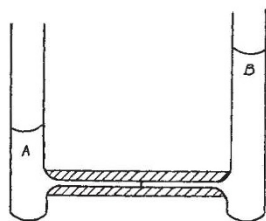


FIG. 2.

where the ends of the liquid column extend into the tubes of a cross-section where capillarity is not displayed, the liquid-liquid interface will move in the direction of the liquid of smaller surface tension.

The pressure developed under this condition is given by

$$(4) \quad P = \frac{2\sigma_{AB} \cos \theta_{AB}}{r}$$

Bartell and Osterhof,¹ in their work on 'wettability' of solids, measured such pressures in compressed

¹ "Colloid Symposium Monograph," vol. 4, p. 240; 1926.

powders, and arrive at the same relationship as in equation (4), but in a complicated manner.

This manifestation of surface phenomena is being utilised in my laboratory in measuring interfacial tensions, angles of contact, and adhesion tension of various liquids against glass.

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Wave-length Shifts in Scattered Light.

RAMAN and Krishnan have recently described a new type of radiation emitted by organic liquids when illuminated with the light of a mercury arc, or with selected lines from such an arc. Lines are found in the spectrum of the scattered light at wave-lengths which are not present in the illuminating source. In the case of benzene the wave numbers of the shifted lines differ from those of the incident lines by amounts which are equal to the wave numbers of certain infra-red absorption maxima of the molecule. Raman and Krishnan state that these lines represent the scattered light of modified wave-length predicted by Kramers and Heisenberg in their correspondence principle treatment of dispersion. I believe this interpretation is correct. However, the evidence that these lines do not constitute a fluorescent emission, following the absorption process after a finite interval, is qualitative. First, Raman states that the radiation scattered with modified frequency from a cloud of carbon dioxide brightens up in the same way as the ordinary scattered light when the cloud is formed. Further, the shifted radiation is polarised nearly as strongly as that which suffers no change of frequency.

These facts indicate that this radiation is coherent, which would presumably not be the case if it were due to absorption followed by emission after a finite time. Of course, the absorption coefficient of benzene is rather small in the region studied, but it may readily be large enough to account for the retention of an amount of energy sufficient to give rise to the very weak modified scattering. In the present state of our knowledge about the mechanism of general absorption in liquids, the possibility cannot be dismissed offhand.

The purpose of this communication is to direct attention to an alternative method of settling this interesting question, independent of assumptions about the coherence properties of the radiation. It consists in determining whether there is a time lag between the reception of the incident light and the emission of the scattered radiation of modified wave-length. Several methods for determining such lags have been described by R. W. Wood (*Proc. Roy. Soc.*, **99**, 362; 1921). In regard to time resolving power, the most efficient of these is the method of Abraham and Lemoine, involving the use of a Kerr cell as a very rapid electromagnetic shutter. Gottling (*Phys. Rev.*, **22**, 566; 1923) has used this method to show that the phosphorescence of barium cyanoplatinites does not commence until 2×10^{-7} seconds after the illumination has commenced. For rhodamine the interval is 2×10^{-8} seconds. It is appreciated that the principal difficulty in applying this method to modified scattering is the small intensity of the light. However, since the modified light can be observed with the aid of colour filters, it is very likely that such observations can be made successfully.

In 1925, Foote and Ruark discussed in *Science* (vol. 61, p. 263) the existence of the scattered wave-lengths of Kramers and Heisenberg in the spectra