SCIENTIFIC SECTION

PHYSICS IN PHARMACY.

PART IV.*

BY JOHN URI LLOYD, WOLFGANG OSTWALD AND WALTER HALLER.

ON THE VARIOUS PHYSICAL CONDITIONS NECESSARY FOR THE FORMATION OF PENDANT AND WETTING DROPS.

1. When two different non-miscible liquids are poured together, they usually separate into two layers, the heavier liquid below, the lighter liquid above the other. The force of gravity seeks to produce a horizontal interface between them.

Many years ago, the senior author found and examined a great number of cases in which the liquids behave altogether differently. For example, in glass tubes the surface of contact (meniscus) does not always form a horizontal plane, but is curved more or less, upward or downward, according to the nature of the liquids, the width of the tube, temperature and the physical condition of the glass surface. With many pairs of liquids, one observes very unique drop formations at the common surface, *e. g.*, drops of heavier liquid which float upon the surface of the lighter liquid (pendant drop), or drops of the lighter liquid creeping along the glass wall until it even may rest below the heavier liquid (wetting drop). These "absurd" formations seem at first to be creations of accident; however, the senior author showed that they were entirely reproducible, and that they formed with complete regularity upon using definite pairs of liquids. Thus, for example, a pendant drop is always formed when chloroform is added to water in a glass cylinder, even after vigorously shaking the two liquids together and then allowing them to settle.

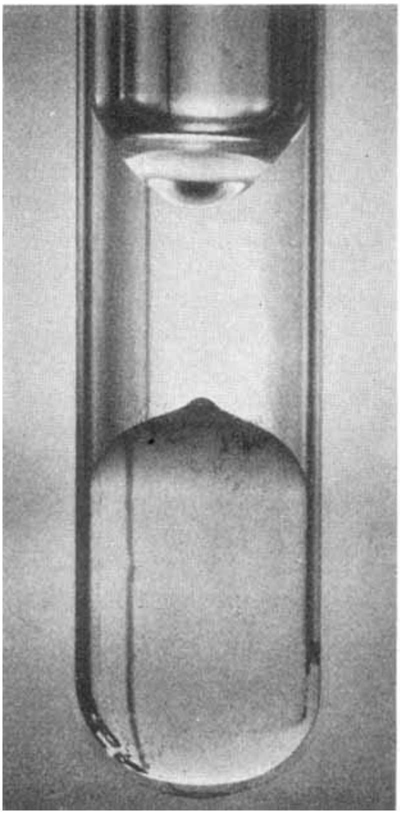
All these phenomena, the curvature of the menisci as well as the odd drop formations, are typical interface phenomena, and are therefore in closest relation with interface tensions. In a preceding article we were able to show, theoretically, in what manner the form and size of pendant drops depend on the interface tension between the liquids. Then the experimentally measured form and size of drops corresponded accurately to the measured value of the surface tension.

2. Of an importance equal to that of the interface tension is the *wetting* of the glass wall by the liquids. In many cases, wetting must be considered the real cause determining the shape of the interface surfaces. For example, the curvature of the meniscus is due to the difference in the wetting abilities of the liquids. The better-wetting liquid seeks to displace the other liquid from the glass wall, and in spreading along the wall, draws along with it the interface (liquid-liquid) like an elastic film. The edge of the interface is drawn upward or downward, *i. e.*, the meniscus is curved convex above or below, according to whether the better-wetting liquid lies above or below the other.

Somewhat more difficult it is to explain the mode of formation of the remarkable drop phenomena, such as pendant drops and wetting drops. Here also, wetting plays a principal part, which is especially evident with the wetting drop. For

* Translated from the German by Dr. Sigmund Waldbott. Presented before Scientific Section, A. PH. A., Miami meeting, 1931.

example, such a wetting drop is formed when a drop of water is put upon chloroform contained in a glass tube. The water readily wets the glass wall, doing so more pronouncedly than does the chloroform; for this reason it creeps downward along the glass wall, displacing the chloroform. When more water is added, the wetting water-ring becomes broader, until finally, after reaching a definite limit of stability, it melts together, forming a massive layer.[1] Evidently, the driving force of the



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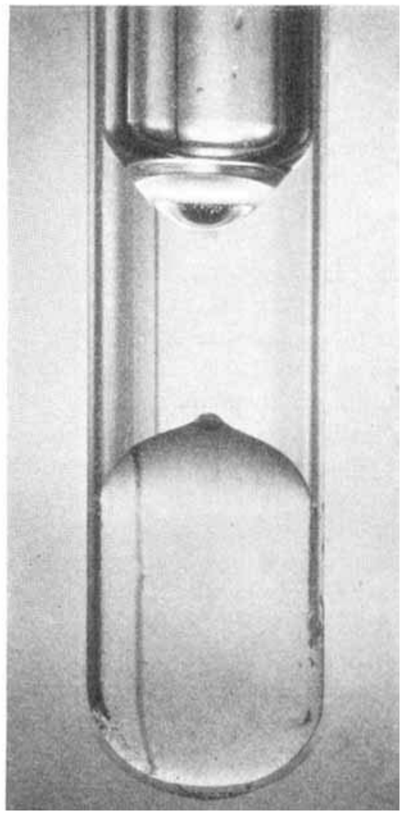

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Fig. 1.—Nitrobenzol under water; pendant drop of nitrobenzol upon the water surface. The nitrobenzol is only partially in wetting contact with the glass walls (note the black lines between nitrobenzol and glass). Fig. 2.—One hour later. The nitrobenzol begins to wet a greater area.

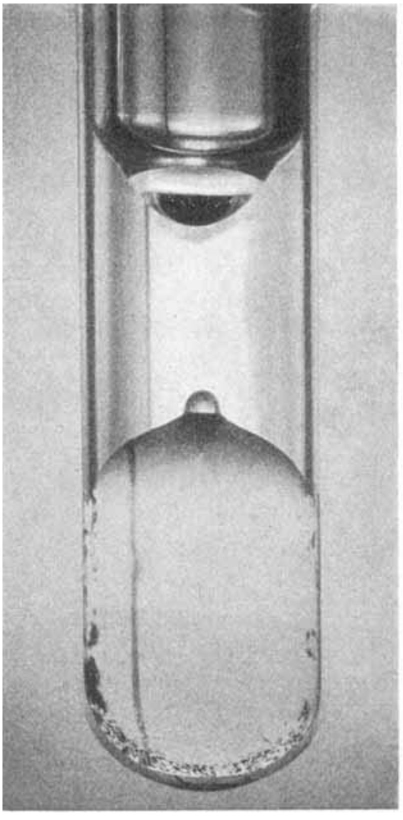
wetting drop consists in the strong wetting power of the liquid.

Considered more closely, the existence of the wetting drop depends not only on the wetting property, but also on the properties of the remaining interfaces involved. In the preceding article of the joint authors, the conditions which the interface tensions must satisfy in order that a wetting drop may form, were deduced by theoretical reasoning based on capillarity. These considerations, which need not be repeated here in detail, resulted in establishing the following conditions:

[1] A detailed description of the phenomenon, with drawings and photos, was given in the preceding article of the authors, JOUR. A. PH. A., 20 (1931), 95.

(1)	$S_{A\text{-glass}}$	$<$	$S_{B\text{-glass}}$
(2)	S_B	$>$	$S_A - S_{AB}$
(3)	S_B	$<$	$S_A + S_{AB}$

$S_{A\text{-glass}}$ is the wetting tension of liquid A.
$S_{B\text{-glass}}$ is the wetting tension of liquid B (wetting drop).
S_A is the surface tension of liquid A.
S_B is the surface tension of liquid B.
S_{AB} is the interface tension between both liquids.



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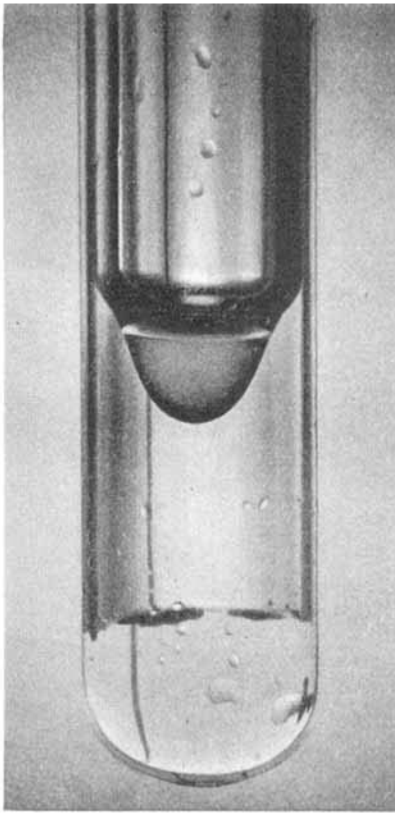

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Fig. 3.—One day later. Now the nitrobenzol is nearly totally wetting the glass wall. Small droplets of water (visible as dark spots at the edges) remain. Fig. 4.—The same nitrobenzol taken out with a fine pipette. Small droplets of wetting nitrobenzol remain attached to the glass wall above the nitrobenzol layer.

Exactly the same conditions prevailed in the formation of the pendant drop.

These equations therefore explain the regular appearance of the strange drop phenomena exhibited by specific liquids, as the senior author has shown, through the fulfilment of very definite physical conditions. Thus it is only necessary to know the different interface tensions to be able to predict whether a pendant drop or wetting drop can form or not. Conversely, whenever a pendant drop or wetting drop has formed, it follows that the interface tensions satisfy the above conditions.

The important part which wetting plays in the remarkable drop phenomena, induced us to investigate the wetting phenomena more in detail, experimentally.

3. MEASUREMENT OF WETTING TENSIONS.

Quite a series of methods exist for the measurement of the wetting tension. It may be determined, for example, from the pressure with which a wetting liquid

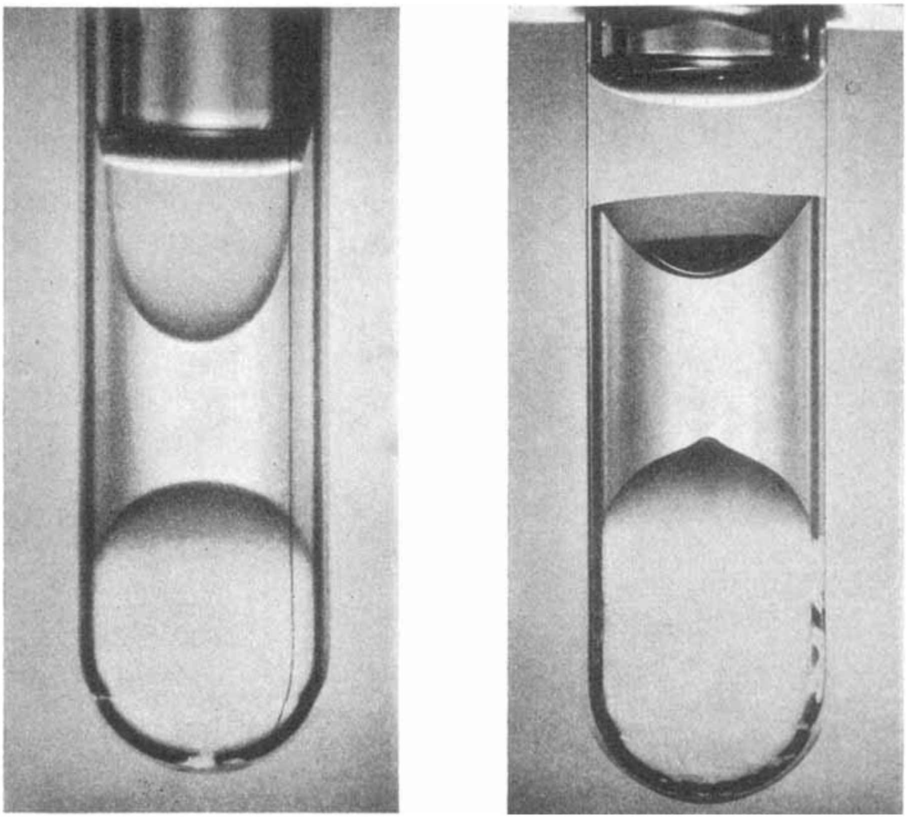

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Fig. 5.—Chlorobenzol under water. Pendant drop of chlorobenzol above. The chlorobenzol wets only in a very small area at the bottom. Fig. 6.—One day later. The chlorobenzol has made a little progress in wetting. The broad black line which is characteristic for water wetting has partially been replaced by the very fine line of chlorobenzol wetting. Chlorobenzol poured upon the surface wets at once (very thin lines) because the glass walls are quite dry.

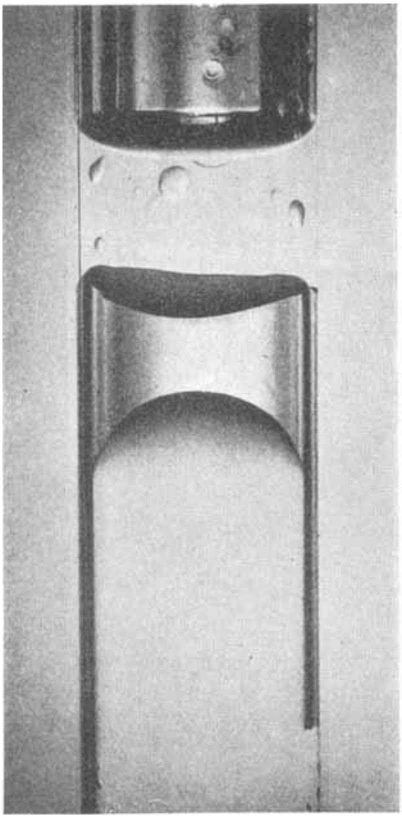
penetrates into capillary spaces; or from the edge angle under which the liquid surface clings to the solid surface, or by different other methods.[1]

However numerous these methods are, their results are frequently unsatisfactory. In carrying out the measurements, difficulties often arise, owing to the fact that wetting is a very complicated process. The wetting tension is exceedingly sensitive toward the slightest irregularity of the solid surface. Even very small traces of impurities alter the wetting tension, which is probably also affected by

[1] A review of the different methods is given by W. Haller in *Kolloid-Z.*, 53 (1930), 247.

thin layers of adsorbed air. Besides, the wetting tension at different points of a solid surface is practically never of equal magnitude.

In order to avoid these difficulties in the measurement of the wetting tension, we have applied a new method which is independent of small irregularities in the surfaces. We connected the liquid with a horizontal capillary tube, and determined the velocity and the negative pressure with which the liquid was sucked into the



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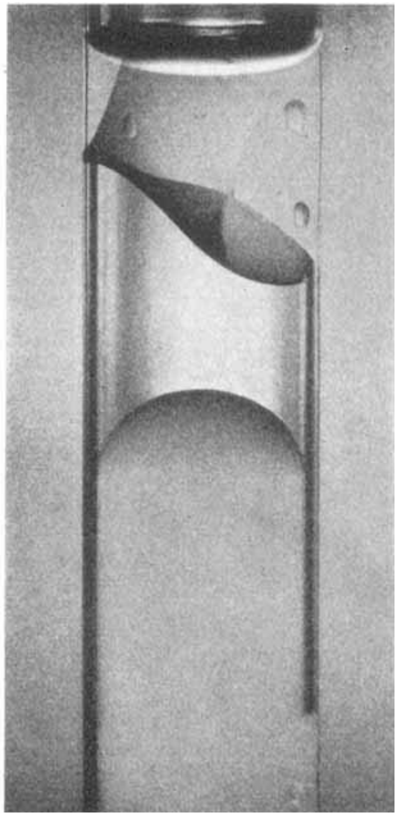

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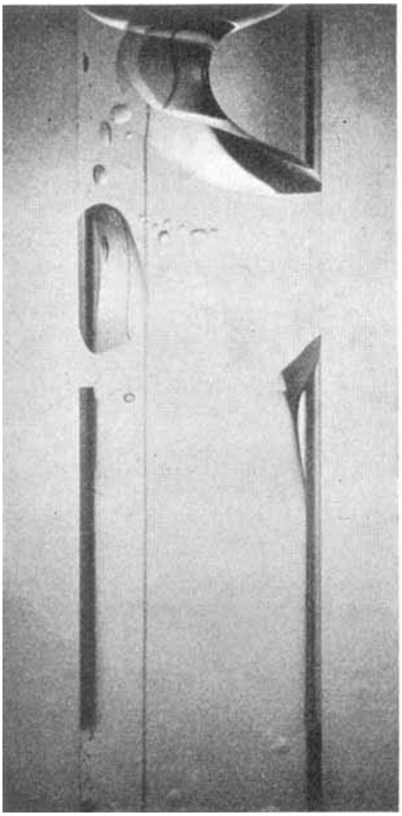
Fig. 7.—The same. Some quantity of chlorobenzol has been added to the chlorobenzol layer below with a fine pipette, so that all menisci were forced to rise. In rising, the meniscus between the upper layer of chlorobenzol and the water has become irregular by the action of the strong hysteresis of wetting which binds the chlorobenzol to the glass. Partially the meniscus has even become concave to the water. Fig. 8.—The same, water added to the middle layer.

capillary tube on account of the wetting tension. During such a measurement the meniscus of the liquid was in motion, and the fact developed that it smoothly passed over the invisible, unavoidable irregularities of the surface, while the stationary meniscus would have been arrested at these spots. From measurements at different velocities, the wetting pressure of the resting meniscus was calculated by extrapolation, and from it the wetting tension of the liquid. The measurements by this method gave very exact and reproducible results. A few results are given in the following table.

Wetting Tensions toward Glass.

i-Amylalcohol	22.7 dyne/cm.	Aniline	39.7 dyne/cm.
N-Heptylacetate	23.9 dyne/cm.	Acetophenone	40.6 dyne/cm.
Petroleum	24.8 dyne/cm.	Glycol	43.9 dyne/cm.
N-Hexanol	25.6 dyne/cm.	Water	50.5 dyne/cm.
Benzylalcohol	37.0 dyne/cm.	Glycerin	62.6 dyne/cm.
Lactic acid	38.5 dyne/cm.		

A more detailed description of this method and additional results have been communicated elsewhere by one of us.[1]



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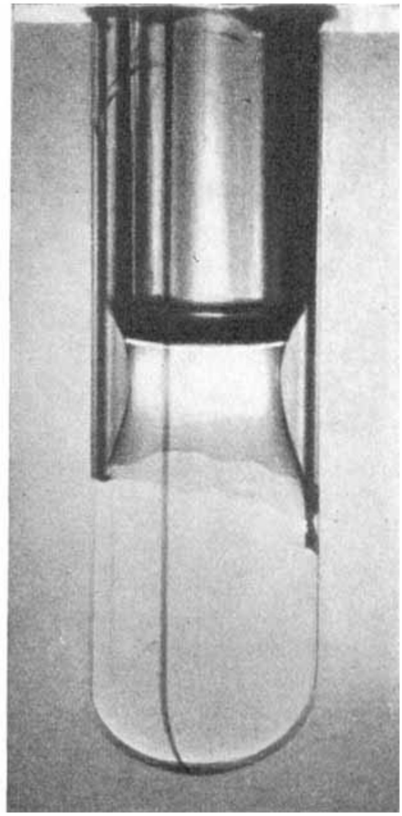

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Fig. 9.—The same. Chlorobenzol added. Fig. 10.—Wetting drop of water on acetophenone. Some water was poured upon a layer of acetophenone. It creeps down along the glass walls forming a ring of wetting water.

4. WETTING DISPLACEMENT.

Two liquids, when in simultaneous contact with a solid body, compete for the wetting surface, and the liquid with the greater wetting tension seeks to displace the other. If, for example, a powdered solid is shaken with two non-miscible liquids, it will be wetted mainly by that liquid which has the greater wetting tension. As the mixture settles, the powder collects in the liquid layer having the greater

[1] W. Haller, *Kolloid-Z.*, 54 (1931), 7.

wetting tension. If the powder is first stirred with the liquid of inferior wetting tension, and is then brought into contact with the better wetting liquid, in this case also it will be ultimately wetted by the better wetting liquid, which displaces the other from the surface of the powder. This phenomenon of *wetting displacement* is of very great importance in practice, chiefly in flotation.

In performing such experiments, it is noted that the displacement of a liquid from the solid surface becomes the more difficult the longer it has been in contact

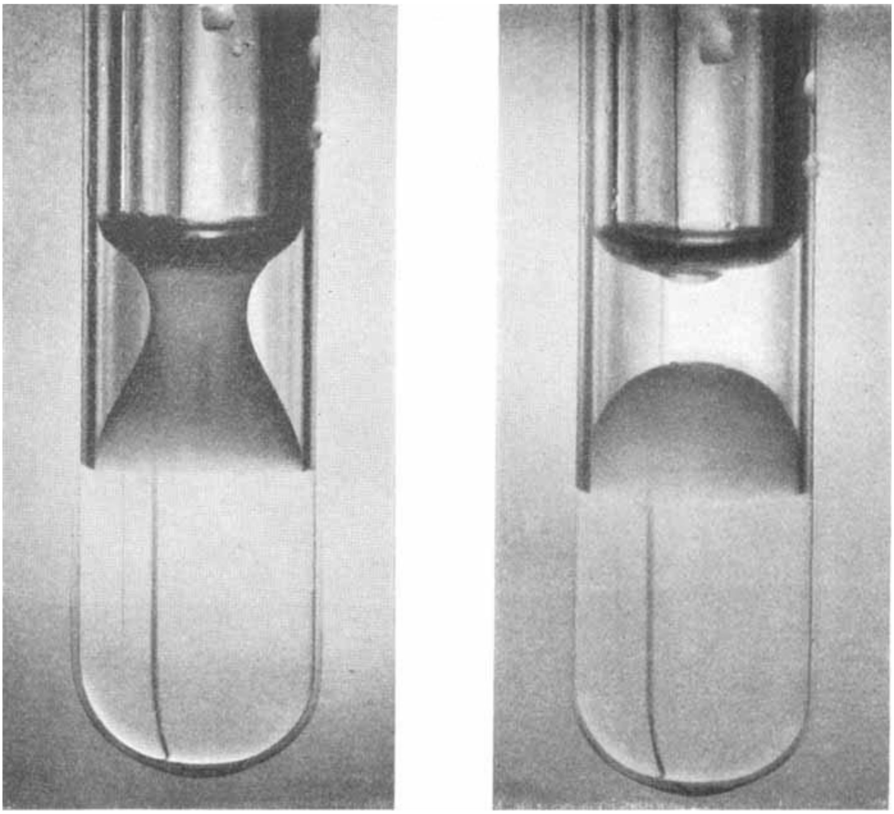

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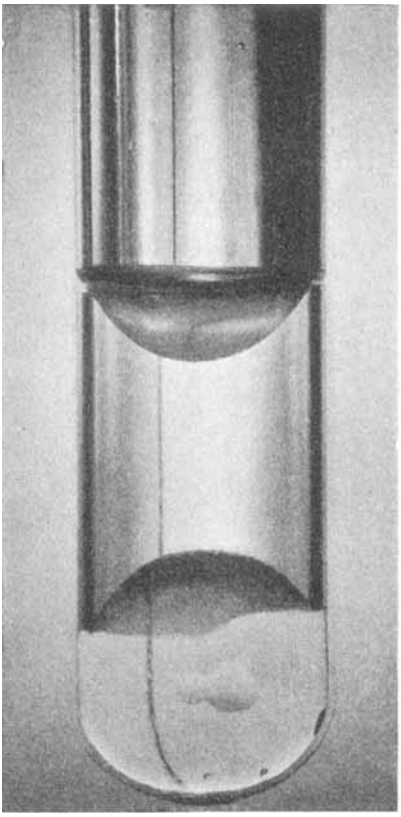
Fig. 11.—The same, more water added. The wetting drop is greater. Fig. 12.—The same. By addition of more water finally the wetting drop unites in the midst of the tube to form a massive layer of water, above which invariably rides a pendant drop. This small pendant drop is analogous to the small remaining drop observed when a drop falls from a capillary.

with it. Thus, for example, F. B. Hofmann[1] found that petroleum which was wetting powdered glass, could be easily displaced by water a few seconds thereafter, but was displaceable by water only with great difficulty after some hours. This changeability dependent on time, renders wetting a rather complicated process, at any rate more complicated than the formation of interfaces between two liquids. With liquid-liquid interfaces a definite surface tension exists after a very short time, and on its magnitude alone depend the area and shape of the interfaces.

[1] F. B. Hofmann, *Z. physik. Chem.*, 83 (1913), 389.

This, however, is not the case with wetting; here it seems very necessary to consider not only wetting tension, but also the other peculiarities of wetting.

In the study of the wetting phenomenon it is true that powders are not a favorable material to use, because the solid surface cannot be directly seen. We therefore adopted the method of rendering the wetting displacement visible on larger surfaces, in glass tubes. This was done successfully with the aid of an especial illumination arrangement which enabled us to observe very plainly the



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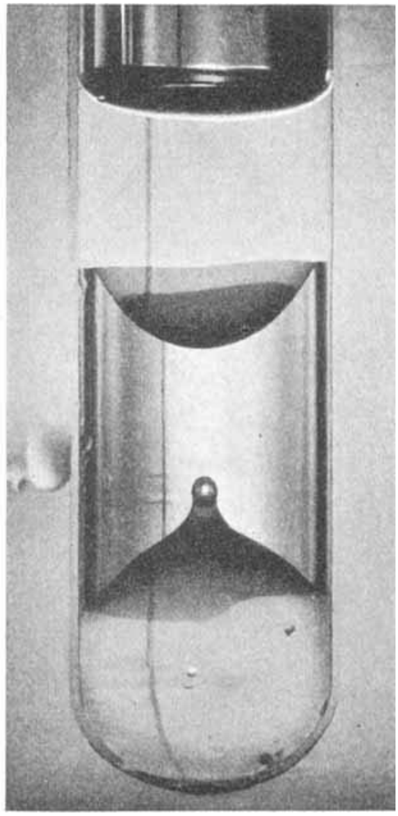

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Fig. 13.—Acetophenone under water. Pendant drop of acetophenone above. Fig. 14.—The same after some hours, some acetophenone poured upon the pendant drop remains there, because it wets there the glass wall at once. A small pendant bubble has formed at the lower interface acetophenone-water.

gradual wetting and the mutual displacement of the liquids. These observations completely confirmed our previously discussed views on the formative origin of the abnormal drop formation.

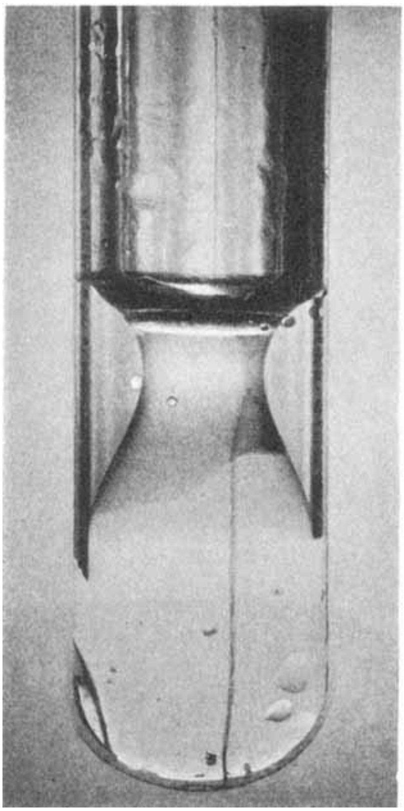
5. METHOD OF RENDERING WETTING VISIBLE.

The observation arrangement was very similar to that used by the authors in a previous study on the shape of menisci.[1] The experimental tube (a test-tube of

[1] John Uri Lloyd, Wo. Ostwald and W. Haller, Jour. A. Ph. A., 18 (1929), 862.

Jena glass) was placed into a basin with plane-parallel walls, which was filled with a mixture of benzylbenzoate and xylol. The mixture was so adjusted that it had the same refractive index as the glass, the contours of which were therefore hardly visible. The experimental tube was illuminated by an incandescent lamp, and the light rendered as diffused as possible by means of a paper screen put into the liquid in the basin; the photographs were taken from the other side.

The advantage of this arrangement was that now the edge parts of the tube



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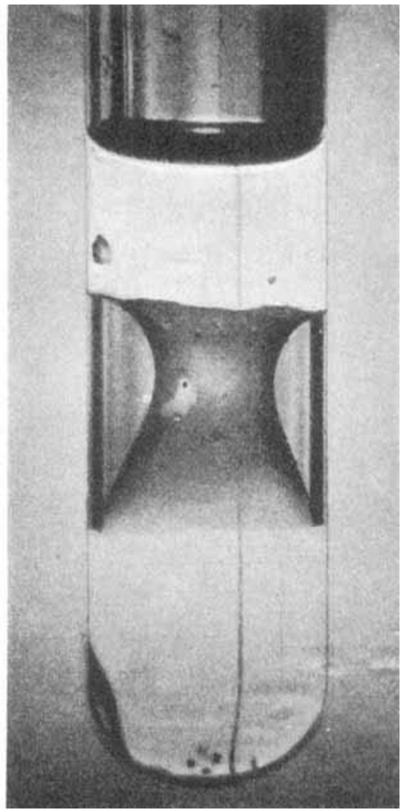

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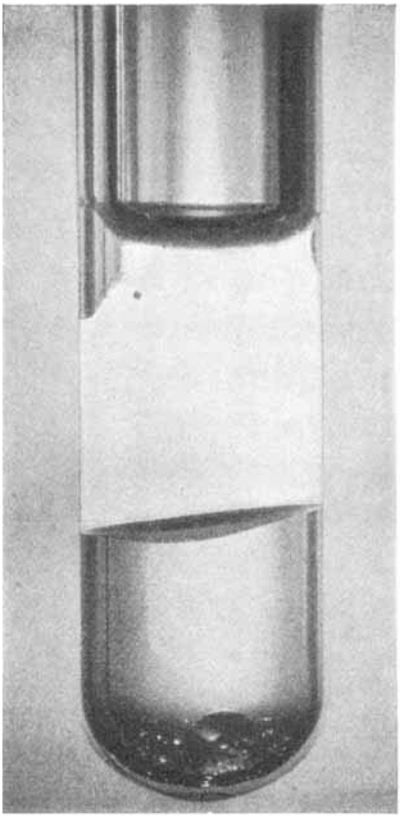
Fig. 15.—From the middle layer of water in Fig. 14 some quantity has been taken off. Finally the two layers of acetophenone touched one another and united, the water remaining as a wetting drop at the glass wall. Fig. 16.—The same, some acetophenone poured upon the wetting drop.

became very distinctly visible, while with ordinary illumination they were not recognizable on account of the strong refraction and reflection of light. By the imbedding into a medium of the same refractive index as glass, optical distortion was reduced to a minimum, therefore deceptive impressions concerning the form of interfaces were excluded.

Of quite especial advantage for our investigations was the fact that there appeared at the edge between liquid and glass wall, narrow dark bands (strips) caused by total reflection. Their width varied from liquid to liquid, which enabled us to recognize with exactness which of the liquids wetted the glass wall. This test was exceedingly sensitive. Even traces of the wetting liquid in the form of thin and otherwise invisible films adhering to the glass wall were revealed by the dark band.

6. A collection of a few photographs obtained by this method is included in this contribution.

Figs. 1–4.—Nitrobenzol was poured into water; in part it settled at the bottom,



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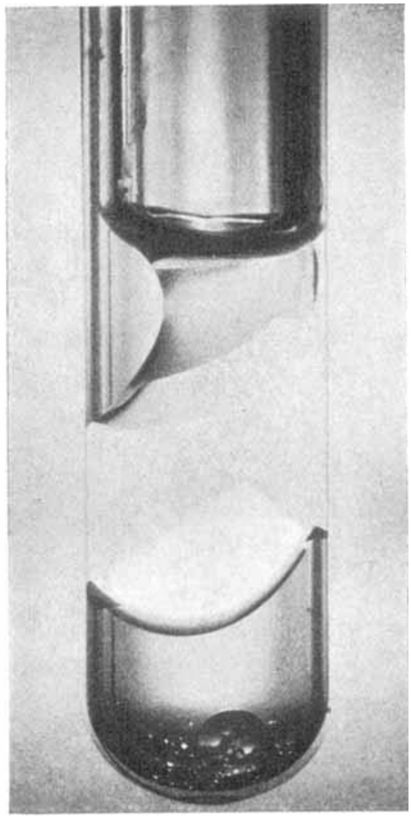

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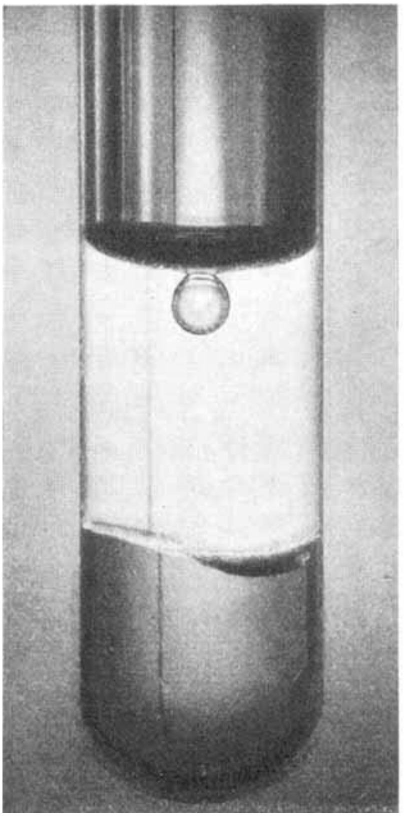
Fig. 17.—Water was placed under a layer of acetophenone with a fine pipette. The water remains below, although it has less gravity than acetophenone. It is held by the hysteresis of wetting. Fig. 18.—The same, but some of the water has now escaped and ascended. This was the result of a path being made by purposely wetting the glass with a wet glass rod. The ascended water forms a half wetting drop.

another part remained at the surface in the form of a pendant drop (*Fig. 1*). Nitrobenzol does not wet as well as water, and a long time elapsed before the water film between the nitrobenzol layer and the glass wall was displaced. This may be recognized by the dark zones in *Figs. 1–3.* Traces of water remained, which are seen in the form of small black specks at the edge. After one day some nitrobenzol was removed from the lower layer by means of a fine pipette; it was now plainly seen that nitrobenzol firmly adhered to the glass, for many small nitrobenzol droplets remained suspended at the wall (*Fig. 4*).

Figs. 5–9.—Especially striking was the hysteresis of wetting when chlorobenzol and water were used. In *Fig. 5,* chlorobenzol forms the lower layer, and a pendant drop but wets the glass only at a small spot at the bottom. After 1 day, a little more chlorobenzol was poured on top of the pendant drop; now it wetted the glass wall at once, because the latter had meanwhile become dry in the air; but below, a large water film still persisted between chlorobenzol and glass (*Fig. 6*). To the lower layer a large quantity of chlorobenzol was now added by means of a pipette, causing all menisci to move upward. It is plainly seen that chlorobenzol also is



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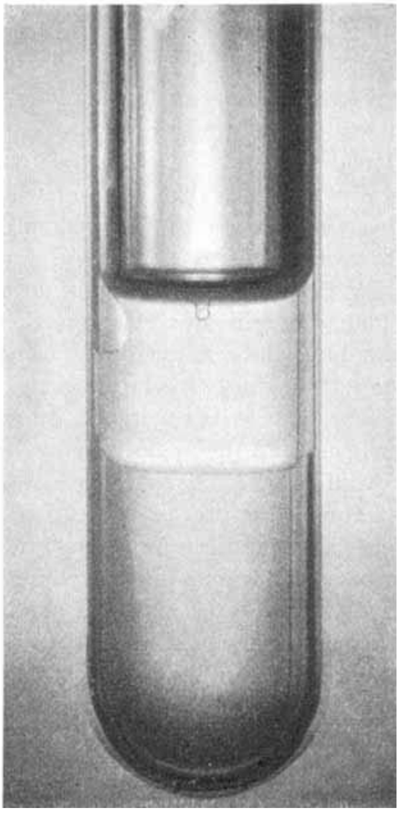

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Fig. 19.—Pendant drop of water above liquid paraffin. Fig. 20.—Pendant drop of water above amylalcohol. Both are exceptions of the theoretical rules of stability. They can only exist under certain conditions. The liquids must not be disturbed and the pendant drop must not come into contact with the glass wall.

displaced from the glass wall with difficulty after it has once wetted it. For this reason, the retreating meniscus of chlorobenzol was curved somewhat concave to water (*Fig. 7*), while normally it is convex.

The tensions involved in the wetting displacement of chlorobenzol were so great that under certain conditions they led to peculiarly distorted formations. *Fig. 8* arose from *Fig. 7* simply upon the addition of a little water by means of a pipette in the space between the two chlorobenzol layers, while in *Fig. 9,* a large quantity of chlorobenzol was added.

Figs. 10–15.—*Figs. 10–12* show the phenomenon of the wetting drop in the example, acetophenone-water. A little water was added to acetophenone. It wetted the glass and moved along the wall between the acetophenone and the glass, visible by the progress of the dark zone, forming a wetting drop (*Fig. 10*). More and more water was added (*Fig. 11*) until the wetting drop finally coalesced into a massive layer (*Fig. 12*). A small part of the acetophenone always remained suspended above the water as a pendant drop, in harmony with the fact that a pendant drop always forms when a wetting drop is capable of being formed.

7. CHANGE OF WETTING DROPS INTO PENDANT DROPS.

Wetting drop and pendant drop are closely related. Theoretically, the same conditions prevail for both, concerning the magnitude of the interface tensions; therefore they always appear with the same pairs of liquids. Experimentally we find that they permit of being converted one into the other, the wetting drop into the pendant drop and vice versa, as we shall see in the following figures.

Fig. 13 is a pendant drop of acetophenone over water. A little acetophenone was poured over it; it wetted the glass wall perfectly, as the latter had become dry on standing, and remained in position above the water (*Fig. 14*). Now the water was taken out slowly by means of a pipette up to the moment where the two menisci touched. The layers merged, the acetophenone flowed from the upper into the lower layer, and the water remained in the form of a wetting drop adhering to the glass wall (*Fig. 15*).

Through the process of wetting, the wetting drop is rather firmly attached to the glass wall, and can move alongside of it only with difficulty. For this reason a layer of acetophenone may be poured upon it without causing the wetting drop to rise (*Fig. 16*). By means of a pipette a layer of water may be placed beneath a layer of acetophenone. The water will be held fast by wetting, remaining below although it is the lighter of the two liquids (*Fig. 17*). It is only when we move the tip of a wet glass rod along the wall, that the water will find an exit upward at this spot, indeed only for a short time. Soon there will be again a closed wetting ring of acetophenone, and the rest of the water remains below, while the water that has risen forms a wetting drop (*Fig. 18*).

8. In conclusion, let us consider a remarkable case of exception as to pendant drops. Ordinarily, a pendant drop can form only when its wetting ability is inferior to that of the other liquid. The reason for this is very simple; if it wetted the glass wall, it would form there a wetting drop, and would gradually flow downward along the wall. If a liquid is to form a pendant drop, it must not wet the wall. This end may be attained in different ways: either its wetting tension is smaller than that of the other liquid, which is the normal case; or the other liquid in consequence of hysteresis (lag) adheres with exceeding firmness to the wall, so that it cannot be displaced even though its wetting tension is smaller.

Thus, for example, we may put paraffin oil into a perfectly dry glass tube and place on its surface a drop of water. In this case, hysteresis is so strong that a pendant drop results (*Fig. 19*), although the water has a much greater wetting tension than the paraffin oil. A similar experiment succeeds with amylalcohol and water (*Fig. 20*). In all these cases, however, equilibria are not attained; the phenomena are those of non-stability.[1]

SUMMARY.

The physical conditions under which pendant and wetting drops are formed, are discussed in detail. From theoretical considerations, we conclude that these formations are stable only if the various interface tensions involved satisfy definite conditions. Of especial importance is the magnitude of the wetting tensions.

In order to test the correctness of the theoretical conclusions, the subject of wetting is investigated in some detail. The known methods of measuring the wetting tension are discussed, and a new method is described, which overcomes certain difficulties of the methods heretofore in use. A few results of the measurements by this method are recorded.

The study of the wetting phenomena invariably shows that wetting is a complicated process, which cannot be characterized by the magnitude of wetting tensions alone. For this reason, wetting was studied more in detail, from its experimental aspect as a phenomenon.

To this end, a special optical arrangement was worked out, by the aid of which, wetting in glass tubes may be rendered very plainly visible. The method also permits proving the existence of very thin wetting films which otherwise could not be seen. The origin of pendant and wetting drops is very closely bound up with the behavior of these wetting films, which is shown in a series of photographs.

The earlier published observations of the senior author were confirmed in every respect.

THE STABILIZATION OF SOLUTION OF ARSENOUS AND MERCURIC IODIDE, U. S. P. X.*

BY WILLIAM J. HUSA.**

RELATION BETWEEN STABILITY AND p_H.

Historical Review.—In 1903, William Duncan (1) reported that the tendency of Donovan's Solution to liberate iodine could be checked by adding sufficient alkali to neutralize the free hydriodic acid, and suggested this method for adoption in the British Pharmacopœia. His suggestion did not receive favorable consideration. Guyot (2) offered this same suggestion for checking the deterioration of a solution of arsenous iodide. In confirmation of these reports, Husa and Enz (3) found that Donovan's Solution was more stable near the neutral point, the rate of deterioration increasing with increasing acidity or basicity.

[1] The contrast between these exceptions and the regular phenomenon may probably be characterized as follows:

The normal phenomena depend solely on the values of the interface tensions, regardless of the order in which the two liquids are mixed. With the 2 anomalies described, exactly the same order of superposition must be observed in order to be successful. Contact of the pendant drop with the glass wall must be especially avoided, because as soon as contact takes place, the laws we derived concerning the magnitudes of interface tensions will go into effect, tending to stability.

* Presented before the Scientific Section, A. PH. A., Miami, Fla., 1931.

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