SCIENTIFIC SECTION

PHYSICS IN PHARMACY.*

PART III.[1]

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ON UNUSUAL DROPS AND BUBBLES.

With the pharmacist, "a drop" has probably more significance than with any other devotee to applied Natural Science. It is an accepted fact that the delicate nature of the living organism on one hand, and the potency of many pharmaceutical preparations on the other, require quantitative treatment not only in pharmaceutical theory, but also in the practice of pharmacy. A pharmacist who fails to measure and to weigh, would be a *contradictio in adjecto*, an impossibility. "A drop" is the smallest *practical unit* of *volumetric measurement* of any liquid preparation. Compared with the unit of the gravimetric method the grain, or gram, "a drop" offers the unusual advantage of being most easily reproduced experimentally.

When pharmaceutical preparations are to be subdivided by weight, comparisons must be made with standard weights, and the quantities must be weighed off in the laboratory before being used. A volumetric subdivision in the form of drops, however, may be performed anew at any moment without requiring, at least in first approximation, a standard drop for comparison. "A drop" is the quantitative unit measure for characterizing and dispensing liquid pharmaceutical preparations of strong potency, a unit easily accessible, the most easily reproducible and in practical pharmacy the most frequently used.

We said above that the drop-volume unit is an *approximate* volumetric unit of measurement. In fact every pharmacist has noted the difference in the size of drops, e. g., of aqueous, alcoholic and ether solutions, decreasing in the order stated. But even in aqueous solutions of different kinds there may be differences in the size of drops produced from the same dropping bottle or dropping tube. For example a sugar solution produces a larger drop than a solution containing small quantities of peptones, or soaps. The speed of the formation of drops may also sometimes influence their size; if, e. g., a peptone solution is made to drop as slowly as possible, the drops will be larger than when drop formation is fast, etc.

It is now known that the forces of *surface tension* are responsible for these differences in the size of drops. Different solutions may not have the same surface tension, therefore may yield drops of different size. A systematic study of these differences among pharmaceutical preparations used in the form of drops seemed to be of interest.

In the formation of an ordinary drop, e. g., from a dropping bottle, evidently *three* interfaces are involved: The interface between liquid and surrounding air or the vapor of the liquid itself, the interface between glass and liquid, and finally that between glass and air, as is shown in Fig. 1.
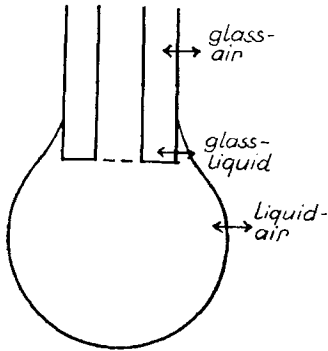

Fig. 1.

Drops of this kind have received detailed theoretical consideration in textbooks on Physics.

The thoughtful and observant pharmacist, however, is confronted in his laboratory with liquid drops of quite another kind and another origin, concerning which nothing is found even in modern textbooks on Physics. The present paper describes such *"unusual drops"* observed by the senior author many years ago, and an endeavor is made to give an explanation of their mode of formation and characteristics. A supplementary chapter will deal with an *"unusual bubble,"* a phenomenon which also requires for explanation the forces prevailing at interfaces.

All the older hitherto unpublished experiments of the senior author dating back several decades, were repeated by the junior authors, with various improvements of method. The fact developed that the greater part of the descriptions of phenomena completely agreed with the results obtained recently; thus the present paper contains pages which although written about 50 years ago, fully hold good to-day. Likewise most of the older drawings were completely verified by the recent investigation. Their number was increased by addition of photographs of phenomena of outstanding interest and importance.

Essentially new are, perhaps, the theoretical discussions at the conclusion of the paper, which develop more in detail the theory only lightly indicated by the senior author.

I.   DROPS AT THE INTERFACE LIQUID-LIQUID.

Experiment.—Into a cylinder pour a little water and benzol. Mix them together by strong agitation, and as they separate it will be seen that the meniscus takes a curved line (Fig. 2). By observing the small globules of benzol as they rise from beneath this curved line, it will be seen that when the center ones strike
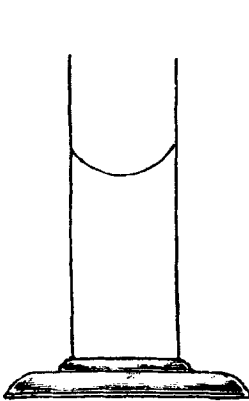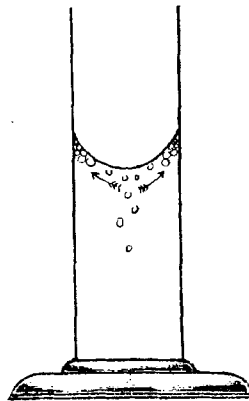

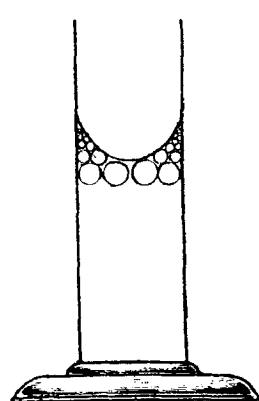Fig. 2.   Fig. 3.   Fig. 4.

the convex surface of the curve in their upward course, they diverge and move towards the glass, pressing upward against the under side of the dividing segment (Fig. 3).

Observe them closely when they strike the glass as they enter the wedge and it will be seen that they force themselves into the tapering triangle. The smaller globules squeezing highest, pass through the successively larger ones beneath them, as shown by Fig. 4.

After a time the large globules, by their great pressure, will burst the films that separate the liquids, escape into and coalesce with the benzol above; but the smaller ones have not the power to do this. They form a fringe next the glass beneath the films that separate the solutions, being thus held prisoners in the capillary wedge.

II. THE WETTING DROP.

Experiments.—Pour a liquid (excepting mercury under air) into a clean, cylindrical glass vessel and the surface presents the appearance of a plane that curves up toward the glass just before contact therewith. Decrease the diameter of the vessel to that of a glass tube and the surface becomes concave.[1] This rule holds good for all liquids of the present series when the surface is exposed to the air. Under other conditions, such as different surface contact, and different materials for containers, however, the reverse may occur, shown as follows: Pour a little chloroform into a tube of about $1/3$ inch in diameter, it assumes the condition previously described. Add now to the glass at just above the surface line, a small drop of water. The water, instead of floating as its gravity would indicate, forces itself about half its bulk below the chloroform, separating the chloroform from the glass. Creeping now downward, the globule of water assumes a wedge shape, as shown by Fig. 5, also by

Fig. 5.

Fig. 6A, raising the overlying chloroform meniscus. Continue adding the water drop by drop, allowing it to flow down the side of the tube and into the preceding water globule.
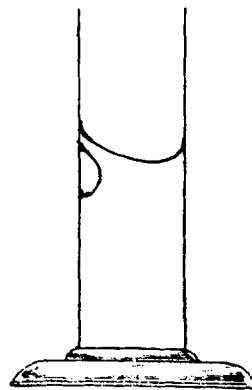
The wedge raises the surface of the chloroform above itself, encircling, as it does so, the side of the tube. (Fig. 6B.) After a time, as water is slowly added, the chloroform presents an appearance like Fig. 6C. A narrow section of chloroform on the side of the tube opposite the water globule only remains to unite the chloroform film above with the chloroform below. (Fig. 6D.) Finally as more water is added, this bond gives way, the water stratum perfects itself, producing a diaphragm across the tube, suddenly uniting in a layer, whereby a globule of chloroform is excised and rests in the cup formed by the surface of the water, while the bisecting water in turn rests on the chloroform below. (Fig. 6E.) If the water is added to the surface at different parts of the glass, just touching the chloroform, the water at the surface line of the chloroform gradually, as water is slowly added,

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[1] Compare Part II of this series, JOUR. A. PH. A., 18 (1929), 867, Figs. 13, 14, 15 or Figs. 16, 17 and 18.

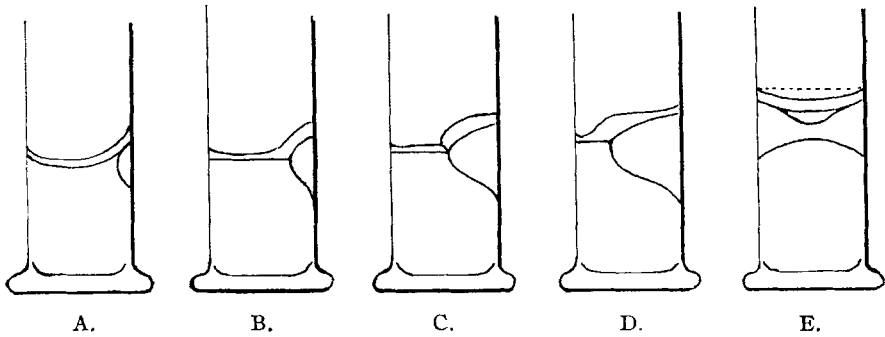A.   B.   C.   D.   E.

Fig. 6.

creeps around the glass, the chloroform finally assuming an hour-glass form, as shown in Fig. 7.

Finally, the central outreaches of the ringlet of water unite, excising a drop of chloroform which rests in the cup above the water. (Fig. 6E.) The chloroform below the water cap has assumed a surface the reverse of the contour presented when it was exposed to the air. It is now convex instead of concave. (Fig. 8.)
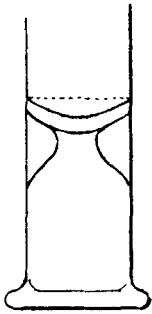
The principle involved may be even more forcefully illustrated with carbon disulphide and glycerin. By this experiment (Fig. 6, A to E and Plate I, A to E), we behold the growth of the convex surface that forms between such liquids and water when they are in contact with each other. It matters little how violently they are mixed, or which is added to the other, on resting, a surface drop (pendant drop) always springs into existence.

Fig. 7.

III.   THE PENDANT DROP.

Experiment.—If into a cylinder containing water a little chloroform be allowed to trickle, drop by drop, down the inner surface of the glass, when it strikes the water, although much heavier it at once separates from the
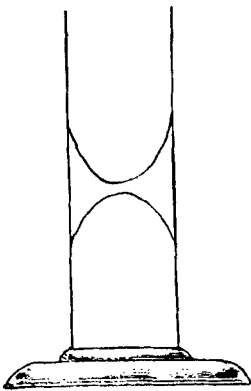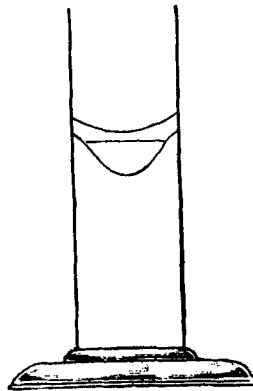

Fig. 8.   Fig. 9.   Fig. 10.

A.   B.   C.

D.   E.

Plate I.

glass and spreads over the surface of the water as a film. Continue adding the chloroform, and the surface floats to the center of the film, coalescing into a globule which rests pendant (Fig. 9) until it becomes heavy enough to overcome the attraction of cohesion of the surface film of the under liquid, when a portion (more than half the drop) breaks from the globule and falls to the bottom. By slowly adding the chloroform at the edge, it is seen to flow regularly to the center of the cup and drop below in fragments (Fig. 10).

A.   B.   C.   D.

Plate II.

This phenomenon so easily produced, seems to have very seldom attracted the attention of scientific authorities.[1] By referring to the preceding pages, "the wetting drop," the reader will meet an attempt to illustrate the manner in which convex surfaces of one class of heavy liquids are produced when water is poured upon them. It will be observed by referring to Fig. 6E of that series that a globule of heavy liquid invariably rides on the surface of the water, as is true of all liquids showing the "wetting drop" phenomenon. Thus, a mixture of carbon disulphide with either glycerin or water, or wintergreen oil with either glycerin or water, or chloroform with either glycerin or water, will produce such surface globules. (See A to E, Fig. 6.) These drops hang pendant if the container be narrow, or if large, float as an inverted cone on and near the center of the lighter liquid. (Plate II, A to D.)

Such globules are not sports, for they obey a natural law, and it is immaterial, as before stated, whether a heavier liquid of this description be poured upon the lighter one, or the reverse, or whether the two liquids are thoroughly incorporated by agitation and then permitted to separate. The phenomenon of the hanging surface drop follows invariably. Indeed, we have failed in every endeavor (at ordinary temperature) to separate the drop from the surface when equal amounts of glycerin and carbon disulphide are mixed under conditions mentioned herein, although with such mobile liquids as chloroform and water, a sudden jar will detach most of it, but never completely.

IV. THE PENDANT BUBBLE.

Experiments.—Pour into a cylinder a stratum of carbon disulphide and then carefully fill the cylinder nearly to the stopper with water, leaving a narrow stratum of air beneath the stopper. Now quickly invert the cylinder and return it at once to the natural upright position, when it will be seen that a part of the air will be excised by the carbon disulphide and held a prisoner. The bubble of air varies in size but seldom will it escape entirely. On jarring the tube it is seen that the bubble is retained with great persistence, and

Fig. 11.

Fig. 12.

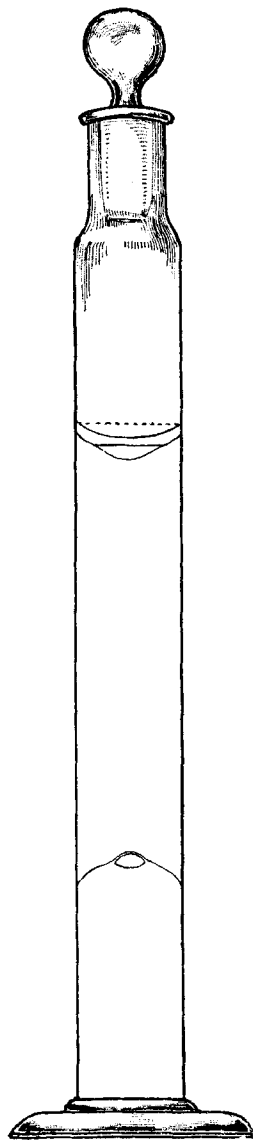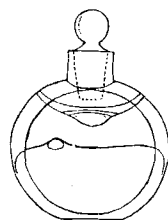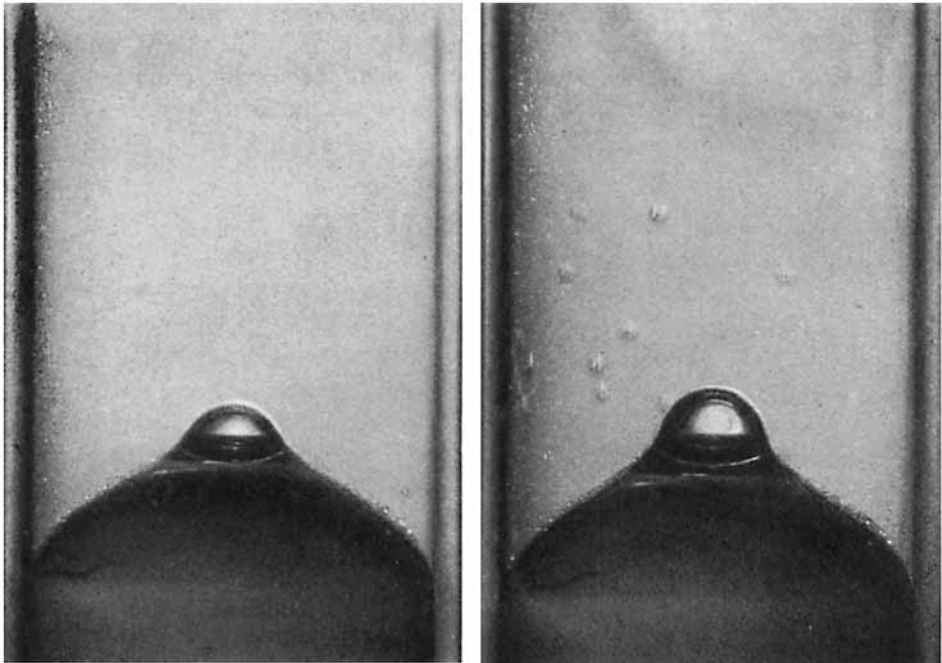[1] The demonstration of a pendant drop (with creosote and water) has been made by Ch. Tomlinson, *Experimental Essays*, London, 1863.

The name pendant drop for a hanging drop in general, has been used by A. M. Worthington, *Phil. Mag.* (5), 19, 46–48 (1885); cf. *References to Capillarity* by S. Waldbott, being Chapter VII of *A Study in Pharmacy*, by J. U. Lloyd (1900); No. 268 (Tomlinson), No. 473 (Worthington).

if it be less than one-tenth of the diameter of the cylinder figured herein, cannot be detached by violence, even by striking the bottom of the tube in the palm of the hand.   (Fig. 11 and Plate III, A and B.)   The same phenomenon can be even better illustrated by using a flat-sided bottle, as it is easier to study the nature of the surrounding mediums through a parallel surface than through a cylinder. (Fig. 12.)

Moving over its surface are often to be seen multitudes of tiny globules apparently resting on a film that differs from the underlying stratum, and which is connected with the surface film of the adjacent carbon disulphide, which in turn reaches to the glass container.   (Fig. 13.)   On closer inspection it is seen that the

A.   B.

Plate III.

mediums about this bubble are in a state of physical activity, and that constant changes are taking place in and about films in this vicinity.   The stratum of water above the dividing films may become (on decreasing the temperature) filled with microscopical globules of carbondisulphide which, falling upon the bubble, move freely over its surface to the edge of the film of carbondisulphide.   They maintain their individualities on the upper film's contour, not underneath it.   (Fig. 14.)
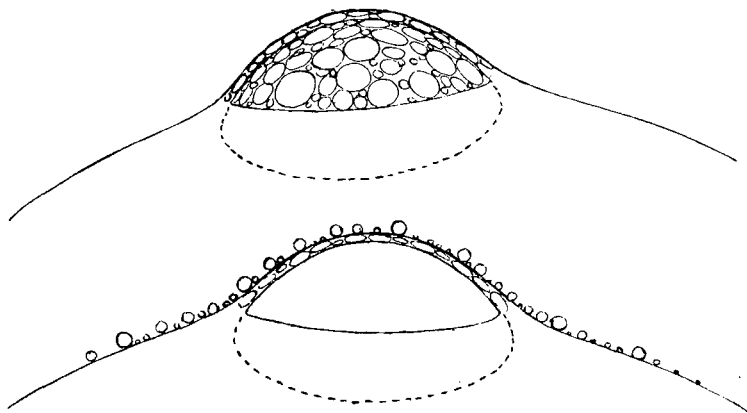
V.   THEORY OF THE PHENOMENA.

A.   General Formulation of the Theory.

The phenomena before described are not the haphazard products of accident, which many investigators probably have thought them to be.   The close

study of the subject, however, has shown that these peculiarities of the interfaces manifest themselves with exceeding *regularity* and are quite specifically dependent on the nature of the liquids. We have noted before that the phenomenon of the "pendant drop" with certain pairs of liquids is always realized, regardless of the manner in which the liquids are brought together, while with some other pairs of liquids this phenomenon was never observable. Without doubt, these phenomena are based on exact laws which are closely connected with the nature of the liquids, and are of especial interest theoretically. We may justly suppose that capillarity of the liquids is the primary determining factor, supplemented perhaps by other physical properties. Selecting the accepted theory of capillarity as the basis of our discussions, we will now endeavor to deduce from this theory some fundamental conditions governing drops and bubbles at interface surfaces.

1. *Drops at the Interface Liquid-Liquid.*—A drop of liquid A can remain suspended in another, foreign liquid B only when the specific gravities of both liquids are equal. Ordinarily, this condition is not fulfilled; the drop will be

Figs. 13 and 14.

pulled upward or downward by gravitation until it strikes the upper or lower boundary of the liquid. This boundary may be formed either by the air above the liquid surface, or by the bottom of the vessel, or by a layer of liquid A, which is situated above or below B, depending on conditions of density.

When the drop moves toward the boundary layer between A and B, it hydro-dynamically pushes before it a coating layer of liquid B, which causes the interface surface somewhat to be arched at its summit, increasing its tension. Thus the first effect of the interface tension is to arrest the drop.

While the drop and layer A are at first separated by a film of substance B, this film gradually becomes thinner, finally is torn at one spot and pulled entirely to one side through the action of surface tension; as a result, the drop merges with layer A. In thus coalescing, surface energy is set free, since the surface of the drop disappears in the liquid mass, and because in addition the tension of the boundary surface has a positive value. (Regarding the possibility of a negative interface tension see Wo. Ostwald, *Grundriss der Kolloidchemie*, 7th ed. (1926), 80.)

Therefore the positive interface tension must be regarded as the driving

force in the merging of drops and liquid layers.   A further condition of the process of coalescence, however, is the formation of a slight defect in the film at some spot thereof.   As long as the interfaces liquid-liquid are complete within themselves and are of uniform tension throughout, the interface tension alone cannot tear the film.

What is the cause of the first tearing of the film?   In the first place, no doubt, it is gravitation of the drop which causes liquid to be squeezed out of the space between drop and layer.   The compressing force is equal to buoyancy, therefore proportional to the volume of the drop (thus proportional to the third power of the radius or the diameter), and the difference in density of the liquids.   Evidently then, the "tearing" pressure becomes rapidly greater with increasing diameter of the drop, since for example in doubling the diameter, the compressing force becomes eight times as great.   For this reason, large drops coalesce faster and more easily than do small drops.

Neither gravitation nor interface tension, however, explain the surprisingly great stability of drops in some pairs of liquids.   It is true, a certain resistance of the drops to merging is noticeable with all liquids, especially with those that easily form emulsions with each other.   Stability of emulsions cannot be explained through the usual notions on interface forces, because under this theory a very small pressure should be sufficient to pierce the separating film.   Thus we are led to the assumption that in very thin films the tension is after all something different from the normal interface tension between larger masses of liquids; we must assume an especial *film tension*, as the senior author has done many years ago.

Discussing such a tension theoretically: The interface tension is a function of the potential difference between molecules in the interfaces and the interior of the liquid.   The molecules at the surface have in general (not always) the greater potential, because their cohesion valences are less saturated than are those in the interior of the liquid.   Now it is certain that in the surface of a film which is thinner than the radius of action of the cohesive forces the molecules are still more "exposed" and must have a much greater potential than in a "massy" surface.   The same is the case with the molecules situated "within" the film.   Therefore with very thin films the potential differences between inner and outer molecules are entirely different from those with liquids in bulk, which recalls the increase of vapor pressure in such layers, and the ready transition of such a thin film into the gaseous state.   Owing to the more "exposed" position of the molecules in the film, the potential difference, and with it the interface tension will generally be greater than in the case with the liquid in bulk.

The thinner the film becomes, the greater the interface tension or preferably speaking, the "film tension" may become.   Thus with the approach of the drop to the interface liquid-liquid the interface energy increases.   The consequence is a *repelling force*, which when it exceeds that of gravitation, prevents the coalescence of drop and layer.

It may be shown that orientated interface layers such as electrical double layers, dipole clouds, layers of coupling substances, etc., whose stabilizing effect upon disperse systems is well known, cause an especially strong increase of the interface tension upon the thinning of the film.   This theory of variable film tension, therefore, includes all other explanations heretofore given for the stability

of disperse system. The theoretical and practical importance of these systems which exhibit such particular interface properties, in addition to the theoretical reasons discussed, justify us in differentiating "film tensions" from the normal "interface tensions."

2. *Drops at the Interface Liquid-Gas.*—(a) *The pendant drop.* A drop of liquid A surrounded by a heavier liquid B, in rising strikes the meniscus of the liquid, the liquid-gaseous interface B-air. In the same manner as with a liquid-liquid interface, the film tension at first retards the drop. When its buoyancy is sufficiently great, it breaks through the film and in the next instant is stretched on account of the action of the different interface
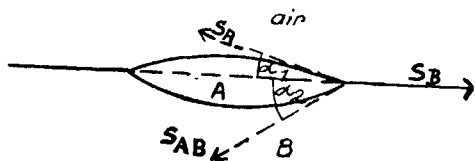

Fig. 15.

tensions. The shape of the resulting lens depends on the relation of the tensions involved. The tensions are in equilibrium when the following relation exists: (Fig. 15.)

$$S_B = S_A.\cos \alpha_1 + S_{AB}.\cos \alpha_2.$$

This equation shows that when $S_B = S_A + S_{AB}$, the angles α_1 and α_2 are equal to zero and the lens is entirely flat; when S_B becomes slightly greater, the drop will spread in the form of a film all over the available surface.

In the characteristic phenomenon of the "pendant drop" we are evidently confronted with the case where S_B is smaller than the sum of S_A and S_{AB}.

The pendant drop forms only when the surface of A does not spread, but also only when it does not contract. If the surface tension of A is very great, the free surface of A seeks to become smaller, which causes the circle of intersection between the drop and the surface of B to be more and more contracted (Fig. 16). This diminishing circular circumference is capable of carrying only a small weight; as a result, more and more of the drop will fall off. However, as long as the relation of interface tensions is such as to prevent *complete* contraction of the free surface of A, a drop however small, will always remain suspended from the surface of B.

Fig. 16.

The shape of this drop like that of all hanging drops, is characterized by the equation already given. When the contractile tension S_A becomes very large, cos α_2 must become smaller and smaller, approaching the limiting value -1; it follows from the vector nature of these quantities that cos α_1 then approaches the limiting value $+1$. The equation for the tension in the extreme case is

$$S_B = S_A - S_{AB}.$$

When these critical values are exceeded, the film of B closes over the drop, and no pendant drop can be formed.

We are now in a position to formulate mathematically two conditions for the formation of the pendant drop:
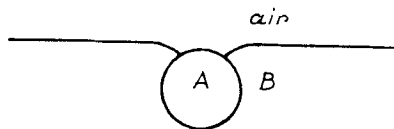
(1)   The drop must not spread:

$$S_B < S_A + S_{AB}.$$

(2)   The drop must not contract:

$$S_B > S_A - S_{AB}.$$

These are two conditions which may be predicted theoretically from the interaction of the three interfaces between A, B and air.

In the usual experiments with suspended drops in narrow glass cylinders, however, additional interfaces come into play, namely, those of Glass-A, Glass-B and Glass-Air. What is their influence upon the pendant drop?

The interface tension of liquids toward glass is nearly always negative (mercury excepted), *i. e.*, the surface of contact tends to become larger. As a consequence, the liquid-air surface is always pulled up high and is under tension; in other words, the liquid *wets* the glass.

The *"wetting tension"* of different liquids is of different magnitude. The better-wetting liquid displaces another not wetting so well and pushes itself forward along the glass wall, carrying the edge of the liquid-liquid interface with it. Since the center of the liquid-liquid interface must lag behind, it naturally follows that the *meniscus must always be convex toward the side of the better-wetting liquid.* It is entirely immaterial whether the better-wetting liquid is heavier or lighter than the other. If it is below the other, the meniscus will be convex below, if above, the meniscus will be convex above.

For the pendant drop, the form of the meniscus is of fundamental importance. We will pour into a glass cylinder a light liquid and upon it carefully, a heavier one in order to note under what conditions a pendant drop may form. When the heavier liquid has a smaller wetting tension than the liquid below it, the meniscus between the two will be convex toward the bottom. The better-wetting liquid pushes upward along the wall, displacing the other liquid from the wall, causing the greater part of the latter liquid since it is heavier, to fall to the bottom through the center of the meniscus. A small remainder gathers in the cavity of the meniscus and there forms the "pendant drop," provided that the tensions S_B, S_A and S_{AB} fulfill the conditions 1 and 2 before explained.

But if the heavier liquid is at the same time the better-wetting one, a meniscus convex above is formed upon carefully producing the layers as before. Then the heavy liquid pushes its way downward along the wall, gradually flowing beneath the lighter liquid. Just as long as some of the heavier, well-wetting liquid is yet on top, the meniscus remains convex upward.

All of the heavy liquid runs off along the wall, and no pendant drop can form in the center of the meniscus. The meniscus will become convex below only at the moment when the surface is entirely cleared; in this case no substance is left to form a pendant drop. Thus, a pendant drop can never be formed when the wetting tension of the heavier liquid is greater than that of the light liquid, even though conditions 1 and 2 may be fulfilled. Therefore the *third* condition for the formation of a pendant drop may be formulated as follows:

(3) $S_{A-Glass} < S_{B-Glass}.$

We shall see further on that these three conditions derived theoretically agree in all cases with the experimental observations on pendant drops.

(b) The wetting drop. The influence of wetting tension between glass and liquids is especially noticeable with drops which adhere directly at the glass wall of the vessel. If we pour a light and well-wetting liquid upon a heavier, poorly-wetting one, the phenomenon of the wetting drop may be observed as recorded before. The well-wetting liquid displaces the other from the glass wall and pushes its way downward although it is less heavy and could float upon the surface of the other. The cause of this phenomenon is the pulling downward of the interface surface by the wetting tension, tending to form a meniscus convex above. However this meniscus can attain its complete form only if the quantity of the upper liquid is large enough to cover it. As long as there is only a small quantity of liquid present, a pendant drop is formed at the glass wall *(the wetting drop)* which leaves the center of the meniscus free. In this manner the peculiar form of the interface of the wetting drop originates, composed of convex and concave menisci.

The physical conditions for the formation of the wetting drop are theoretically the following:

(1) Liquid B of the wetting drop as we have seen must wet better than liquid A beneath it. For the wetting tensions, therefore, the relation must hold:
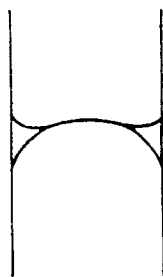
$$S_{A-Glass} < S_{B-Glass}.$$

(2) If the remaining free surface of A were contractile, the ring-like wetting drop B would become a skin uniformly covering liquid A. Consequently formation of the wetting drop is possible only if the surface tension of A is smaller than the sum of the tensions S_B and S_{AB} which act in opposite direction (Fig. 17). Thus the 2nd condition governing formation of the wetting drop is

$$S_A < S_B + S_{AB} \quad \text{or} \quad S_B > S_A - S_{AB}.$$

Fig. 17.

(3) The hour-glass form of the meniscus in the wetting drop is caused by the tension of the free surface of A pulling the other interfaces toward the center, forming a constriction. Now if the free surface of B contracted, the free surface of A would have to spread to the edge and could no longer maintain the tension of the ring of B. Liquid B would then fall apart into small droplets, or would spread flatly along the wall of the vessel. Therefore the wetting drop in its typical form can be generated only if the surface of B does *not* contract, thus when

$$S_B < S_A + S_{AB}.$$

Comparing the conditions deduced with those holding good for the pendant drop, we find that they are the same. In fact liquids which satisfy these conditions, invariably show both phenomena, the wetting drop as well as the pendant drop.

3. Bubbles at the Interface Liquid-Liquid.—The problem of bubbles at liquid-liquid interfaces is entirely similar to the problem of drops.

Assuming a bubble of air or vapor to rise in liquid A, striking the liquid-liquid interface between A and another liquid B. As in the case of the rising drop, the bubble pushes before it a coat of liquid A which at first rests as a thin film between the bubble and the interface. In this case, also, the tension of the film will prevent the further rising of the bubble unless buoyancy is strong enough to cause the interfaces to be torn.

It is true that here it is difficult to decide whether the bubble is held back by a peculiar film tension or by the normal interface tension. If for example the film did not possess any particular firmness, buoyancy would readily pierce it, it is true, but the bubble would nevertheless remain suspended in the interface. This is because if the volume of the bubble were to intersect the interface, three different interfaces would meet, readily adjusting themselves in an equilibrium of tension. To this, buoyancy adds a strong vector acting perpendicularly upward; as a result the all-supporting liquid-liquid interface is stretched in upward direction (Fig. 18). We note that the bubble is held by the interface surface; it is true not through film tension but through the interface tension.

B.   *Quantitative Comparison between Theory and Experiment.*

We shall now examine whether these general theoretical notions concerning drops and bubbles at interface surfaces actually correspond with experimental observations; first whether those tensions which permit of being calculated from the experiments are actually equal to the normal surface tensions of theory, qualitatively and quantitatively, selecting for examination a few quite special cases. In a subsequent paper we intend to take up more in detail the especially important problem of wetting tensions, experimentally as well as theoretically.

Fig. 18.

(1)   *The Pendant Drop.*—The tensions holding the pendant drop in suspension, may be calculated by different methods.

(a)   *From the weight of the pendant drop:* (cf. Plate II). The interface between the drop and liquid B tends to be curved convex downward on account of the weight of the hanging drop. The strongest downward pull is exerted upon the meniscus line at the edge of the drop, because along this line the total weight of the drop must be carried by the interface. The meniscus line at the edge becomes the steeper the greater the weight of the drop and the smaller the carrying interface tension.

If α is the deviation of the meniscus line from the horizontal, then the force of the interface tension S_{AB} pulling upward at the edge of the meniscus is

$$K = 2\,\pi r \,.\, S_{AB} \,.\, \sin\,\alpha.$$

This force must be equal to the weight G of the hanging drop, therefore

$$2\pi r \,.\, S_{AB} \,.\, \sin\,\alpha = G \text{ and}$$

$$S_{AB} = \frac{G}{2\pi r \,.\, \sin\,\alpha}$$

G is equal to the product of the drop volume v and the difference of densities $d_A - d_B$ of the two liquids. The volume of the drop is best obtained from the enlarged photograph of the drop by measuring the meridional area and applying Guldin's rule.
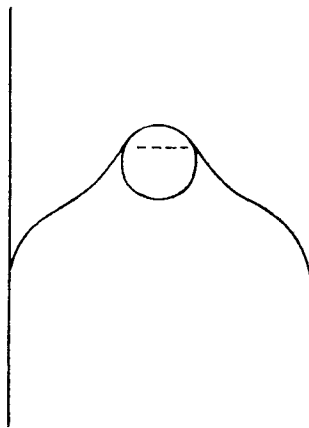
For the pendant drop chloroform-water illustrated in Plate II-B, the following result was obtained:

$$V = 0.166 \text{ cc.} \qquad\qquad G = 0.081 \text{ g.}$$
$$r = 0.518 \text{ cm.} \qquad\qquad \sin \alpha = 0.75$$
$$S_{AB} = 0.333 \text{ g./cm.} = 32.6 \text{ dyne/cm.}$$

This value agrees well with that obtained by means of a different method,[1] of the interface tension between chloroform and water, namely, 33.3 dyne/cm.

(b)　*From the curvature of the drop.* The interface tension S_{AB} may also be calculated from the curvature of the drop. The curvature becomes the more pronounced the smaller the interface tension, and the greater the hydrostatic pressure causing the drop to bulge. In the center where the curvature is strongest, the pressure is equal to the product of the entire height of the drop and the difference in densities $d_A - d_B$.

This hydrostatic pressure is exactly compensated by the curvature pressure of the interface. The magnitude of the curvature pressure may be calculated from the curvature and the interface tension, as follows (Fig. 19):
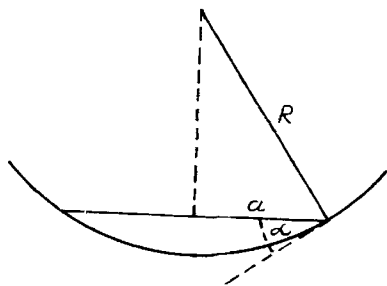

Fig. 19.

Consider a plane (horizontal) section through an evenly curved portion of the interface. The normal (vertical) component of the interface tension force attacking at the circumference of the circular section line, is

$$K = 2\pi a \,.\, S_{AB} \,.\, \sin \alpha.$$

The sectional area upon which this force acts, is

$$f = \pi a^2;$$

the curvature pressure therefore is

$$P = \frac{K}{f} = 2\, S_{AB} \,.\, \sin \alpha / a.$$

Let R be the curvature radius of the interface, then we readily obtain

$$\sin \alpha / a = 1/R \text{ and } P = 2 \,.\, S_{AB}/R.$$

This pressure is equal to the hydrostatic pressure

$$h \,.\, (d_A - d_B)$$

and we have finally

$$S_{AB} = \tfrac{1}{2} \,.\, R \,.\, h \,.\, (d_A - d_B).$$

From the photograph of Plate II-B the following values were derived for the apex of the pendant drop:

$$R = 0.28 \text{ cm.} \quad h = 0.45 \text{ cm., and from this}$$
$$S_{AB} = 30.2 \text{ dyne/cm.}$$

Correspondingly, the hanging drop in Plate II-A gave

$$R = 0.51 \text{ cm.} \quad h = 0.26 \text{ cm., therefore}$$
$$S_{AB} = 31.7 \text{ dyne/cm.}$$

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[1] Reynolds, *J. Chem. Soc.*, 119 (1920), 460.

Both values are in sufficient agreement with the magnitude of the surface tension between chloroform and water, = 33.3 dyne/cm. (Reynolds: see foregoing.)

(2) *The Pendant Bubble.*—We have concluded above that the tension retaining a bubble at the interface of two liquids, is in any case the tension of the interface liquid-liquid, regardless of whether there rests a film upon the bubble or not. We will verify this theoretical conclusion by endeavoring to calculate the magnitude of the tension from the experimental data.

The bubble causes the interface to be arched until the vertical component of the interface tension exactly compensates the buoyancy of the bubble. If the force of buoyancy is K_A, the relation must exist: $K_A = 2\pi r . S_{AB} . \sin \alpha$. As Fig. 18 shows, r must be the radius of the small circle along which the interface liquid-liquid "intersects" the bubble.

The buoyancy may be calculated from the volume of the bubble and the densities of the displaced liquids. Since the upper and lower sections of the bubble are in contact with different liquids, the density must have a value intermediate between the values d_A and d_B, obtained by dividing the density interval in inverse ratio of the partial volumes referred to.

The total volume of the bubble is calculated from its radius R, and we have:

$$K_A = V . d = 4/3\pi . R^3 . d = 2\pi r . S_{AB} . \sin \alpha$$

and from this

$$S_{AB} = \frac{2 R^3 . d}{3r . \sin \alpha}.$$

For the pendant bubble in Plate III-A (carbondisulphide-water) the following values were obtained:

$$R = 0.20 \text{ cm.} \qquad r = 0.17 \text{ cm.}$$
$$\sin \alpha = 0.78 \qquad d = 1.2 \text{ g./cc.}$$
$$S_{AB} = 47.5 \text{ dyne/cm.}$$

This value quite closely approaches that obtained by another method[1] for the interface tension between carbondisulphide and water, namely, 49.3 dyne/cm.

Thus we reach the conclusion that a quantitative comparison of the theory presented, with a few special experimental examples shows a strikingly good concordance.

SUMMARY.

I. Former investigations of the senior author on drops and bubbles at interfaces were repeated and completely verified. Peculiar phenomena of drops and bubbles are observed which very regularly appear at interfaces and are by no means haphazard products. The drop formations described here are the following:

Drops at the interface between two liquids, and drops at the surface of a foreign liquid, either in center position (the *pendant drop*) or in marginal position (the *wetting drop*).

Besides, air bubbles are described being attached at the interface between two liquids.

II. Endeavoring to explain these phenomena from the point of view of the accepted capillary theory, the following results were obtained:

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[1] Reynolds, *J. Chem. Soc.*, 119 (1920), 460.

(*a*) The great resistance of small drops to coalescence with the bulk of the liquid cannot be explained by the usual interface tensions. A resistant film seems to coat the interface. Purely theoretical considerations lead to the conclusion that the tension of thin films is greater than the interface tension of the liquid in bulk. The particular properties of the film tension explain the stability of emulsions.

(*b*) The *pendant drop* can form only when the interface tensions stand in a definite relation to one another. Theory permits the derivation of three conditions for the interface tensions of the "pendant drop." The same conditions hold good also for the formation of the "wetting drop."

(*c*) In this connection the case of the "pendant bubble" is also treated theoretically, and is explained by interface tension.

III. From a few photographs of drops and bubbles the forces are calculated which are active in these formations. The results show that the tensions agree very well with the interface tensions, which confirms our theory.

RESEARCHES ON CHINESE MATERIA MEDICA.*

BY K. K. CHEN,[1] PH.D., M.D.

While numerous noteworthy discoveries for the healing of the sick have been made during recent years, medical science still owes much to the people of the past for the accumulated knowledge of many remedies and cures. Primitive medicine almost always involves empiricism and sometimes superstition, but is often based on some keen observation. Such an observation, when confirmed and well appreciated, then becomes a sound principle in modern medicine. An example of this kind can be found in the prevention of smallpox in civilized communities. It is true that Edward Jenner (1796) was the first person to introduce vaccination, but the observation that inoculation of cowpox débris confers immunity against smallpox was previously known to the Orientals and Europeans, especially among milkmaids. It was from the latter that Jenner obtained the information, then conceived the idea of vaccination as a prophylactic measure against smallpox, and finally achieved his discovery.

We can recall another example in the introduction of the foxglove or digitalis for the treatment of heart diseases. The leaves of this plant were long known to diminish the body fluids in dropsy, but it was not until 1775 that William Withering actually initiated its use in medical practice. It was an old family recipe from which Withering derived his knowledge and which led him to investigate the therapeutic value of digitalis, which has now become an indispensable drug to relieve the symptoms of cardiac disorders.

Chinese civilization, like other ancient civilizations, is rich in curative measures. Its materia medica up to 1596 included 1871 drugs. Such drugs as camphor, cinnamon (*Cinnamonium cassiæ*), anise (*Illicium verum*) and rhubarb (*Rheum officinale*), which have been known in China for centuries have been admitted to modern pharmacopoeias. There are, however, many other drugs that in China

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* Read before the Committee on the Promotion of Chinese Studies of the American Council of Learned Societies on Dec. 30, 1930, at Cleveland.

[1] From Lilly Research Laboratories, Indianapolis, Indiana.