through the relay. In the original filling of the bath in this case, then, the mercury and platinum must not be in contact until after the stopcock is closed, when the wire is screwed down so that it just makes contact. As this contact is broken, owing to the cooling of the bath, the relay current is also broken, which causes current to flow through the sounder, drawing down its arm and allowing warmer water to flow in until contact is again made, when the weight carries down the unattracted arm and pinches the rubber tube.

The advantages of this apparatus are as follows:

Any temperature, between 0.1° and 90°, can be maintained, with an accuracy of a few hundredths of a degree, in one form of bath, which is simple, easy to adjust and inexpensive.

A small and transparent bath can be employed without sacrifice of delicacy.

A series of determinations, such as specific gravities, each at a different temperature, can be made in a day, for but a short time is required to change from one constant temperature to another.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY No. 185.]

THE WEIGHT OF A FALLING DROP AND THE LAWS OF TATE. III. AN APPARATUS FOR RAPID AND ACCURATE DETERMINATION OF THE WEIGHT OF A FALLING DROP OF LIQUID.

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Introduction.

The results obtained in the previous researches of this series,[1] employing the cumbersome and elaborate apparatus necessary for the calculation of the weight of a falling drop from the very accurately determined volume of a single falling drop of the liquid, and its density, have shown that for all the (6) liquids studied[2] the weight of the drop is strictly proportional to the surface tension of the liquid at that temperature; and can be substituted very satisfactorily for the latter in the relationship of Eötvös, as modified by Ramsay and Shields.

Since, contrary to the conclusions of all the other investigators in this field, the weight of a falling drop of liquid from any one tip is thus found to

[1] Morgan and Stevenson, THIS JOURNAL, 30, 360–76; *Z. physik. Chem.*, 63, 151–70 (1908). Morgan and Higgins, *Ibid.*, 30, 1055–68; *Ibid.*, 64, 170–86 (1908).

[2] Work with the new apparatus on about 50 new liquids, in place of contradicting this, confirms absolutely all the conclusions, with regard to this relationship, reached in the two previous papers.

be strictly proportional to its surface tension, determined by capillary rise, or any other accurate method; and since from the surface tension of a liquid, and consequently from its drop weight, the molecular weight and some of the physical constants of the liquid can be accurately calculated,[1] it is quite evident that a simple, yet accurate, laboratory apparatus for the determination of the weight of a falling drop of liquid would be of value in the study of the liquid state.

The object of this paper is to present the specifications for such an apparatus, so simple and easy to operate (in contrast to capillary rise and other methods) that it can serve, for general laboratory purposes, in much the same way as the freezing-point and boiling-point methods; and yet, at the same time capable of giving results fully as accurate as those by Morgan and Higgins, *i. e.*, with a mean error of but a few hundredths of 1 per cent.

What at first appeared to be a very simple problem, however, was soon found in reality to be a very complicated one. This discovery, together with the delays in the work of glass blower and grinder, and the definit setting aside of a year and a half for a thorough testing of the method in the hands of several observers, in order to bring to light, if present, any unforeseen errors or defects, is the cause of the somewhat considerable delay in the publication of the description of this simpler form of apparatus. In its final form, as here presented, consequently, all difficulties have been avoided or eliminated, so that at length an apparatus is at hand with which any one can confirm readily (and with even a smaller mean error) the results already presented on the weight of a falling drop, or those to be presented in the future.

In order to duplicate accurately the results of Morgan and Higgins it was at once recognized that the only satisfactory, simple method possible was one based upon the direct determination of the weight of a number of falling drops; for the observation of the number of drops falling from a definit weight of liquid is only fairly accurate, even when the evaporation is reduced to zero; and here it was desired to obtain results of the greatest possible accuracy, at temperatures up to within a few degrees of the boiling point. For such a method it is clear that the following conditions must be fulfilled, if the results of Morgan and Higgins are to be duplicated:

1. Perfect and absolute control of the speed of formation of the drop up to the instant of its fall,[2] and the ability to weigh accurately any number of fallen drops.

[1] In later papers of this series will be considered the relationship existing between molecular weight and the physical constants and the drop weight from any one tip.

[2] It is quite evident, though apparently disregarded by most investigators, that *the weight of a falling drop can only be proportional to its surface tension when the drop*

2. Avoidance of, or compensation for, any loss of liquid by evaporation from either the hanging drop, or from the drops which have already fallen, at temperatures even up to within a few degrees of the boiling point; this to include also any of the evaporation which is possible owing to the difference of vapor pressure caused by the difference in curvature of the liquid surfaces, *i. e.*, hanging drop and liquid from the fallen drops.

3. Exact knowledge of the temperature (and assurance of its constancy) of the liquid as it forms the drop.

4. Assurance that the tip is always horizontal; or at any rate is always exactly in the same position, if it is not horizontal.

5. Certainty that succeeding drops are always identical; in other words, the avoidance of errors which might be due to consecutive dropping, and consequently not observed when the weight of the first, perfect drop is found, as in the method of Morgan and Higgins.

These conditions, together, naturally, with the possibility of cleaning the apparatus thoroughly, without destroying its setting, were recognized at once as essential features of any accurate method for finding the weight of a falling drop of liquid; and all are very satisfactorily fulfilled in the form of apparatus which is here advocated.

It is unnecessary here to show how the above difficulties were met one by one, and avoided; to sketch the various other forms which were found for one reason or another to be inadequate and discarded; or to consider the almost numberless other difficulties which were encountered; so that we can proceed at once to the description of the apparatus, and the method of carrying out a determination with it.

The Apparatus.

The essential parts of the apparatus are shown in section in Fig. 1. Since it is more satisfactory for the worker to set up the apparatus for himself, rather than to allow the maker to attempt it, the details are entered into more fully here than would otherwise be necessary. Be-

is caused to fall by its own weight alone, and is not blown out from the tube by an excess of pressure applied to it through the tube. In other words, when the weight of the hanging drop *just exceeds* the surface tension of the liquid, which maintains the drop form, it ruptures and falls. And yet many investigators state that to avoid evaporation losses they have caused the drops to fall rather rapidly; which violates the above premise, and, in general, causes more liquid to fall than otherwise would.

Since it is only at the instant of fall that this condition must in general be fulfilled, the drop can be formed very rapidly, and checked just before it is allowed to fall, so that it is only the weight of the drop itself which causes the rupture; or. the drop can be formed very slowly throughout its entire life, as was the case in the work of Morgan and Higgins, where the viscosity of the liquid in the very long capillary buret absolutely and automatically prevented anything but a very slow and uniform speed of formation.

This question is considered again later.

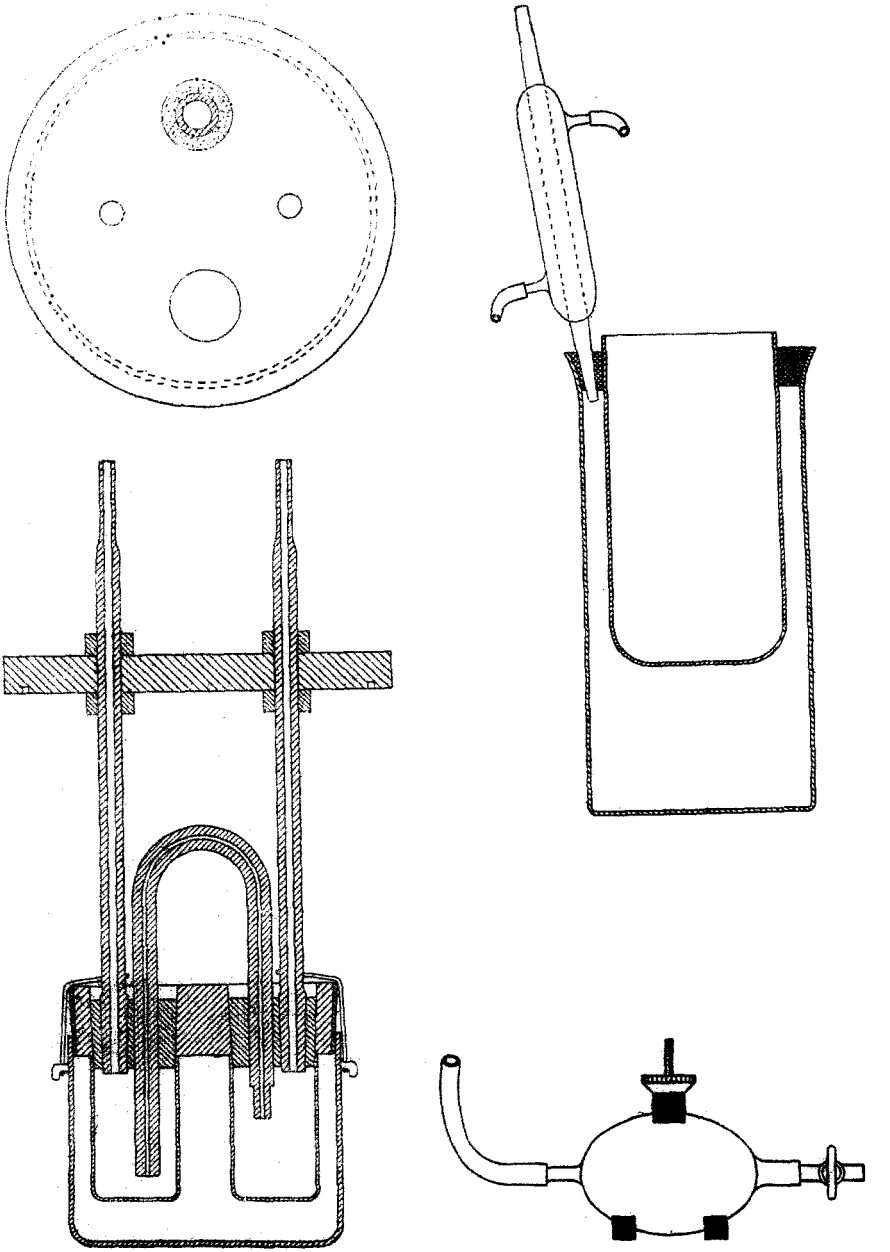

Fig. 1.

fore being cemented together the apparatus consists of the following separate pieces:[1]

One glass disk (7 × 1.5 cm.), in which there are three holes; one of these, 1 cm. in diameter, is 5 mm. from the edge of the plate, lying on one diameter; the other two are side by side, on the other diameter, with their edges separated by 7 mm., and are slightly smaller at the bottom than at the top, where the diameter is 2.2 cm. There are four hooks of wire cemented into holes in the lower side of this plate, one each on opposit sides of the two large holes.

Two plugs which are so ground into the two holes of the disk that their tops lie 6 mm. below the top of the plate, while at the bottom they project 8 mm. below the plate. In each of these plugs there are two 6.5 mm. holes.

Two light weighing vessels (3.5 cm. deep), which are provided with light ground-in glass stoppers. These are also ground to fit tightly on the lower projections of the plugs (when the latter are in position), where they are held by rubber bands fastened to the wire hooks on the plate.

One capillary dropping tube (6 mm. in diameter, with a bore of 0.2 mm.[2]) which is bent in Π-shape, one end being 9 mm. in length, while the other, the tip side, is 7.0, the separation of the legs being such that if one leg is put through the inner hole of the one plug, the other falls into the adjacent hole of the other plug, when these are in position in the disk. The tip side is ground down, concentric to the bore, to the diameter desired for the tip, for a distance of 0.5–1 cm. The tip itself has a straight, sharp edge, as is shown in the figure, and must be handled with the greatest of care.[3]

Two ventilation tubes, 15 cm. long and 6 mm. in diameter, with a bore of 2–3 mm. At the upper end these are drawn out to one-half the diameter, while the lower ends are ground into the outer hole of the plugs, so as to extend 1–2 mm. below them.

One air vessel, 4 cm. high and large enough to fit loosely on the glass disk. A pair of glass hooks are attached on opposit sides of this vessel, near the top.

[1] The apparatus in this form can be obtained from Messrs. Eimer and Amend, of New York City. Without the very skillful work of their grinder, much of the work on drop weight done in this laboratory would have been utterly impossible, and I wish here to acknowledge my indebtedness to his skill.

[2] The bore here should be such that liquid even in very small amounts forms a thread, and consequently can be removed completely from the bore by suction or pressure.

[3] Such straight-edged tips could not be obtained at the time of the work of either Morgan and Stevenson or Morgan and Higgins, but the grinder has since discovered that by first beveling the edge, and then just grinding it off, sharp edges, free from chips and flaws, can readily be obtained.

One air tube, 14 cm. long and 1 cm. in diameter, the lower end of which is ground into the third hole of the glass disk. The top of this hole should be larger than the bottom, *i. e.*, it should be funnel-shaped at the top, so that amalgam may be packed around the tube, after it is in position, to protect the cement from the effects of water. The object of this air tube is to prevent a vacuum being formed in the air vessel when the apparatus cools, after being removed from a warm bath.

One glass cover disk to hold together the above parts. This is 1 cm. thick and 10.5 cm. in diameter, with a 9.5 cm. groove, 3 mm. deep, parallel to the edge. In this disk there are two pairs of holes, one pair on each diameter. Two of these holes are 8 mm., the other two, 2.2 cm. in diameter.

One stiff rubber compression bulb, provided at one end with a tube carrying a stopcock, and attached at the other to a meter of rubber compression tubing, 5 mm. in diameter, with a bore of 1 mm. This is so arranged in an Ostwald clamp that it may be compressed or expanded with great delicacy by the turning of the milled screw head.

One reading glass (8–10 cm. in diameter), on a stand, by the aid of which the formation of the drop may be followed.

It is well to have duplicates made of the tip tube, the weighing vessels, and the air vessel, so that in case of an accident no time will be lost.

To assemble the apparatus, the plugs are first cemented into the holes in the disk with "stratina" or any other glass cement, care being taken that they are in such a position that the tip tube will slide through the adjacent holes; and the ventilation tubes, when pushed into the outer ones, will also enter the corresponding (8 mm.) holes in the cover disk. After the plugs are cemented into the disk, and the ventilation tubes into the plugs, all is allowed to stand until the cement has hardened. The two vessels, the weighing vessel on the tip side, and the supply vessel on the other, are now fitted perfectly air-tight to the projecting ends of the plugs, using lanolin, since in the setting up suction is to be applied for a long period and the rubber tube from the bulb connected to the tip ventilation tube, while the top of the other ventilation tube is plugged by a piece of rubber tubing containing a glass rod. All is now in readiness for the fastening in of the tip tube. In order to do this most conveniently, the disk is set upon two parallel pieces of wood fastened together at the ends with two blocks, so that the plate can rest solidly upon the pieces of wood, while the vessels slip between them.

The tip tube is to be so arranged that the shoulder formed by the grinding down to form the tip reaches at least to the bottom of the plug, or extends slightly below it. It can be held temporarily in this position by allowing the supply end to rest upon a piece of folded paper, of the proper thickness, placed in the bottom of the supply vessel. A piece of asbestos cord is now shredded out and the finer pieces packed around

the tip tube, on both sides, with a small chisel-shaped awl, until it is firmly held in the proper position. The holes here should be about 0.5 mm. larger than the diameter of the tip tube, so that the lengths of asbestos can be packed around both legs uniformly. This is really more satisfactory than attempting to have the legs ground into the holes, for that is not only difficult to accomplish, but, if once accomplished, makes the tip tube too rigid to stand the changes in temperature necessary, and causes it in time to crack at the bend. After the joints have been packed with asbestos, "stratina" is placed on the upper layer and suction applied with the rubber bulb. Any leak in the joints is now made apparent. In case there be such, the cement is allowed to harden, still applying suction, and more asbestos and "stratina" supplied until the apparatus is tight enough to stand, without change, the full suction of the bulb over night. It is probable, here, that when properly set up the "stratina" does not penetrate the lower layers of the asbestos, for the use of such an apparatus for a year, using volatil liquids, even within a few degrees of their boiling point, has never shown any trace of substance dissolved by the vapors. In case difficulty is experienced in this respect, however, the tip side may be raised so that the shoulder is just within the plug, when a ring of lead, cut from a sheet, may be packed in, which will prevent any such action, except for the vapors of corrosive liquids.

The air tube is now fastened into the third hole of the disk with "stratina," the dry cement both here and on the plugs being covered with a layer of plaster of Paris moistened with linseed oil (or a mixture of barium sulfate, graphite, and linseed oil) and then packed tightly with an amalgam made by dissolving tin foil to saturation in mercury at 70°. Or the amalgam alone can be used for this purpose. These protect the cement from the action of water; and yet can be readily removed with a knife blade, in case of accident, so that the apparatus can again be taken apart by simply soaking in hot water.

Next, after removing the rubber tubes, the upper extremities of the air and ventilation tubes are passed through the holes in the cover disk, which is to be fastened 10–11 cm. above the other one, the air tube being fastened by a rubber stopper in one of the large holes, while each ventilation tube is cemented to two tightly fitting blocks of wood or glass, which lie one above, and the other below the plate, to which they are to be cemented. It is more convenient to secure the tubes in this way, indirectly to the top, than to have them fit directly and tightly into the cover, for then the holes would have to be smaller in diameter than they are, and there would be danger, if they were not separated by exactly the correct distance, of breaking the tubes in putting on the cover.

A piece of rubber tubing such as is used for Gooch crucibles is now slipped over the edge of the lower disk, overlapping both above and below,

and is built up with other pieces, if necessary, until the air vessel fits water-tight on the lower few millimeters—thus leaving enough of the upper edge of the disk exposed to furnish a grip for one hand when taking off the air vessel, after a determination, and so to remove any danger of shearing off the ventilation tubes with the twisting strain. Or short pieces of a heavy glass rod may be cemented into two holes, on opposit sides of the upper surface of the disk, for this purpose; but the former plan has been found to be quite satisfactory, especially if the disk be a few millimeters larger at the top than at the bottom, *i. e.*, is cork shaped.

The next and final step in the setting up is to find what position of the cover is necessary to cause the bottom of the tip to be horizontal, so that it may always be placed in that position for every determination. This may be readily done when putting on the cover disk by being assured that this is parallel to the bottom of the tip, before cementing it fast. Then it will be only necessary to see that the cover is level in two directions before each determination. To do this most readily, a microscope cover glass is temporarily fastened on the bottom of the tip with a drop of glycerol, and the cover moved until observation of the edges of the two surfaces, from all directions, shows it to be parallel to the tip, when it is cemented. If this has not been done in the setting up, it is necessary to find with a level mounted on three legs (two of which are adjustable) the unlevelness of the cover which is necessary to make the bottom of the tip horizontal. Before each determination, then, the adjusted level, fixed previously in the proper position, must be placed on the three marks on the cover, and this raised or lowered until the bubble is fixed on its mark.[1]

The Temperature Bath.

In order to find the temperature of the drop which is forming and falling, it is necessary that the apparatus be immersed in water below the bend of the tip tube. The temperature of the tip tube itself, or the exposed parts must, naturally, be the temperature of the liquid as it drops, for in going slowly through this mass of glass, the small amount of liquid must quickly get into equilibrium with it, even though the temperature of the supply liquid be slightly different. Heating in an air bath, which would allow the use of a much simpler form of dropping apparatus, is not feasible, although much time was expended in discovering it. For this reason, it may be concluded that this form of apparatus, devised for use in a water bath, is the simplest possible, if the temperature is to be fixed exactly.

[1] In the nine pieces of apparatus which are in constant use in this laboratory, this has been necessary, owing to the fact that the ventilation tubes were ground into the cover, thus allowing only one position for that, which was usually not the correct one. These levels were made especially by W. and L. E. Gurley, of Troy, N. Y.

The water bath, which must, of course, be transparent, would best be the one for all temperatures, from 0–90°, very recently described by Morgan.[1] In this the apparatus itself would be set upon a brass ring (2–3 cm. deep) which just fits into the groove in the cover plate, and is fastened permanently into the cover of the water bath, which would have to be fixed so that it could be raised and lowered, in order to reproduce the unlevelness of the top which is requisit to level the tip. This can be done by the use of small pieces of wood or card, or the bath itself can be placed upon a stand fitted with three leveling screws.

If such a bath is not at hand, the one shown in the figure may be used, which is heated by the vapor of a boiling liquid. The water vessel here is 18 cm. high and 9.5 cm. in diameter, its top fitting into the groove of the cover disk; or the top may be placed upon a brass ring which is held in place in a larger water vessel with a cork. The outer vessel is a 2.5 liter Jena beaker, the bottom of which is covered with a layer of glass beads to facilitate the bubbling. The cork ring of the outer vessel is provided with a condenser, and is wrapped tightly with tinfoil to prevent the vapor from condensing in it and splitting the beaker. By pouring a layer of plaster of Paris over this tinfoil-covered cork ring, after the water vessel is in place, and coating this with a layer of the tin amalgam, the loss of vapor is reduced to a minimum, and solutions, as well as pure liquids, can be used as the boiling liquid. On any one day, using ether or chloroform, for example, the temperature of the water bath can be retained constant to within a tenth of a degree. From day to day, however, the temperature obtained will naturally change with changes in the barometric pressure. The first heat for ether and the second for chloroform, on the usual small electric stove give very satisfactory results. Just as in the above water bath, the tip here is leveled by aid of pieces of wood or card, or the stove is placed upon an adjustable stand.

Making a Determination of the Weight of a Falling Drop.

Before using the apparatus, the dropping tube and the ventilation tubes should be thoroughly cleansed with bichromate-sulfuric acid, water, alcohol, and ether (especial care being taken that all traces of lanolin are removed) and dried in a current of air. The weighing vessel, *i. e.*, the one on the tip side, is now cleaned and wiped dry with a piece of cheesecloth and placed in position on its plug, and a rubber band, which is attached to one hook, passed over its end and hooked around the other. The tube from the bulb is now connected to the tip ventilation tube, and pressure applied to the bulb, with its stopcock closed, by turning the screw head of the clamp. Sucking the drop over in this way allows a regulation which is utterly impossible when blowing it over, and further, the escape of vapor is thus blocked by the liquid on the one side and the bulb on the

[1] See the preceding paper.

other. Still retaining pressure on the bulb, the supply vessel, one-half full of the liquid to be investigated, is next put upon its plug, and fastened by a rubber band, as the other was. The purpose of the air pressure here is to prevent the liquid rising in the bore of the capillary to any distance above the surface of the supply liquid, until the determination is about to be made, when the liquid will flow through the *dry* bore, and thus cannot, by any possibility, drive before it small threads of liquid, such as might form, and remain unobserved, if the liquid at first filled the bore, and was then driven back. The air vessel is now put tightly in position on the disk, to protect the two vessels from the water of the bath, and fastened on each side by a rubber band running from the hook, around the lower part of the ventilation tube, and then around the hook again.

The apparatus is then put into the constant-temperature bath and allowed to stand until it has attained the proper temperature, *i. e.*, from 20–40 minutes. It should never be allowed to remain any longer than necessary in the water, and especially not over night, for, if it is, a leak is likely to develop, which will necessitate at least a new packing with amalgam, if not a new setting of the tip. The thermometer bulb should always be just at the bend of the tip tube, and midway between the two legs; it is held by a cork in the second large hole of the cover. A small thermometer placed in the air tube, with its bulb within the air vessel, sometimes shows a difference of 0.2°, but the correct temperature of the liquid, as it drops, as mentioned above, is that of the tube through which it passed, *i. e.*, that of the outside thermometer. While standing in the bath, the top is brought, by use of a level, to the position necessary to assure the constant, horizontal, position of the bottom of the tip. During this period of waiting, pressure must still be applied to the bulb, to keep the meniscus in the lower part of the supply end of the tip tube. Naturally, if the temperature is higher than that of the room, this object will be attained automatically, for the air in the weighing vessel warms more rapidly than the liquid, and having no other outlet, forces that back in the bore.

The temperature now being fixed, the bottom of the tip in its proper position, and the bulb one-half compressed; the liquid is sucked over very slowly, by releasing the pressure screw, until it forms a drop on the tip. It is here that the perfect and absolute control of the drop is apparent, when viewed through the reading glass; especially if the apparatus is placed against a light background, when the bright spot of light in the drop shows increases and decreases that could not be observed in any other way. It is well at this time to practice controlling the drop (*i. e.*, not attempting to make a weighing at first), as it will save much time and trouble later. When a weighing is to be made, the drop, once formed on the tip, is allowed to hang there, being kept at as near its maximum

size as possible, for 5 minutes. This is for the purpose of saturating the weighing vessel with vapor, so as to free the first drop which is to fall from changes due to evaporation, which might make its speed control difficult. At high temperatures, *i.e.*, near the boiling point, the amount of liquid necessary to saturate the weighing vessel with vapor is at times equal to the weight of one falling drop.

After the drop has hung for 5 minutes, 30 consecutive drops are allowed to fall, the count being kept on a tally register. *It must be borne in mind here that each drop at the instant of its fall must be forming with infinitesimal speed, and hence finally fall of its own weight alone.* The bright spot in the drop, seen through the reading glass against an illuminated white background, must be followed very closely during the formation, and the greatest care exerted, especially at the very last instant, to see that the above condition is fulfilled. The speed of formation, except at this final moment, may be comparatively rapid, so that the fall of the 30 drops will not necessarily require more than 15–30 minutes. Perhaps the best method of taking the drop is to start with such a suction on the bulb that the drop forms rather rapidly, and then gradually and continuously to decrease it until the bright spot shows only the slightest possible increase in size, and the drop falls of its own weight alone. When the last drop has fallen, the remaining portion on the tip is forced back very slowly until the meniscus is just at the tip end of the bore, the bore itself remaining full. When the liquid is anywhere near its boiling point, and perhaps it is best in all cases, the total time which has elapsed from the bringing over of the evaporating drop to the instant when the meniscus is fixed in the tip, is taken.

The apparatus is now removed from the bath and placed with the cover resting on a rubber-covered ring (an opening which allows the apparatus to be slipped in quickly), roughly dried with a towel, and the air vessel taken off. All this should be done as rapidly as possible. Next the supply vessel is removed, care being taken that the liquid in the capillary remains with its meniscus at the tip, which should be watched closely throughout. Then the supply end of the tip tube is touched with a piece of cheesecloth (if necessary the bulb being slightly compressed) until the liquid in the bore is drawn, as a column, and not broken up into threads, into the cloth, without the loss of any of the vapor which takes its place. When assured that there is no trace of liquid left in the capillary bore, a small glass containing water at room temperature (or iced for very volatil liquids) is raised around the weighing vessel so that the water rises a little higher than the liquid within it; it is retained in in this position for 1 minute. This causes the condensation of the vapor in the vessel, tip tube and ventilation tube, and also removes to the main amount any of that which may already have condensed

on the plug or on the tip—and in addition cools the liquid itself, so that the loss by evaporation during the removal of the vessel from its plug and the immediate insertion of the glass stopper is reduced to a minimum. This transfer should always be made as rapidly as possible, notwithstanding, and in the same way each time.

In weighing the vessel which contains the liquid that has fallen, the most satisfactory method is to wipe it to constant weight with a piece of cheesecloth, *i. e.*, after the first, approximate weight has been obtained, the vessel and stopper are wiped again and again, until further wiping does not change the weight, observed immediately after the wiping. The glass stopper of the vessel must naturally fit tightly, else losses on the balance will be observed, in case the liquid is volatil; while for very volatil liquids (boiling within 5–15° of room temperature) a cork must be substituted for the glass stopper, and a preliminary test made to show that no loss is observable after the vessel, which has stood for 10 minutes on the balance, is wiped and weighed.

The weight observed here, it must be remembered, is not, of course, the weight of the vessel plus that of the 30 drops, for it is increased by the weight of the vapor formed from the hanging drop in 5 minutes, and decreased by that of the vapor lost, both from the hanging drop and from those that have fallen, which may not have been condensed by the cold water. We cannot then simply subtract the weight of the empty vessel, plus that of the vapor formed from the hanging drop in 5 minutes, and expect to have the weight of 30 drops, except when the temperature is such that there is practically no evaporation, *i. e.*, when the vapor pressure at that temperature amounts to but a few millimeters. Furthermore, there may have been a distillation from the hanging drop to the liquid of those which have fallen, or *vice versa*—this would not be accounted for.

In order to take into account all these possible complications, and to eliminate them, the weighing vessel is cleaned and wiped dry and then replaced in position, after the tip ventilation tube and the tip tube have been cleaned with ether and dried with a current of air; and the apparatus set up again, exactly as before, and placed in the bath at the same temperature. Then, once again, when the temperature equilibrium is established and the cover leveled, a drop is run over and allowed to hang for 5 minutes; and then 5 consecutive drops are caused to form and fall, exactly as they did in the case of the 30. Here, however, the liquid is not immediately run back, but the 6th drop is allowed to hang at its maximum size (nearly), until the same total time has elapsed (from the running over of the evaporating drop to the fall of the last one) as in the case of the 30, when it is drawn back until the meniscus is just at the tip. The

apparatus is now removed, everything being done exactly as it was before, and the weighing vessel and stopper wiped to constant weight.

This weight, of course, will not be the weight of the vessel and 5 drops alone, but is the weight of these plus the vapor of 1 drop hanging for 5 minutes, *minus exactly the same total weight lost by evaporation, from every source, in the 30-drop determination.* By subtracting the weight of this 5-drop *blank* from the weight of the 30 previously determined, we must have the weight of 25 drops of the liquid falling from the tip in question, from which we can find the weight of a single falling drop, unaffected by evaporation, even though the temperature lies within a few degrees of the boiling point. Naturally, if the evaporation from the fallen drops is so great that the 5 drops no longer cover the bottom of the vessel, and present the same evaporating surface as the 30 did, 10 drops may be used as the blank, in which case the subtraction would give the weight of 20 in place of that of 25.

Whether or not all the possibilities of loss have been considered here, it is not possible to decide; it is quite certain, however, that this method of using a blank gives consistent results at all temperatures, even to within 4° of the boiling point.

In using this method it is very necessary with a new liquid to be assured that perfect control is possible at the very last instant before the fall of the drop, for otherwise a false result will be obtained. The question of the control of the drop usually resolves itself into a question of the size of the tip, and its relation to the size of the drop formed upon it. Thus the volume of a drop of carbon tetrachloride is so small that it is impossible to control it readily on a tip larger than 4.6 mm., for it suddenly spurts at the last instant and leads to results that are too large. This can always be predicted, however, from observation of the first drop. Thus far in the work no liquid has been found which can not be controlled easily on a tip of this size, while all liquids, with one or two exceptions, can be controlled easily on tips up to 6 mm. or larger.

Another necessary precaution is to see that the second and succeeding drops are identical in size, *i. e.*, that consecutive drops lead to the same result as a single drop. It is sometimes observed with pyridine that the second drop is smaller than the first. The remedy for this, and it should always be used at least once with a new liquid, is after the first drop has fallen to run the remainder back until the meniscus is just at the tip, and to start the second drop from there, and to continue in this way until the desired number of drops have been obtained. This difference is usually to be observed through the glass as a change in the profile of the drop. It is possible that this result is due to the fact that the remaining drop as it settles back into place after the fall assumes a different form from that which it would assume if it formed from the bore by

slowly collecting. Whatever the cause, however, the method advocated eliminates it; while in all other cases this method gives the same result as the regular one.

In the next paper of this series will be considered the standardization of a tip, and the calculation, from the drop weight, of surface tension and the molecular weight; while in the succeeding ones, which will appear in the immediate future, will be presented the results already obtained with the fifty or more liquids examined, using tips of various diameters.

LABORATORY OF PHYSICAL CHEMISTRY.

SOLUBILITY OF OXYGEN IN SEA WATER.

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It is a well recognized fact that oxygen is less soluble in sea water than in fresh water, and that in brackish water the solubility is intermediate, varying with the amount of chlorine present. In studying the pollution of the waters of harbors it is often desirable to express the amount of oxygen present in terms of "per cent. of saturation." Inasmuch as the proportion of sea water varies considerably in different samples it is not easy to determin this percentage on account of the lack of convenient tables showing the amount of oxygen dissolved in saturated waters containing different amounts of chlorine. For this reason the authors have investigated the literature on the subject and have prepared a convenient table for use.

One of the earliest investigations of the solubility of oxygen in sea water was made by Prof. William Ditmar, of Anderson's College, Glasgow, in connection with the Challenger expedition.[1] His method consisted of boiling off the dissolved gases, collecting and analyzing them. His results have been much used. They show the variations in the amount of oxygen in "sea water" dissolved at different temperatures, but do not state fully the corresponding amounts of chlorine in the water used for the experiments.

In connection with the study of the amount of dissolved oxygen in the Thames River, Clowes and Houston carried on some experiments on the solubility of oxygen in distilled water, sea water, and mixtures of the two in different proportions, at temperatures between 13.8° and 16° C.[2]

The data thus secured, taken in connection with the known variations

[1] "Report on Composition of Sea Water," by William Dittmar, *Challenger Report, Physics and Chemistry*, 1, 168. See also page 58 of the Report of Letts and Adeney on the "Pollution of Estuaries and Tidal Waters," Appendix 6 of the "Report of the Royal Commission on Sewage Disposal, 1908."

[2] Report to the London County Council by Dr. F. Clowes and Dr. A. C. Houston on "The Experimental Bacterial Treatment of London Sewage, 1892-1903," page 225.