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XXXV.—*A Microscopical Method of Determining Molecular Weights.*

By George Barger, Scholar of King's College, Cambridge.

This research, a preliminary account of which has been given in the Proceedings (1903, 19, 121), originated in Professor Errera's laboratory at Brussels, where experiments were being carried out on the hereditary adaptation of fungi to strong salt solutions. The fungi were grown in hanging drops of the solutions; each drop was suspended from the lower surface of a coverslip, which was separated from the slide by a cardboard frame, the chamber thus produced being

moistened from time to time with distilled water. The experiments generally lasted a few weeks, and it was noticed that the drops of the salt solutions invariably increased in size. This phenomenon was explained by Prof. Errera in the following manner. As the vapour pressure of the salt solutions was less than that of pure water at the same temperature, and as the drop was confined in a closed space, moistened by pure water, a condensation of vapour took place on the drop. Prof. Errera then asked me to study the effect quantitatively, and for this suggestion and for the kindly interest he has taken in the work I wish to express my hearty thanks. My earliest experiments were made either with small flasks or with small crystallising dishes, which could be completely closed by ground glass plates, but as the results were only of a qualitative character, I finally determined to study the behaviour of the drops in a capillary tube, so that their change in thickness could be measured under the microscope.

Description of the Method.

A solution of known strength of the substance, the molecular weight of which is unknown, is compared with standard solutions of a substance of known molecular weight, a series of drops taken alternately from the two solutions being introduced into a capillary tube (length 6—8 cm.; bore 1·5 mm.).

After the drops have been measured, the tube is put aside for some time varying from a few minutes to a day, and then another measurement is taken. If there is a decided difference in the vapour pressure of the two solutions employed, one series of drops will be found to have increased, while those alternating with them have decreased. In that case we can decide whether the solution experimented with contains more or less molecules than the standard solution, and so arrive at two limits for the unknown molecular weight.

The theory of the determination is very simple. Each drop is placed between two others of a different solution, and can evaporate on either side into a small, closed air-chamber. This chamber is soon saturated with vapour, which can condense freely on the drops. If the vapour pressures of the two solutions are equal, the evaporation will equal the condensation, and there will be no change in volume of the drops. If, on the other hand, the vapour pressures are unequal, there will be a gradient of vapour pressure in the air spaces; some drops will therefore be in contact with an atmosphere the vapour pressure of which is greater than their own. Condensation will take place on these drops and they will increase. The others, alternating with them, will have a vapour pressure greater than that of the adjoining

air spaces; these drops will evaporate and thus decrease. Hence there is a distillation from the drops of the one series to those of the other series, although all are at the same temperature.

By measurement, we can tell which drops increase, and hence ascertain which solution has the smaller vapour pressure. If the solvent is identical in both cases, and if the solutes are non-volatile, the solution with the smaller vapour pressure will have the greater concentration of molecules and *vice versâ*, and thus the determination of the molecular weight is rendered possible.

Preparation of Solutions.

The supply of the substance, the molecular weight of which is to be determined may be very limited, but good results have been obtained with as little as 30 milligrams. The substance is weighed out in a minute stoppered bottle or cylinder. A known volume of the solvent is then added from a pipette, for instance, a one c.c. pipette graduated in hundredths. It is generally easier to add enough of the solvent to dissolve the substance completely and then weigh the solution. To obtain the volume of the solution, we must know its density, but as the solution is generally dilute, we may, without great error, take its density as being equal to that of the pure solvent. The density of the solvent is easily estimated by a hydrometer.

It is best to express the concentration of the solution thus prepared by volume, and not by weight, as it is easier to make up the other (standard) solutions by volume.

The choice of the standard substance is determined by the following circumstances:

1. In the first place, it should neither be associated nor dissociated under the conditions of the experiment, that is to say, it should actually have the molecular weight deduced from its formula.

2. Secondly, the standard substance must neither combine with the solvent, nor with the other solute (for a certain amount of mixing of the two solutions is inevitable).

3. Thirdly, both the standard and the unknown substance should be very much less volatile than the solvent employed.

4. Fourthly, if the unknown substance is colourless, it is useful to employ a coloured substance as standard, for then one can always see at a glance to which solution a given drop belongs, and to what extent mixing has taken place.

Benzil and azobenzene are two good substances for work with organic liquids. They can be easily obtained pure, are freely soluble in most solvents, have normal molecular weights, and give coloured solutions.

With water, I have most frequently used cane sugar and boric acid. The latter substance has the advantage of not being attacked by moulds, so that its solutions can easily be kept unchanged; its electrolytic dissociation is so slight as to be negligible. The standard solutions are conveniently made up in 10 c.c. graduated stoppered measuring cylinders. It is then easy to obtain a solution of any desired intermediate strength by mixing two others. Sometimes it may be desirable to dilute a solution of known strength very slightly with the pure solvent. In that case, to the known volume of the solution the calculated quantity of the solvent from a one c.c. pipette graduated in hundredths can be added, this procedure being much more accurate than taking the difference between the two readings of the measuring cylinder.

With regard to choice of solvent, the method allows considerable latitude. The solvent need have neither a constant melting point nor a constant boiling point. Therefore, its purity is not an essential condition. Ether saturated with water, wet acetone (b. p. 56·7—65°) alcohol with 10 per cent. water, acetic acid with 20 per cent. water, can all be used successfully.

Boiling point determinations with acetone and pyridine, for instance, require specially purified samples of these substances, whereas by the microscopic method an approximate value of the molecular weight can easily be found in a short time. The best proof that a solvent of constant boiling point is not required is given by the experiments with light petroleum (b. p. 50—60°; see below).

Although the solvent need not be pure, it is obviously essential that all the solutions for one determination should be made up from the same sample. Very volatile solvents cannot be used, for with them it is impossible to fill tubes with any degree of accuracy. I have performed a few experiments with ether and obtained satisfactory results, but cannot recommend this solvent on account of the difficulty of manipulation. With a little care, carbon disulphide may be employed. If, on the other hand, the solvent is not sufficiently volatile, the experiment takes too long. Xylene is one of the least volatile solvents which can conveniently be used.

The *capillary tubes* are best prepared by drawing out soft glass tubing of $\frac{1}{2}''$ bore into capillaries of 1—2 feet long, which should be cut into smaller pieces, having a smooth, regular edge, in order that the tube may be closed tightly with the finger while it is being filled. The internal diameter of the capillaries should be between 1 and 2 mm., preferably about 1·5 mm. The influence of the bore will be discussed later.

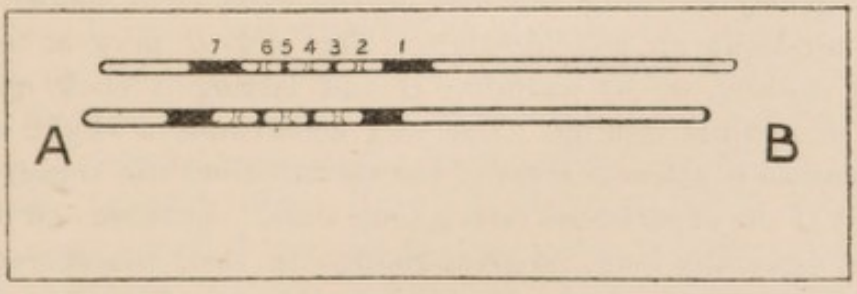
The *filling of the tubes* requires a little practice, but when this has been obtained it can be done quite rapidly. The tube is taken between

the middle finger and thumb, and its upper end, which should be rounded, is closed with the index finger. The other end is then dipped below the surface of one of the two solutions (which in the following experiments is always the standard one). By lifting the index finger very slightly, enough liquid is admitted into the tube to make a column of about 5 mm. long. The index finger is again pressed against the tube, so as to close it, and the tube is then held in a slanting position, with the open end uppermost. By again diminishing the pressure of the finger on the closed end, some air is allowed to escape, and the column of liquid slides down the tube. Its progress is regulated by the amount of slant given to the tube. When the column has travelled about 3 mm., it is stopped by closing the tube again with the finger. The tube is now once more held vertically, and its open end is made to touch the surface of the second solution, while the upper end is still closed by the index finger. This time only a minute drop enters, for the capillary forces are soon balanced by the increase in the pressure of the air inside the tube. The tube is then again held in a slanting position, and the small drop allowed to slide down a short distance, and so on.

Most organic solvents wet the glass and slide down the tube with ease, but with water, especially in narrow tubes, the drop descends very slowly or not at all. This difficulty can be overcome by previously wetting the tube with the first solution to be employed. The drops can also be sucked into the tube by heating the free end and then closing it with the finger. The air, on cooling, contracts, and the drop is forced in.

For the sake of uniformity, I always use tubes with 7 drops; when sealed, the tubes have the following appearance (natural size):

FIG. 1.



A is the end which has been dipped in the various solutions.

B is the end which is closed by the finger.

In the diagram, the drops are numbered in the order in which they have entered the tube, and the drops of the standard solution are shaded black. The first and last drops are about 5 mm. long, and are not measured, for they generally decrease by evaporation

into the air-spaces at *A* and *B*. They are also the ones most liable to become heated while sealing the tube; for this reason, they are made rather large, in order that their concentration may not so easily be changed by evaporation. The drops 2, 4, and 6 contain the substance the molecular weight of which is being determined.

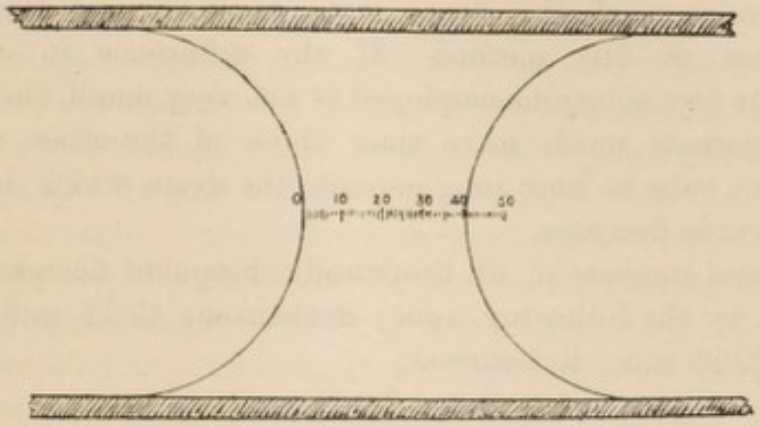
To ensure a rapid interchange of vapour with small differences of concentration, the drops should be close together—say 2 or 3 millimetres apart—but they must not be too close, or they will mix. The thickness of the drops 2—6 is limited by the size of the micrometer scale. Thicker drops can be measured with a lower objective, but then the measurements are, of course, less accurate. With a little practice, drops of the right thickness can easily be obtained. Water gives some difficulty on account of its high surface tension. If too much liquid has been sucked up, the excess can always be removed by means of filter paper. With some heavy liquids in wide tubes, the capillary rise is not great enough, in which case the end of the tube is dipped well under the surface of the liquid, and the pressure of the finger on the other end is slightly diminished until the right quantity of liquid has entered. The same procedure is sometimes necessary with very volatile solvents, the vapour of which may expand by the warmth of the hand, and so tend to drive out drops which have already entered.

When all the drops are in the tube, they are allowed to slide down until the last drop is about 1 cm. distant from the end *A*, and then this end is sealed carefully in the lower part of a small Bunsen flame, and withdrawn immediately. With volatile solvents (acetone, carbon disulphide, &c.), it is advisable to let the last drop get more than 1 cm. from the end *A* before sealing, but there is an objection to letting the drops slide so far down the tube, as will be seen later. Tubes with volatile liquids are best closed by means of soft paraffin wax, at least at the end *A*. A plug of the wax is introduced, and then, by gently warming the end of the tube, it is melted, so as to become air-tight on solidification. The end *B* may be closed by ordinary sealing, or by warming it and letting it suck up a little melted wax while cooling. The wax constitutes a slight source of error, because it attracts some of the solvent from the terminal drops, especially if the experiment lasts a long time. As these end drops are, however, especially long, no great change in their concentration need be feared. Instead of paraffin wax, fusible metal may be used, preferably d'Arcet's alloy with mercury, which melts at 45°. The difficulty here is in getting the alloy into the ends of the tube, owing to the negative capillarity of metals. It can perhaps best be accomplished by means of another thinner capillary, which is dipped into the melted alloy, and then, with some of the metal adhering, it is used to plug up the larger tube.

After the tubes have been filled, the drops are measured. For ease in handling and for purposes of identification, they are fixed to a microscope slide (3″ by 1″) by means of thick Canada balsam. Each slide is numbered and can take at least half a dozen tubes. The slides are placed in a glass Petri dish about $3\frac{1}{2}$″ square, and enough water is placed in the dish to cover the tubes, so that the drops are always at the same temperature, and do not move owing to the expansion of the air between them.

Under the microscope, the drops and scale present the following appearance:

FIG. 2.



A sharp image is obtained if the microscope is focussed to the level of the centre of the tube. The menisci then become exceedingly distinct, and the distance between them (which is the minimum thickness of the drop) can be measured. The Petri dish is moved till one of the menisci almost coincides with the zero of the scale; a drop of water between the stage and the dish allows the latter to be moved small distances without jerking. The exact coincidence of the meniscus with the zero is obtained by moving the eye-piece (with the scale in it) transversely in the tube of the microscope, in which it has a little play. As we are only concerned with the *direction* of the change in the drops, not with its *magnitude*, the scale need not be standardised. The distance between the menisci can now be read off to tenths of a scale division. As the micrometer has 50 divisions, 5 numbers below 500 are obtained for each tube. I use a $\frac{3}{4}$″ objective (Leitz, No. 3); with a lower one, larger drops can be measured on the scale, but the accuracy is correspondingly decreased. With higher objectives, the drops have to be inconveniently small, and the focussing also becomes difficult. The eye-piece should be a strong one, in order to magnify the scale as much as possible. I use a Leitz No. 4 eye-piece; a Zeiss micrometer disc is placed on its diaphragm. With a No. 3 objective, the magnification is about 65 diameters, so that a scale division is equivalent to 17 μ, and an accuracy of 3 μ is easily obtained.

The time during which the tubes have to be kept before a definite result is obtained varies greatly with the nature of the solvent, the difference in concentration of the solutions, &c.

The changes in the various drops of the same tube are by no means regular. Sometimes all the drops increase if the difference in concentration between them is small. The reason for this is that in filling the tube some of the solution adheres to its walls. This solution forms a dew of minute, convex drops, whereas the large drops, which are measured, have a concave surface. Now, other things being equal, the vapour pressure of a convex surface is greater than that of a concave one (Lehmann : *Molecularphysik*, vol. ii, p. 151). Hence the general tendency of the drops is to increase, and this limits the sensitiveness of the method. If the difference in concentration between the two solutions employed is not very small, the drops of one solution increase much more than those of the other solution, and often, if the tube be kept long enough, the drops which increase least will afterwards decrease.

This initial increase of all drops and subsequent decrease of some is illustrated by the following tube : azobenzene (0·19 mol.) and ethyl benzoate (0·20 mol.) in benzene :

Time.	Readings in tenths of scale divisions.				
12.15 p.m.	321	264	289	279	215
2.15 p.m.	325	272	292	297	214
5.30 p.m.	321	289	286	310	210

As already mentioned, solvents with very high boiling points cannot be used, because the change in the drops occurs too slowly. Theoretically, there is no good reason why tubes should not be kept for an indefinitely long time, so that even the smallest difference of vapour pressure might be demonstrated. In practice, I find, however, that when the difference between the two solutions is small, or when the solvent is insufficiently volatile, the changes in the drops are irregular.

The possibility of keeping tubes at temperatures other than the ordinary naturally suggests itself in this connection. I hoped by this means to apply the method to all high boiling solvents, but my experiments so far have not been successful. The difficulty arises from the necessity of cooling the tubes again before measuring. By cooling, the air spaces between the drops become super-saturated, and the solvent is condensed on the walls of the tube, which, being on the outside, are coldest. Hence, generally, all the drops are smaller than before they were heated.

If the tubes have not been heated too much and if they have been

cooled slowly (for instance, immersed in a large water-bath), good results may nevertheless be obtained. I have kept tubes with water or with acetic acid at a temperature of 37°, and in this way the change in the drops is more rapid than at the ordinary temperature. The temperature of the determination can therefore be varied within certain limits ; possibly this may be of use in studying the change of molecular weight with the temperature, for example, of substances which undergo association.

Consideration of the Probable Errors.

The effect of the various manipulations on the accuracy of the method will now be considered. Solutions can be prepared, the concentration of which is accurately known. The only difficulty arises when the supply of the substance is very limited. Through frequent use, the concentration of a solution may gradually undergo a change, for while a tube is being filled, the bottle containing the solution is left open. If the solvent is volatile, it may evaporate ; if hygroscopic, it may attract water from the air ; in the first case, the vapour pressure of the solution will always be lowered ; in the second case, it will only be lowered with low boiling solvents (acetone, alcohol).

If accuracy is desired, it is advisable, after an approximate value has been found, to repeat the last steps in the determination with freshly prepared solutions.

The error due to increased concentration of the solution can be overcome by weighing the residue left on evaporating a small quantity of the solution. This is most easily done with volatile solvents where it is at the same time of most importance. For the ordinary determinations in this paper, no such special precautions were taken, and the same standard solutions generally served for all the work with a given solvent. The principal object was to find a short and easy method of wide application, not necessarily a very accurate one.

The errors produced in filling the capillaries are as follows. Each drop remains for a moment at the end of the tube before it slides down and is placed between the drops of the other liquid. During this short time, it is exposed to the same influences as the solutions in an open bottle. It may evaporate and absorb moisture ; it presents a relatively large surface to the air, and so may change its vapour pressure. The time of exposure is, however, very short, and may be made approximately equal for the drops of both solutions. The two errors will then balance each other, as we are only concerned with the difference between the two solutions.

Some experiments were performed to study this source of error,

choosing acetone as solvent, because it is both volatile and hygroscopic.

Normal tube, both series of drops composed of benzil in acetone, 0·10 mole.,* and all exposed for 2—3 seconds.

3.21 p.m.	347	310	346	283	491
3.37 p.m.	351	312	345	290	490
4.3 p.m.	357	318	342	298	492

A similar tube, but with the 2nd, 4th, and 6th drops exposed for 10 seconds (the 1st and 7th drops were not measured).

	+	−	+	−	+
3.21 p.m.	349	401	366	330	388
3.37 p.m.	353	400	371	331	391
4.3 p.m.	367	392	382	326	396

It will be seen that whereas the first tube gives no clear result (theoretically, the drops ought not to change at all), the second tube shows that those drops which were exposed for 10 seconds have become distinctly more concentrated than the others.

To get an idea of the amount of concentration, two different solutions of benzil in acetone (strengths 0·09 and 0·10 mole.) were next used.

1. Normal tube, 0·10 benzil as standard (that is, drops 1, 3, 5, 7).

	−	+	−	+	−
11.59 a.m.	422	509	491	414	478
12.09 p.m.	420	510	488	416	476
12.57 p.m.	416	520	478	421	471

2. A similar tube with drops of 0·09 mole. exposed for 5 seconds.

	−	+	−	+	−
1.6 p.m.	346	392	331	394	328
1.16 p.m.	346	396	331	400	324
1.55 p.m.	342	402	330	412	336

3. Same as above, but drops of 0·09 mole. exposed for 10 seconds.

	−	+	−	+	−
11.59 a.m.	251	236	246	217	241
12.10 p.m.	250	240	250	220	246
12.57 p.m.	251	250	248	222	250

* Throughout this paper the term "mole." signifies a concentration of one gram-molecule per litre.

4. Same as before, but drops of 0·09 mole. exposed for 15 seconds.

1.6 p.m.	249	341	222	269	165
1.16 p.m.	253	341	224	269	176
1.55 p.m.	258	349	225	275	193

From these experiments, it would appear that by an exposure of a quarter of a minute a change of something like 10 per cent. is produced in the concentration of an acetone drop, for only the last tube of the series does not clearly indicate which solution is the stronger. As this time is far in excess of the ordinary differences which occur in filling a tube, the error can only be a slight one. At the same time, it may be one of the reasons for the occasional irregular behaviour of drops in the tube. Sometimes (when the difference between the two solutions is small) there is no regular alternation of increase and decrease, so that no conclusion can be drawn. In that case, the experiment must be repeated.

We now come to the chief interference with the concentration of the drops, namely, their *mixing* with one another. Each drop, as it slides down the tube, leaves a portion of itself behind on the walls. This is shown (in a dry tube) by the decrease of the first drop. The succeeding ones travel over a part which has already been wetted, so they retain their original thickness. As each drop is composed of a different solution from its predecessor, it becomes to some extent mixed with the other solution. That this is so can be easily shown by alternately using a colourless and a coloured solution. For instance, with a potassium permanganate solution and pure water all the drops become pink or red, and the only difference between them is in the intensity of their colour. By making the drops slide up and down the tube a number of times, the mixing becomes more complete, and the difference in their colour disappears.

At first sight, this might seem to be a fatal objection to the method, but such, however, is not the case. The mixing which takes place lessens the difference in concentration between the two series of drops. It cannot, however, obliterate this difference, still less produce a difference in the opposite direction, and the method is only concerned with the *direction* of the difference, not with its *absolute magnitude*. To return to the permanganate solution and water : the drops which were originally composed of pure water will become dilute permanganate solutions ; they can never be more concentrated than the other original permanganate drops. Even if an infinite amount of water were added to one drop of permanganate, the resulting mixture would never be pure water.

A difference must, therefore, always remain, and it must remain on

the same side as between the original solutions employed; if we can observe any regular changes in the drops, we shall be able to conclude which solution has the greater vapour pressure.

Although the mixing of the drops does not impair the reliability of the method, it makes it less sensitive. The rate of change depends on the difference between the concentration of the drops, and this difference is decreased by mixing. The mixing should therefore be reduced to a minimum, and it may be useful to consider what conditions will tend to make it so.

Firstly, the amount of liquid which adheres to the walls of the tube varies with the nature of the solution, and seems to depend on its viscosity as well as on its surface tension.

Secondly, the amount of mixing depends on the diameter of the tube. Suppose this diameter to be $2r$ and the average thickness of the film of liquid which adheres to the walls of the tubes to be δ (depending on the nature of the liquid), then, if the drop travel along the tube for a distance l, it will have lost $2\pi r\delta l$ (supposing δ to be small compared with r). If the average thickness of the drop be d, its volume will be $\pi r^2 d$. The proportional loss will be $\frac{2\pi r\delta l}{\pi r^2 d} = \frac{2\delta l}{rd}$, and this will approximately represent the amount of mixing. In order to reduce this to a minimum, l should be small, d and r should be large; δ is presumably a constant for a given liquid.

1. l should be small; this means that the drops should slide along as short a piece of the tube as possible.

The distances of each drop from the end of the tube by which it was admitted should be a minimum; the drops must, therefore, be close together, yet not so close that they come into contact and mix. The end drop must be near the entrance of the tube, yet not too close lest it becomes heated when the tube is sealed.

2. The thickness of the drop should be the greatest which can still be measured on the micrometer scale (except in the case of the first and last drops).

3. The tube should be fairly wide, yet sufficiently narrow to allow of the formation of stable drops by surface tension.

It is easy to show that the above general conditions are correct by comparing the behaviour of a coloured and a colourless solution in tubes of widely different bore. Iodine in chloroform and pure chloroform were used for this purpose. The extent of the mixing is indicated by the difference in shade of the two solutions after they have been made to slide up and down the tube a number of times. The difference between the drops sooner becomes imperceptible in the narrow capillary than in the wide one. In the same way, the influence of l and of d can be shown.

There is yet another reason why the drops should be close together; their proximity favours the rapid interchange of vapour. This may be inferred from the experiments of Stefan (*Sitzungsber. Wiener Akad.*, 1873, 68, 385) on the rate of evaporation in vertical capillaries. The rate is inversely proportional to the distance of the liquid surface in the tube to the mouth of the tube, and a similar law probably applies to the drops.

It may be asked whether the thin film of liquid which adheres to the walls of the tube does not constitute a permanent means of communication between neighbouring drops. In practice, no such interchange was ever detected (unless the drops actually touch each other). This is probably because the thin layer of liquid sticking to the side of the tube soon breaks up into a number of convex drops, which tend to disappear (as the vapour tension of a convex surface is greater than that of a concave one). Oily liquids which wet the glass with difficulty (ethylene dibromide, aniline) do not leave a uniform film adhering to the walls of the tubes, but a few relatively large drops, which makes it less convenient to work with these liquids.

The next possible source of error is in the closing of the tube. In most cases, the simplest plan is to seal it by holding the end in the lower part of a Bunsen flame. The flame should be steady and the tube should be removed from it as soon as it is completely sealed. The drops nearest the flame are liable to become slightly heated by this process, but the heating only lasts a very short time, so that no appreciable effect can be observed. With liquids such as ether and carbon disulphide and with chloroform (which seems to attack the glass), I prefer to close the tube with melted paraffin wax. In these cases, the heating effect is negligible, but a different error is introduced, because the paraffin wax attracts the organic solvent from the end drop and so gradually concentrates the latter. The end drop is, however, very large, in order that its concentration should only change slowly, whereas with volatile solvents, the change in the measured drops takes place very quickly, before the error due to the paraffin has time to make itself felt. The large size of the end drop is, of course, also useful in counteracting the error due to heating.

Occasionally the tube may turn out to be imperfectly closed; this is at once detected when the tube is measured under water by the movement of the drops and the entrance of the water. In that case, another tube had better be prepared.

In handling the tubes, they must not be jerked or dropped, for this produces sudden and irregular changes in the drops. If the tube is inconveniently long, it must not be scratched with a file, but a piece can be drawn off in a Bunsen flame.

The last error to be considered is the change in the shape of the

drops. The method presupposes that any change in the least diameter (that is, the distance measured) is accompanied by a corresponding change in the volume of the drop. Hence the curvature of the meniscus must remain the same.

This is invariably the case with nearly all organic solvents, but occasionally with water and some less volatile liquids the curvature changes, especially on one side of the drop and if the tube is not quite clean. It does not necessarily follow that the apparent change in the drops is in opposite direction to the real one, but they may become quite out of proportion. This change in the curvature of the meniscus is of rare occurrence and need only be considered with a few solvents; it can, moreover, be readily detected.

Attempted Improvements and Applications of the Method.

As was said in a previous section, the method only depends on knowing the direction of change in the drops (whether increase or decrease), not the amount of this change. Theoretically, if all the conditions were known, it should be possible to calculate the amount of this change, or, conversely, calculate at once from any observed change the difference in molecular concentration between the drops. It should, moreover, be possible to find the concentration of the unknown solution by interpolation, knowing its behaviour to two known solutions.

A good deal of time was spent in experimenting in this direction, with scarcely any result. The chief aim was to know the influence of the difference in concentration of the drops on their rate of change, the other conditions being kept constant.

To eliminate the variations in the diameter, pieces of thermometer tubing of uniform bore were used. The drops were placed at approximately equal distances from one another. All the solutions contained the same solute, and differed only in strength. The temperature was kept constant, and a special method of filling the tubes with capillary syringes was used in order to prevent mixing. The tubes were closed with wax.

Another attempt to study the change in the drops quantitatively was to use capillary tubes of about 6—10 mm. long, which were slightly constricted in the middle, so that they would, at this point, retain by capillarity a measured drop of a solution. These tubes were put horizontally into a Petri dish filled with distilled water without being sealed. In this way, mixing was excluded, as in the previous plan. These experiments did not even show a constant rate of change when all the known conditions were constant. The only

general statements which can be made about this rate of change in the drops is that it increases with the temperature, with the difference in concentration and with the proximity of the drops, and that the influence of the diameter of the tube is doubtful.

There are a few special problems which might perhaps be solved by the present method, such as the ionisation of salts in mixtures of an ionising with a non-ionising solvent. Similarly, the method may be used in studying association in mixtures of associative and a non-associative solvent (for example, alcohol and benzene). Some preliminary experiments on this are given at the end of the paper.

So far, I have mainly devoted myself to showing that the new method is reliable, widely applicable, and sufficiently accurate to be of real practical use in organic chemistry.

Results.

The value of a new quantitative method can only be proved by the results obtained with it; a large number of determinations with various solvents have therefore been made.

In the experimental records, I have not only mentioned in each case the strength of the two standard solutions—the one hypertonic, the other hypotonic to the unknown solution—but the actual changes which were observed in the drops are also given. In this way, the personal factor has been eliminated.

In order to illustrate the degree of sensitiveness, and by way of showing the accuracy obtainable in the micrometer readings, some measurements are first given with different urea solutions in 90 per cent. alcohol.

I. *Odd drops* 0·095 *mole.; even drops* 0·10 *mole.*

Concentration	0·095	0·10	0·095	0·10	0·095	0·10	0·095	0·10	0·095
Apr. 7, 11 a.m.	312	340	384	76	376	448	417	361	128
12 a.m.	312	340	378	82	369	448	413	360	126
1 p.m.	312	342	376	86	368	449	413	361	126
2 p.m.	311	344	372	92	362	449	413	361	125
3 p.m.	310	345	372	96	360	451	413	362	126
4 p.m.	308	346	370	100	358	450	412	362	128
5 p.m.	306	346	367	102	358	450	410	360	126
6 p.m.	304	348	366	105	356	450	408	361	130
Apr. 8, 10 a.m.	272	342	363	114	356	452	402	368	149

II. *Odd drops* 0·10 *mole.; even drops* 0·095 *mole.*

Concentration	0·10	0·095	0·10	0·095	0·10	0·095	0·10	0·095	0·10
Apr. 7, 11 a.m.	233	255	189	240	248	256	240	270	262
12 a.m.	235	253	190	236	248	256	239	267	261
1 p.m.	235	252	194	236	250	257	239	268	261
2 p.m.	335	250	195	234	250	258	239	265	263
3 p.m.	233	250	197	232	250	260	240	264	265
4 p.m.	232	250	199	232	251	261	240	262	266
5 p.m.	230	248	201	231	252	262	240	261	264
6 p.m.	230	247	202	230	252	262	240	261	265
Apr. 8, 10 a.m.	206	232	202	228	256	268	242	262	285

III. *Odd drops* 0·24 *mole.; even drops* 0·25 *mole.*

Concentration	0·24	0·25	0·24	0·25	0·24	0·25	0·24	0·25	0·24
Apr. 3, 1 p.m.	73	360	364	347	384	367	345	371	379
2.30 p.m.	75	367	356	342	382	368	341	372	372
4 p.m.	75	372	353	350	380	369	340	374	372
5.30 p.m.	73	375	351	354	377	367	336	373	365
Apr. 4, 10 a.m.	77	373	345	361	385	370	333	378	364
Apr. 6, 10 a.m.	36	344	325	358	408	354	342	382	372

The changes in the drops of the foregoing three tubes are very slight, yet they are so regular as to show the great accuracy of the measurements. The tables illustrate a further point: the drops on the right hand side, that is, those which have travelled furthest up the tube and have the greatest chance of becoming mixed, show, generally, a smaller rate of change than the other drops on the left. For this reason, I have confined myself to five measured drops. The first and the last drop in each tube, as seen in the preceding tables, do not behave in a regular manner. Therefore, the five above-mentioned drops were enclosed between two large ones which were not measured.

To economise space, in all further cases the *change* in the drops is alone recorded, not their actual measurement. For the same reason, the changes for those standard solutions which were most nearly isotonic with the unknown solution are alone given. By way of example, other concentrations of the standard solution have been included in the case of the first two determinations (glucose and mannitol in water). With these exceptions, therefore, only those tubes have been included which have the slowest rate of change. All the other tubes gave results more quickly on account of the greater difference between the two solutions contained in them.

Water.

Glucose, 25·02 grams per litre (0·139 mole.).

Cane sugar	0·05 mole.	18 hours	+230	−97	+71	−79	+71	+548
„ „	0·10 „	18 „	+26	−18	+25	−31	+30	+130
„ „	0·12 „	21 „	+6	−4	+9	−4	+4	+27
		46 „	+21	−22	+13	−10	+15	
„ „	0·13 „	3 „	+3	+1	+8	0	+2	
		22 „	+8	+3	+5	−1	+5	+16
		70 „	+18	+4	+15	−1	+10	
„ „	0·14 „	22 „	−1	0	−2	+2	−2	−7
„ „	0·15 „	18 „	−3	+8	0	+9	−4	−24
„ „	0·20 „	18 „	−41	+55	−57	+53	−45	−251
„ „	0·25 „	25 mins.	−3	+2	+1	+3	+1	
		18 hours	−75	+85	−81	+65	−78	−384

In the above and all subsequent tables of measurements, the first column gives the concentration of the standard solution, the second that of the time from the beginning of the experiment (where several times are given with one concentration, these times all apply to the same tube). The next column gives the changes observed during that time in five drops. The figures denote tenths of a micrometer scale division. As has already been said in the description of the method, the first, third, and fifth of these drops contain the substance the molecular weight of which is being determined (glucose in this case). The other two are composed of the standard solution, and in addition the whole series of five are enclosed between two large drops of the standard solution which are not measured. In the last column is shown the change between the aggregate thickness of the three glucose drops and that of the two cane sugar drops (in a period of about 20 hours). These figures show at once that the glucose solution is somewhere between 0·13 and 0·14 mole. They also show that the rate of change in the drops is greatly influenced by the difference between their concentrations.

Assuming the molecular weight of cane sugar to be 342, we have now for glucose M between $\frac{25{\cdot}02}{0{\cdot}14}$ and $\frac{25{\cdot}02}{0{\cdot}13}$.

M between 179—192. Mean 186; $C_6H_{12}O_6$ requires 180.

Mannitol, 15·69 grams per litre (0·0862 mole.).

Cane sugar	0·064 mole.	24 hours	+5	−7	+4	−7	+10	+33
„ „	0·072 „	24 „	+4	−4	+3	−2	+3	+16
„ „		48 „	+7	−5	+5	−5	+10	
„ „	0·080 „	24 „	0	−1	0	+1	+1	+1
		48 „	+2	−1	+1	+3	0	+1
„ „	0·088 „	24 „	−2	+5	−1	+3	−4	−15
		48 „	−1	+3	−1	+4	−1	
„ „	0·096 „	24 „	−2	+12	−7	+4	−5	−30

The mannitol solution is practically isotonic with the cane sugar of 0·080 mole.

$$M = \frac{15{\cdot}69}{0{\cdot}08} = 196\ ;\ C_6H_{14}O_6 \text{ requires } 182.$$

Mannitol, 11·41 grams per litre (0·063 mole.).

Cane sugar	0·056 mole.	8 hours	+1	+1	+1	+3	−2
		24 „	−2	+4	−3	+6	−6
„ „	0·060 „	8 „	+1	−1	+2	+2	+2
		24 „	0	−1	+1	−1	+2

Molecular weight of mannitol = 190—204, mean 197 ; $C_6H_{14}O_6$ requires 182.

Boric Acid as Standard.

Cane sugar, 95·76 grams per litre (0·28 mole.).

Boric acid	0·30 mole.	22 hours	0	−13	+12	−15	+12
„ „	0·29 „	17 „	−5	+14	−4	+8	+1

Molecular weight of cane sugar = 319—331, mean 325 ; $C_{12}H_{22}O_{11}$ requires 342.

In the foregoing and following calculations, no allowance has been made for the electrolytic dissociation of boric acid, but if ionisation is considered, then the result for cane sugar approaches more nearly to the theoretical value.

Urea, 12·00 grams per litre (0·20 mole.).

Boric acid	0·195 mole.	15 hours	+9	−5	+7	−11	+24
„ „	0·20 „	21 „	−1	+7	−1	+5	+1

Molecular weight of urea = 60—61·5 ; CH_4ON_2 requires 60.

Tartaric Acid, 30·00 grams per litre (0·20 mole.).

Boric acid	0·19 mole.	21 hours	+3	−1	+8	−2	+5
„ „	0·20 „	21 „	+4	+4	+3	+4	+10
		45 „	+4	+13	+9	+6	+19
other tube)	0·20 „	96 „	+10	+8	+8	−2	−1
	0·21 „	21 „	−6	+19	−3	+3	0

Molecular weight = 143—157 ; $C_4H_6O_6$ requires 150.

Succinic Acid, 18·29 grams per litre (0·155 mole.).

Boric acid	0·15 mole.	23 hours	+4	−4	+10	−15	−18
„ „	0·16 „	24 „	+2	+17	−1	+12	+1

Molecular weight = 114—122 ; $C_4H_6O_4$ requires 118.

Mannitol, 29·12 grams per litre (0·16 mole.).

Boric acid	0·165 mole.	22 hours	+10	−7	+9	−10	+11
„	0·17 „	18 „	−5	+8	−2	−4	0

Molecular weight = 166—171 ; $C_6H_{14}O_6$ requires 182.

Catechol, 15·95 grams per litre (0·145 mole.).

Boric acid	0·13 mole.	15 hours	+22	−9	+18	−5	0
„	0·14 „	23 „	−20	+19	−3	+30	−10

Molecular weight = 114—123 ; $C_6H_6O_2$ requires 110.

Glucose, 28·8 grams per litre (0·16 mole.).

Boric acid	0·17 mole.	18 hours	+14	−40	+33	−27	+38
„	0·175 „	21 „	−1	+3	−2	+1	−5

Molecular weight = 165—170 ; $C_6H_{12}O_6$ requires 180.

The following two determinations show electrolytic dissociation :

Potassium Nitrate, 10·1 grams per litre (0·10 mole.).

Boric acid	0·19 mole.	21 hours	+11	−18	+8	+1	+2
„	0·195 „	21 „	−1	+11	−31	0	0

i (van't Hoff's coefficient) = 1·92.

Sodium Chloride, 5·85 grams per litre (0·10 mole.).

Boric acid	0·17 mole.	21 hours	+10	−3	+10	−10	+18
„	0·175 „	24 „	+1	+1	−5	0	0
„	0·18 „	45 „	0	+13	+1	+18	−3

Taking the salt to be isotonic with 0·175 mole., $i = 1·75$.

Tryptophan. For a specimen of this substance, I have to thank Dr. F. G. Hopkins of Cambridge (*J. Physiol.*, 1903, **29**, 451).

Boric acid	0·075 mole.	1 day	+19	−1	+10	−1	+
Cane sugar	0·085 „	2 days	+3	+19	+1	+10	−1

Two c.c. of the solution left, on evaporation, 0·0368 gram of tryptophan

$$M = \frac{0{\cdot}0368}{0{\cdot}002 \times 0{\cdot}08} = 230\,;\ C_{11}H_{12}O_2N_2 \text{ requires } 204.$$

Alcohol.

The experiments were performed either with commercial "absolute" alcohol (99·5 per cent.), or with 90 per cent. methylated spirits.

α-Naphthol as Standard; 99·5 per cent. Alcohol.

Azobenzene, 30·94 grams per litre (0·17 mole.).

α-Naphthol	0·16 mole.	100 mins.	+13	−13	+20	−11	+1
„	0·18 „	125 „	−26	+21	−30	+32	−1

Molecular weight = 172—193; $C_{12}H_{10}O_2$ requires 182.

Phenyl Salicylate, 38·52 grams per litre (0·18 mole.).

α-Naphthol	0·17 mole.	50 mins.	+1	−3	+4	−3	+
„	0·19 „	90 „	−17	+14	−2	+5	−

Molecular weight = 203—227; $C_{13}H_{10}O_3$ requires 214.

Salicylic Acid, 24·84 grams per litre (0·18 mole.).

α-Naphthol	0·17 mole.	45 mins.	+5	−3	+5	−1	+
„	0·19 „	90 „	−10	+10	−12	+12	−

Molecular weight = 131—146; $C_7H_6O_3$ requires 138.

Benzoic Acid, 21·96 grams per litre (0·18 mole.).

α-Naphthol	0·17 mole.	30 mins.	+3	−1	+2	−1	−
„	0·19 „	90 „	−7	+4	−7	+1	−

Molecular weight = 115—129; $C_7H_6O_2$ requires 122.

Catechol, 19·80 grams per litre (0·18 mole.).

α-Naphthol	0·17 mole.	45 mins.	+5	−4	+3	−3
„	0·19 „	80 „	−3	+5	0	+9

Molecular weight = 104—116; $C_6H_6O_2$ requires 110.

Resorcinol, 19·80 grams per litre (0·18 mole.).

-Naphthol	0·17 mole.	80 mins.	+11	−9	+11	−3	+6
„	0·19 „	80 „	−10	+23	−22	+16	0

Molecular weight = 104—116; $C_6H_6O_2$ requires 110.

Quinol, 19·80 grams per litre (0·18 mole.).

-Naphthol	0·17 mole.	45 mins.	+4	−3	+11	−5	+6
„	0·19 „	80 „	−2	+7	−1	+6	0

Molecular weight = 104—116; $C_6H_6O_2$ requires 110.

Cinnamic Acid, 26·64 grams per litre (0·18 mole.).

-Naphthol	0·17 mole.	30 mins.	0	−5	+13	−9	+3
„	0·19 „	30 „	−2	−3	−5	−2	−8
		15 hours	−24	+40	−32	+37	−30

Molecular weight = 140—157; $C_9H_8O_2$ requires 148.

Acetanilide, 24·30 grams per litre (0·18 mole.).

-Naphthol	0·17 mole.	90 mins.	+4	0	+8	−4	+5
„	0·19 „	110 „	−8	+20	−17	+31	−19

Molecular weight = 128—143; C_8H_9ON requires 135.

Diphenylamine, 30·42 grams per litre (0·18 mole.).

α-Naphthol	0·17 mole.	60 mins.	+11	−7	+13	−9	+8
„	0·19 „	125 „	0	+7	−7	+6	+1

Molecular weight = 160—178; $C_{12}H_{11}N$ requires 169.

The error in the preceding ten determinations in no case exceeds per cent., but a greater deviation from the theoretical value was ound with the following substances: hippuric acid, diphenyl, dinitro-enzene, and urea. These all gave values which were more than 10 er cent. too high as compared with α-naphthol in absolute alcohol.

It was repeatedly found that the molecular weight of urea was too igh as compared with other substances. Urea is therefore not a ood standard. This is further illustrated by the first of the following ree determinations, all of which were carried out in 90 per cent. methylated spirit.

Urea as Standard; 90 per cent. Alcohol.

Phenyl Salicylate, 38·52 grams per litre (0·18 mole.).

Urea	0·18 mole.	20 hours	0	−6	+12	−10	+18
„	0·19 „	2 „	−2	+2	0	0	−3
„	0·20 „	2 „	−2	+6	−1	+5	−7

The change with 0·19 mole. is not very decisive. The phenyl salicylate solution gives values between 0·18 and 0·20 mole. (probably between 0·18 and 0·19). Taking the values 0·18 and 0·20, we get:

Molecular weight = 193—214; $C_{13}H_{10}O_3$ requires 213.

Phenyl Salicylate as Standard; 90 per cent. Alcohol.

Azobenzene, 29·12 grams per litre (0·16 mole.).

Phenyl salicylate	0·15 mole.	130 mins.	+8	−3	+21	+2	+
„	0·16 „	90 „	−13	+23	−13	+7	−2

Molecular weight of azobenzene = 182—194; $C_{12}H_{10}N_2$ requires 182.

Benzil, 23·10 grams per litre (0·11 mole.).

Phenyl salicylate	0·115 mole.	70 mins.	+20	−19	+18	−40	−
„	0·12 „	120 „	−6	+7	−10	+6	−

Molecular weight of benzil = 193—201; $C_{14}H_{10}O_2$ requires 210.

Acetone.

The acetone used for all the experiments contained water and boiled between 56·7° and 65°. Various substances were used as standard.

With Phenyl Salicylate as Standard.

Salicylic Acid, 27·40 grams per litre.

Phenyl salicylate	0·18 mole.	35 mins.	+12	−10	+15	−26	+
„	0·19 „	20 „	−7	+7	−10	+12	−

Molecular weight = 124—131, mean 127; $C_7H_6O_3$ requires 138.

Picric Acid, 45·80 grams per litre.

Phenyl salicylate	0·20 mole.	11 mins.	+11	−7	+8	−11	+
„	0·21 „	48 „	−3	0	−6	+5	−

Molecular weight = 217—229, mean 223; $C_6H_3O_7N_3$ requires 229.

Benzil, 42·00 grams per litre.

Phenyl salicylate	0·20 mole.	22 mins.	+54	−76	+93	−71	+75
„	0·21 „	15 „	−8	+71	−67	+88	−47

Molecular weight = 200—210, mean 205 ; $C_{14}H_{10}O_2$ requires 210.

Phenol, 18·8 grams per litre.

Phenyl salicylate	0·17 mole.	40 mins.	+6	0	+6	−2	+6
„	0·18 „	30 „	−8	+24	−22	+29	−14

Molecular weight = 103—111, mean 107 ; C_6H_6O requires 94.

With Salicylic Acid as Standard.

Phenol, 18·8 grams per litre.

Salicylic acid	0·16 mole.	20 mins.	+48	−12	+3	−2	+11
„	0·17 „	20 „	−21	+75	−48	+27	−21

Molecular weight = 111—119, mean 115 ; C_6H_6O requires 94.

The two values for phenol are a good deal too high. This is because the vapour pressure of phenol is not negligible at the ordinary temperature. To further illustrate this point, I made some determinations with aniline as standard. Although two substances having approximately the same boiling point need not have nearly the same vapour pressure at the ordinary temperature, yet the boiling point gives a general indication as to the volatility of the substance.

With Aniline as Standard.

Phenol, 18·8 grams per litre.

Aniline	0·19 mole.	80 mins.	+22	−3	+16	−19	0
„	0·20 „	120 „	−4	+14	+1	+5	−14

Molecular weight = 94—99, mean 97 ; C_6H_6O requires 94.

Nitrobenzene, 24·6 grams per litre.

Aniline	0·19 mole.	25 mins.	+2	−5	+16	−15	+2
„	0·20 „	25 „	−13	+1	−13	+17	−21

Molecular weight = 117—123, mean 120 ; $C_6H_5O_2N$ requires 123.

Ethyl Benzoate, 30·00 grams per litre.

Aniline	0·19 mole.	50 mins.	+30	−2	+7	−11	+10
,,	0·20 ,,	20 ,,	−5	0	−5	+2	−5

Molecular weight = 143—150, mean 146; $C_9H_{10}O_2$ requires 150.

The last three determinations give good results. The boiling points of phenol, nitrobenzene, and ethyl benzoate are close to that of aniline. With the same standard, the molecular weight of a considerably less volatile substance is found to be too low.

Phenyl Salicylate, 38·52 grams per litre (0·18 mole.).

Aniline	0·21 mole.	60 mins.	0	−30	+70	−92	+175
,,	0·22 ,,	—	−6	+12	−7	+2	−11

Molecular weight = 175—182, mean 178; $C_{13}H_{10}O_3$ requires 214.

In the same way, the molecular weights of salicylic acid and of catechol are found to be more than 10 per cent. too low when these substances are compared with aniline. Conversely, for camphor and phenetole, which are more volatile, values are found which are a good deal too high.

As a last example of a determination in acetone solution, I give that of a new substance kindly given me by Dr. Ruhemann (Trans., 1903, 84, 1133).

Dimethoxybisketocoumaran.

Owing to the small quantity available (0·04 gram) the process was slightly modified. The strength of the solution of the substance was determined after it had been rendered isotonic with a solution of benzil.

1·0415 grams of the solution left a residue of 0·0315 gram of the substance. The density of the acetone was 0·794; hence the volume of this solution was 1·312 c.c. and the solution contained 24·01 grams per litre.

The following readings were obtained:

With benzil,	0·0775 mole.	23 mins.	+9	−7	+31	−19	+19
,,	0·080 ,,	30 ,,	0	+4	0	+4	−3
,,	0·0825 ,,	13 ,,	−4	+13	−3	+7	−8

The solution of the new substance was therefore between 0·0775 and 0·080 mole.

Taking 0·0775 as the value, we get $M = \frac{24{\cdot}01}{0{\cdot}0775} = 309$. $C_{18}H_{14}O_6$ requires 326.

Acetic Acid.

Glacial acetic acid was used, with benzil as standard substance.

Acetanilide, 18·90 grams per litre (0·14 mole.).

Benzil	0·135 mole.	23 hours	+45	−68	+95	−105	+160
„	0·145 „	23 „	−10	+36	−20	+12	−89

Molecular weight = 130—138, mean 134; C_8H_9ON requires 135.

Triphenylmethane, 34·16 grams per litre (0·14 mole.).

Benzil	0·135 mole.	45 hours	0	−9	+2	−3	+5
„	0·145 „	21 „	−58	+30	−30	+29	−31

Molecular weight = 236—253, mean 245; $C_{19}H_{16}$ requires 244.

Picric Acid, 27·48 grams per litre (0·12 mole.).

Benzil	0·115 mole.	19 hours	+10	−4	+23	−6	+7
„	0·12 „	19 „	−16	+21	−31	+37	−10

Molecular weight = 229—239, mean 234; $C_6H_3O_7N_3$ requires 229.

Diphenyl, 21·56 grams per litre (0·14 mole.).

Benzil	0·10 mole.	17 hours	+10	−4	+23	−6	+7
„	0·11 „	21 „	−16	+21	−31	+37	−10

Molecular weight = 196—216, mean 206; $C_{12}H_{10}$ requires 154.

The last of these determinations was repeated, but the same high value was found, this inaccuracy differing markedly from the exact results obtained in the three preceding examples.

The following is an example of a determination in a mixed solvent namely, 80 per cent. acetic acid, 20 per cent. water:

Acetanilide, 29·83 grams per litre.

Urea	0·20 mole.	17 hours	+6	+1	+12	−3	+5
„	0·208 „	17 „	−4	+24	−6	+8	−1

Molecular weight = 143—147, mean 145; C_8H_9ON requires 135.

Benzene.

In all the experiments except the last, azobenzene was used as standard substance; in this case, it was benzil.

Benzil, 42·00 grams per litre (0·20 mole.).

Azobenzene	0·19 mole.	4 hours	+4	−9	−2	−6	+7
,,	0·21 ,,	30 mins.	−13	+5	−8	+11	−3

Molecular weight = 200—221; $C_{14}H_{10}O_2$ requires 210.

Diphenyl, 30·80 grams per litre (0·20 mole.).

Azobenzene	0·19 mole.	100 mins.	+7	−2	+5	+3	+10
,,	0·20 ,,	18 hours	−32	+11	−20	−2	−13

Molecular weight = 154—162, mean 158; $C_{12}H_{10}$ requires 154.

Triphenylmethane, 48·80 grams per litre (0·20 mole.).

Azobenzene	0·20 mole.	30 mins.	+4	−10	0	0	+3
,,	0·215 ,,	3 hours	−2	+9	−8	+4	−2

Molecular weight = 227—244, mean 235; $C_{19}H_{16}$ requires 244.

Diphenylamine, 33·80 grams per litre (0·20 mole.).

Azobenzene	0·19 mole.	100 mins.	+3	0	+4	+1	+4
,,	0·21 ,,	100 ,,	−1	+6	−4	+3	0

(With 0·20 mole., no definite result could be obtained.)

Molecular weight = 161—177; $C_{12}H_{11}N$ requires 169.

α-Nitronaphthalene, 34·60 grams per litre (0·20 mole.).

Azobenzene	0·18 mole.	75 mins.	+9	−7	+1	−3	+1
,,	0·20 ,,	5 hours	−10	−2	−13	+8	−12

(With 0·19 mole., no definite result could be obtained.)

Molecular weight = 173—192, mean 183; $C_{10}H_7O_2N$ requires 173.

m-*Dinitrobenzene*, 32·26 grams per litre (0·192 mole.).

Azobenzene	0·18 mole.	75 mins.	+7	0	−2	−4	+6
,,	0·19 ,,	2 hours	+1	0	−21	+3	−4

Molecular weight = 170—179, mean 175; $C_6H_4O_4N_2$ requires 168.

Ethyl Benzoate, 30·00 grams per litre (0·20 mole.).

Azobenzene	0·18 mole.	70 mins.	+16	0	+5	−2	+7
,,	0·19 ,,	5 hours	0	+25	−3	+31	−5

Molecular weight = 158—167, mean 162; $C_9H_{10}O_2$ requires 150.

Ethyl benzoate is slightly volatile; phenetole is still more so, and accordingly gives a higher molecular weight.

Phenetole, 23·42 grams per litre (0·192 mole.).

Azobenzene	0·16 mole.	40 mins.	+12	−1	+5	+1	+12
,,	0·17 ,,	150 ,,	−9	+16	−1	+40	−14

Molecular weight = 138—146, mean 142; $C_8H_{10}O$ requires 122.

Triphenylguanidine, 28·70 grams per litre (0·10 mole.).

Azobenzene	0·09 mole.	65 mins.	+53	−2	+8	−8	+1
,,	0·10 ,,	130 ,,	−7	+9	−1	+6	−3

Molecular weight = 287—319, mean 303; $C_{19}H_{17}N_3$ requires 287.

The following acids show association in benzene solution:

Benzoic Acid, 24·40 grams per litre (0·20 mole.).

Azobenzene	0·10 mole.	85 mins.	+6	−3	+3	−1	+2
,,	0·11 ,,	70 ,,	0	+6	−4	+1	0

Molecular weight = 222—244, mean 233; $C_7H_6O_2$ requires 122.

Cinnamic Acid, 29·60 grams per litre (0·20 mole.).

Azobenzene	0·17 mole.	45 mins.	−31	+27	−22	+20	−27

The change in the drops is a large one in a small time.
The molecular weight is considerably above 174; $C_9H_8O_2$ requires 148.

Azobenzene, 20·02 grams per litre (0·11 mole.).

Benzil	0·10 mole.	4 hours	+12	−44	+18	+3	+17
,,	0·12 ,,	4 ,,	−15	+13	+2	+22	−1

Molecular weight of azobenzene = 167—200; $C_{12}H_{10}N_2$ requires 182.

Chloroform.

With chloroform, there was often some difficulty in sealing the tubes; the glass was attacked, and did not fall together very easily. Hence paraffin wax was always used to close the capillaries.

Phenyl Salicylate as Standard.

Benzil, 42·00 grams per litre (0·20 mole.).

Phenyl salicylate	0·19 mole.	2 hours	+16	−19	+30	−23	+52
,,	0·21 ,,	2 ,,	−11	+4	−8	+4	−2

Molecular weight = 200—220; $C_7H_{10}O_2$ requires 210.

m-*Dinitrobenzene*, 33·60 grams per litre (0·20 mole.).

henyl salicylate	0·21	mole.	2	hours	+19	−6	+3	−6	+14
„	0·22	„	3	„	−4	+3	−7	+18	−21

Molecular weight = 153—160; $C_6H_4O_4N_2$ requires 168.

Benzil as Standard.

Triphenylmethane, 24·40 grams per litre (0·10 mole.).

Benzil	0·095	mole.	2	hours	+19	−6	+3	−6	+14
„	0·105	„	3	„	−4	+3	−7	+18	−21

Molecular weight = 232—256; $C_{19}H_{16}$ requires 244.

Diphenyl, 15·40 grams per litre (0·10 mole.).

Benzil	0·095	mole.	1	hour	+4	−8	+1	−6	+2
„	0·105	„	1	„	−6	+2	−4	+4	−1

Molecular weight = 146—162; $C_{12}H_{10}$ requires 154.

Diphenylamine, 16·90 grams per litre (0·10 mole.).

Benzil	0·09	mole.	10	mins.	+7	+1	+7	+2	+7
„	0·095	„	2	hours	−5	+3	−1	+3	−3

Molecular weight = 178—188; $C_{12}H_{11}N$ requires 169.

m-*Dinitrobenzene*, 16·80 grams per litre (0·10 mole.).

Benzil	0·09	mole.	2	hours	+31	−22	+16	0	+37
„	0·095	„	3	„	−2	+14	−3	+11	−1

Molecular weight = 177—187; $C_6H_4O_4N_2$ requires 168.

Phenyl Salicylate, 21·40 grams per litre (0·10 mole.).

Benzil	0·09	mole.	40	mins.	+3	−2	+6	−3	+8
„	0·095	„	2	hours	−8	+5	−1	+6	−5

Molecular weight = 225—238; $C_{13}H_{10}O_3$ requires 214.

α-Nitronaphthalene, 17·30 grams per litre (0·10 mole.).

Benzil	0·09	mole.	90	mins.	+15	−1	+3	0	+6
„	0·10	„		—	−12	+9	−5	+6	−7
„	0·095	„	(gave no distinct result)						

Molecular weight = 173—192; $C_{10}H_7O_2N$ requires 173.

Caffeine (anhydrous, dried at 110°), 19·4 grams per litre (0·10 mole.).

Benzil	0·10	mole.	3 hours	+10	−9	+4	−6	+10
,,	0·105	,,	1 hour	−8	+4	−2	+6	−7

Molecular weight = 185—194 ; $C_8H_{10}O_2N_4$ requires 194.

Caffeine (with water of crystallisation), 21·2 grams per litre (0·10 mole.).

Benzil	0·105	mole.	2 hours	+6	−4	+28	−12	+28
,,	0·11	,,	2 ,,	−3	+4	−1	+2	−1

Molecular weight = 193—202 ; $C_8H_{10}O_2N_4,H_2O$ requires 212.

Cocaine (crystalline, dried at 110°), 30·3 grams per litre (0·10 mole.).

Benzil	0·105	mole.	50 mins.	+2	−22	+13	−17	+17
,,	0·11	,,	—	−6	+9	−6	+5	−10

Molecular weight = 275—289 ; $C_{17}H_{21}O_4N$ requires 303.

Piperine (air-dried crystals), 28·5 grams per litre (0·10 mole.).

Benzil	0·105	mole.	45 mins.	+14	−8	+16	−2	+2
,,	0·11	,,	100 ,,	−2	+10	−5	+4	−4

Molecular weight = 259—271 ; $C_{17}H_{19}O_3N$ requires 285.

Quinine (precipitated, dried at 120°), 32·4 grams per litre (0·10 mole.).

Benzil	0·09	mole.	50 mins.	+5	−3	+6	−5	+20
,,	0·095	,,	2 hours	−24	+27	−20	+30	−22

Molecular weight = 341—360 ; $C_{20}H_{24}O_2N_2$ requires 324.

Phenylbenzylmethylethylammonium Iodide.

For a specimen of this salt, I am indebted to Mr. H. O. Jones (Trans., 1903, 83, 1419). Two determinations were made.

I. *Triphenylmethane as Standard.*

0·0487 gram of the iodide was dissolved in 2 c.c. of chloroform, this being equivalent to 24·35 grams per litre.

Afterwards 2·358 grams of the solution left 0·0370 gram of salt, dried at 70°. Density of chloroform = 1·502.

This gives a concentration of $\frac{37 \times 1{\cdot}502}{2{\cdot}358} = 23{\cdot}6$ grams per litre. Mean concentration = 23·9 grams per litre.

Triphenylmethane	0·07 mole.	30 mins.	+22	−11	+20	−22	+42
„	0·075 „	70 „	+4	+4	+2	+5	+9
„	0·08 „	30 „	−5	+4	−3	+3	−3

Taking the concentration to be 0·075 mole.: $M = \frac{23·9}{0·075} = 319$.

II. *Azobenzene as Standard.*

0·2008 gram of salt in 8 c.c. = 25·1 grams per litre.

Azobenzene	0·07 mole.	35 mins.	+15	−10	+4	0	+3
„	0·075 „	23 „	−3	+2	−1	0	−5

Mean = 0·725 mole.

$$M = \frac{25·1}{0·0725} = 346\ ;\ C_{16}H_{20}NI \text{ requires } 353.$$

α-*Phenylbenzylmethylallylammonium Iodide.*—This salt, for a sample of which I am indebted to Mr. H. O. Jones, is of special interest because Wedekind, its discoverer, has recently found that by the ebullioscopic method its molecular weight is one-third of the normal value (*Zeit. physikal. Chem.*, 1903, 46, 235).

Triphenylmethane as Standard.

0·2771 gram of salt in 4·70 c.c. = 59·0 grams per litre (0·162 mole. theoretically).

Triphenylmethane	0·17 mole.	—	−16	+13	−8	+9	−6
„	0·15 „	70 min.	−1	+9	−3	+3	−4

This was within a few hours of making up the iodide solution. The molecular weight of the salt is greater than the normal value. Next morning, the determination was continued:

Triphenylmethane	0·15 mole.	20 mins.	+6	−1	+3	−2	+5
„	0·17 „	15 „	−1	+4	−1	+5	−5
„	0·155 „	1 hour	+10	−4	+3	−5	+15

Taking the numbers 0·155 and 0·17 (intermediate concentrations giving uncertain results), it was found that the values for the molecular weight ranged between 335 and 381 (mean 358); $C_{17}H_{20}NI$ requires 365.

A second determination was made.

0·5450 gram of salt in 7·60 c.c. of chloroform = 71·71 grams per litre (0·196 mole.).

Within 2 hours of making up this solution :

Triphenylmethane	0·150 mole.	—	+8	−2	+14	−28	+26
,,	0·165 ,,	35 mins.	−23	+20	−23	+9	−12

Molecular weight = 435—478, mean 457.

The salt is therefore associated, as in the previous determination. The new solution (71·71 grams per litre) was now directly compared with the old one (59·0 grams per litre), which had been made some days previously.

The old solution as standard	7 mins.	−8	+9	−5	+10	−11

The new solution contains, therefore, less molecules. Two days later this had changed :

The old solution as standard	95 mins.	+10	−5	+5	−6	+34

The molecular weight in the new solution had diminished. The following numbers were obtained :

Triphenylmethane	0·21 mole.	7 mins.	−8	0	−2	+7	−2
,,	0·238 ,,	15 ,,	+18	−1	+2	−1	+21

Molecular weight between 301 and 341, mean 321.

The effect of heat was next tried. The second iodide solution was divided into two parts, one of which was kept overnight at the ordinary temperature, the other at 37°, both in tightly stoppered bottles in the dark. The determinations were made on the following day, the solution which had not been heated being taken as standard :

30 mins.	+22	−16	+17	−9	+15

The molecular concentration of the solution has been, therefore, considerably increased by heating. This explains the fall in the molecular weight observed by Wedekind in employing the ebullioscopic method.

Carbon Disulphide.

Triphenylmethane was used as standard. The other substances were used in solutions of 0·20 mole.

Azobenzene, 36·4 grams per litre.

Standard	0·19 mole.	15 mins.	+13	−14	+14	−17	+6
,,	0·20 ,,	100 ,,	−26	−2	−28	+5	−2

Molecular weight = 182—192, mean 187 ; $C_{12}H_{10}N_2$ requires 182.

Diphenyl, 30·8 grams per litre.

Standard	0·20 mole.	35 mins.	+3	+1	+4	0	+8
,,	0·21 ,,	45 ,,	−7	+3	−12	0	−32

Molecular weight = 147—154, mean 150; $C_{12}H_{10}$ requires 154.

Phenyl Salicylate, 42·8 grams per litre.

Standard	0·18 mole.	50 mins.	+2	−7	−4	−8	+1
,,	0·19 ,,	—	−15	−11	−19	+6	−30

Molecular weight = 225—238, mean 232; $C_{13}H_{10}O_3$ requires 214.

α-Nitronaphthalene, 34·6 grams per litre.

Standard	0·18 mole.	—	+5	−1	0	+4	+10
,,	0·19 ,,	15 mins.	−18	−2	−30	+7	−16

Molecular weight = 172—192, mean 182; $C_{10}H_7O_2N$ requires 173

Ethyl Benzoate, 30·0 grams per litre.

Standard	0·19 mole.	25 mins.	+2	−7	0	12	+2
,,	0·20 ,,	35 ,,	−14	+17	−6	1	−7

Molecular weight = 150—158, mean 154; $C_9H_{10}O_2$ requires 150.

Phenetole, 24·4 grams per litre.

Standard	0·18 mole.	15 mins.	+9	−3	+5	−1	+3
,,	0·19 ,,	35 ,,	−16	+1	−1	+17	0

Molecular weight = 128—136, mean 132; $C_8H_{10}O$ requires 122.

The behaviour of the last two substances is interesting, since ethyl benzoate is very slightly volatile, and phenetole rather more so. In benzene, for instance, solutions of 0·20 mole. behave as if they were respectively between 0·18 and 0·19 mole. and between 0·16 and 0·17 mole. Carbon disulphide is much more volatile than benzene, so ethyl benzoate and phenetole approach more nearly to the theoretical values. As the latter substance is the more volatile of the two, it gives a greater difference from the theory than the former.

Benzoic Acid, 24·4 grams per litre.

Standard	0·10 mole.	30 mins.	+45	−77	+60	−40	+37
,,	0·11 ,,	—	−8	+9	−4	+8	0

Molecular weight = 222—244, mean 233; $C_7H_6O_2$ requires 122.

Phenol, 18·4 grams per litre.

Standard	0·10 mole.	—	+5	+1	+5	+1	+4
,,	0·11 ,,	12 mins.	−1	+5	−1	+1	−2

Molecular weight = 167—184, mean 180; C_6H_6O requires 94.

It will be seen that, while ethyl benzoate and phenetole give normal values, the substances with which they are closely connected, namely, benzoic acid and phenol, have almost double the normal molecular weight. This association was to be expected in a non-hydroxylic solvent like carbon disulphide. When the hydrogen of the hydroxyl is replaced by ethyl, the association disappears.

Sulphur.

The determination of the molecular weight of sulphur in carbon disulphide gave the following numbers:

Triphenylmethane,	0·14 mole.	14 mins.	+4	−8	+6	−20	+5
,,	0·15 ,,	35 ,,	−1	+18	0	+5	−2

After these results had been obtained, the strengths of the standard solutions were checked. Of the solution called 0·15 mole., 5 c.c. left on evaporation 0·2030 gram of triphenylmethane. Its concentration had, therefore, changed during the determination to 0·166 mole., and the other solution, obtained from it by dilution, was in reality 0·155 mole. The mean = 0·160 mole. may be taken to represent the strength of the sulphur solution.

Of this, 1·70 c.c. left on evaporation 0·0738 gram of sulphur, that is, 43·4 grams per litre.

1·00 c.c. left on evaporation 0·0432 gram of sulphur, that is, 43·2 grams per litre.

Mean, 43·3 grams per litre. 0·160 gram-molecules = 43·3.

Molecular weight of sulphur = 270 = $S_8 - S_9$.

This is in close agreement with the value previously obtained by E. Beckmann (*Zeit. physikal. Chem.*, 1890, 5, 8) who finds as an average $S_8 = 256$.

Light Petroleum.

A fraction boiling between 50° and 60° was obtained from ordinary light petroleum by distilling once with a Young's still-head. All the substances were tried at a concentration of 0·10 mole., on account of the sparing solubility of certain of them. Azobenzene was used as standard in all cases.

Triphenylmethane, 24·4 grams per litre.

Azobenzene	0·10 mole.	40 mins.	+5	−1	+1	−6	+3
„	0·108 „	25 „	+1	+9	+1	+11	−6

Molecular weight = 226—244, mean 235; $C_{19}H_{16}$ requires 244.

Diphenyl, 15·4 grams per litre.

Azobenzene	0·09 mole.	14 mins.	+8	+1	+4	0	+5
„	0·10 „	150 „	−10	+14	−21	+30	+3

Molecular weight = 154—169, mean 162; $C_{12}H_{10}$ requires 154.

Diphenylamine, 16·9 grams per litre.

Azobenzene	0·09 mole.	100 mins.	+2	−15	+59	−29	+36
„	0·10 „	40 „	−1	+7	−8	+26	+6

Molecular weight = 169—186, mean 178; $C_{12}H_{11}N$ requires 169.

Phenyl Salicylate, 21·4 grams per litre.

Azobenzene	0·10 mole.	40 mins.	+5	−1	+1	−6	+3
„	0·108 „	—	+1	+10	+4	+10	0

Molecular weight = 198—214, mean 206; $C_{13}H_{10}O_3$ requires 214.

The above non-volatile substances give quite satisfactory values for their molecular weight, but this is not the case with the following substances, the vapour pressure of which at the ordinary temperature is not negligible.

Camphor, 15·2 grams per litre.

Azobenzene	0·07 mole.	15 mins.	+6	−14	+7	−10	+5
„	0·08 „	85 „	−11	+21	−12	+37	−6

Molecular weight = 190—217, mean 203; $C_{10}H_{16}O$ requires 152.

Naphthalene, 12·8 grams per litre.

Azobenzene	0·07 mole.	15 mins.	+6	−1	+9	−4	+2
„	0·08 „	130 „	−11	+48	−59	+47	−2

Molecular weight = 160—183, mean 171; $C_{10}H_8$ requires 128.

Phenetole, 12·2 grams per litre.

Azobenzene	0·07 mole.	15 mins.	+3	−5	+1	0	0
„	0·08 „	85 „	−9	+58	−47	+30	−13

Molecular weight = 152—174, mean 163; $C_8H_{10}O$ requires 122.

Ethyl Benzoate, 15·0 grams per litre.

Azobenzene	0·08 mole.	85 mins.	+29	0	+20	0	+30
„	0·09 „	—	−1	+10	−4	+20	−2

Molecular weight = 167—187, mean 177 ; $C_9H_{10}O_2$ requires 150.

As might have been expected, ethyl benzoate gives a result most nearly approaching to the real value, because it is the least volatile of this series. As petroleum is a non-hydroxylic solvent, phenols, acids, &c., are associated in it, and give high values for their molecular weights. This is shown by the following examples :

Thymol, 15·0 grams per litre.

Azobenzene	0·07 mole.	30 mins.	+4	−6	+1	−10	−3
„	0·08 „	35 „	−1	+12	−13	+30	−18

Molecular weight = 188—214, mean 201 ; $C_{10}H_{14}O$ requires 150.

Trichlorophenol, 19·7 grams per litre.

Azobenzene	0·07 mole.	35 mins.	+15	+2	+25	+3	+20
„	0·08 „	35 „	−1	+9	−3	+27	−3

Molecular weight = 246—281, mean 263 ; $C_6H_3OCl_3$ requires 197.

Pyridine.

The pyridine, which was a commercial specimen containing a little water, boiled at 115—118°. Benzil and azobenzene were used as standard substances. Of the other substances, solutions of 0·20 mole. were prepared.

Diphenylamine, 33·8 grams per litre.

Benzil	0·19 mole.	90 mins.	+4	0	+1	0	+1
„	0·20 „	5 hours	−2	+1	−1	+1	−3

Molecular weight = 169—178 ; mean 174 ; $C_{12}H_{11}N$ requires 169.

Cinnamic Acid, 29·6 grams per litre.

Benzil	0·19 mole	17 hours	+20	−28	+26	−10	+31
„	0·20 „	95 mins.	−1	+2	−11	+20	−8

Molecular weight = 148—156, mean 152 ; $C_9H_8O_2$ requires 148.

Salicylic Acid, 27·6 grams per litre.

Benzil	0·19 mole.	7 hours	+8	−1	+4	−20	+30
„	0·21 „	7 „	−3	+8	+1	+5	+1

Molecular weight = 131—145, mean 138; $C_7H_6O_3$ requires 138.

Triphenylmethane, 48·8 grams per litre.

Benzil	0·18 mole.	20 hours	+28	−12	+12	−6	+22
„	0·19 „	2 „	−10	+27	−26	+34	−25

Molecular weight = 257—271, mean 264; $C_{19}H_{16}$ requires 244.

Azobenzene, 36·4 grams per litre.

Benzil	0·18 mole.	20 hours	+16	−21	+10	−19	+15
„	0·19 „	16 „	−20	+38	−127	+130	−13

Molecular weight = 192—202, mean 197; $C_{12}H_{10}N_2$ requires 182.

Acetanilide, 27·0 grams per litre.

Benzil	0·18 mole.	5 hours	+3	−7	+2	−5	+2
„	0·19 „	16 „	−21	+9	−9	+17	0

Molecular weight = 142—150, mean 146; C_8H_9ON requires 135.

α-Nitronaphthalene, 34·6 grams per litre.

Benzil	0·18 mole.	5 hours	+9	−6	+2	−9	+7
„	0·19 „	2 „	−3	+2	−8	+5	−4

Molecular weight = 182—192, mean 187; $C_{10}H_7O_2N$ requires 173.

α-Naphthol, 28·8 grams per litre.

Benzil	0·21 mole.	22 hours	+16	−28	+39	−22	+17
„	0·22 „	5 „	−4	+8	−4	+5	0

Molecular weight = 131—136, mean 134: $C_{10}H_8O$ requires 144.

Judging from the comparatively small errors in the values for cinnamic and salicylic acids and for α-naphthol, the association in pyridine does not seem very marked, which is in accordance with the results obtained by Ross Innes (Trans., 1901, 79, 261).

Abnormal results were obtained for the following: *m*-dinitrobenzene, phenyl salicylate, diphenyl (more than 10 per cent. too high), picric acid, succinic acid, thiocarbanilide (more than 10 per cent. too low).

With azobenzene as standard, the error for *m*-dinitrobenzene and for diphenyl was 5—10 per cent.

Ether.

The ether was previously saturated with water to avoid the effect of atmospheric moisture. The tubes were sealed with paraffin wax.

Diphenyl, 30·8 grams per litre (0·20 mole.).

Benzil	0·18 mole.	4 mins.	+8	−3	+4	−2	0
,,	0·22 ,,	5 ,,	0	+5	+1	+8	−2

Molecular weight of diphenyl = 140—171 ; $C_{12}H_{10}$ requires 154.

Quinol, 22·0 grams per litre (0·20 mole.).

Benzil	0·18 mole.	4 mins.	+5	−3	+2	−2	+26
,,	0·22 ,,	4 ,,	−10	+1	−3	+5	−4

Molecular weight of quinol = 100—122 ; $C_6H_6O_2$ requires 110.

Xylene.

Triphenylmethane, 51·24 grams per litre (0·21 mole.).

Benzil	0·17 mole.	55 mins.	+15	−6	+1	−3	+1
,,	0·223 ,,	—	−24	+12	−9	+10	−4

Molecular weight of triphenylmethane = 230—301, mean, 265 ; $C_{19}H_{16}$ requires 244.

Association in Mixtures of an Associative and a Non-Associative Solvent.

As the microscopic method is particularly suited for work with mixed solvents, it seems desirable to study with its help the problems of association. The results of some preliminary experiments are here communicated, and although no special attention was paid to accuracy, the values show the general nature of the association in mixtures.

The object in view was to determine the molecular weight of acids, phenols, &c., in mixtures of varying composition of two solvents, the boiling points of which are not very remote, and in one of which the substance has a normal molecular weight, whereas it is associated in the other.

Such pairs of solvents are : ether and carbon disulphide, methyl alcohol and chloroform, ethyl alcohol and benzene, &c. Determinations were carried out with the second and third pairs, using cinnamic and benzoic acids respectively as solutes. In both cases, the concentration

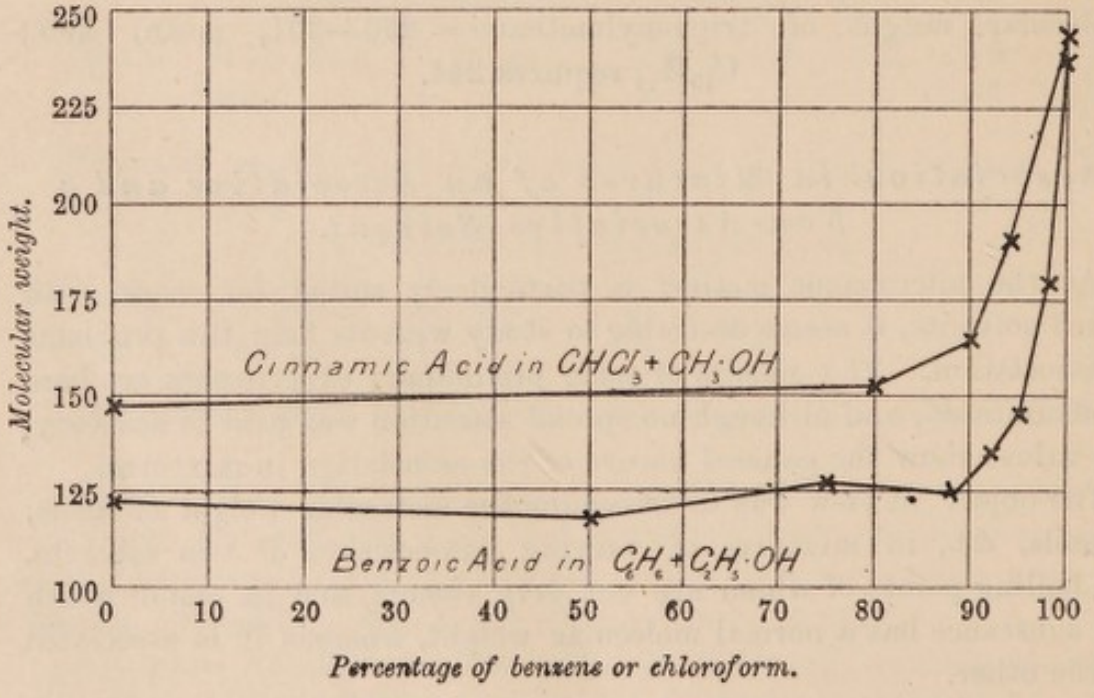
was 0·20 mole., the standard substance was benzil, and the tempera ture was 16°.

Mixtures were made containing the two solvents in known proportion by volume, and with each mixture the cinnamic (or benzoic) acid solution was prepared, together with the necessary benzil solutions.

Benzoic acid in crystallisable benzene and absolute ethyl alcohol 24·4 grams per litre.

50 per cent. benzene	benzil 0·204 mole.	5 mins.	+4	−2	+1	−1	+7	mean = 0·208
	,, 0·212 ,,	30 ,,	−8	−1	−5	+3	−4	M. W. = 117
75 per cent. benzene	,, 0·19 ,,	2 hours	+5	−11	+6	−8	+1	mean = 0·192
	,, 0·195 ,,	1 ,,	−2	+6	−2	+3	−9	M. W. = 127
87·5 per cent. benzene	,, 0·19 ,,	—	+16	−1	+9	+2	+8	mean = 0·196
	,, 0·202 ,,	4 ,,	−39	+41	−3	+9	−3	M. W. = 124
92 per cent. benzene	,, 0·175 ,,	1 ,,	+8	−16	+3	−14	+8	mean = 0·18
	,, 0·185 ,,	18 ,,	−28	+31	−11	+53	−30	M. W. = 136
95 per cent. benzene	,, 0·16 ,,	½ ,,	+1	−5	0	−3	+1	mean = 0·17
	,, 0·18 ,,	1 ,,	+1	+3	−1	+4	−5	M. W. = 144
98 per cent. benzene	,, 0·13 ,,	—	+9	+3	+7	+4	+11	mean = 0·135
	,, 0·14 ,,	—	+3	+10	−5	+14	−5	M. W. = 181
100 per cent. benzene	,, 0·095 ,,	1 ,,	+2	−1	+3	0	+1	mean = 0·103
	,, 0·112 ,,	2 ,,	−1	+8	0	+7	−1	M. W. = 237

Among the results given in an earlier section of this paper there



will be found for the molecular weight of benzoic acid in pure benzene 233, and in alcohol 122, both in concentrations of 0·20 mole.

II. Cinnamic acid ; 29·6 grams per litre ; methyl alcohol and chloroform not specially purified.

80 per cent. chloroform	benzil	0·19 mole.	50 mins.	+4	−7	+1	−11	+5	mean = 0·195
	,,	0·20 ,,	12 ,,	−7	+1	−3	+1	−2	M. W. = 152
90 per cent. chloroform	,,	0·175 ,,	40 ,,	+2	−4	0	+1	+3	mean = 0·18
	,,	0·185 ,,	55 ,,	+5	+1	−3	+12	−3	M. W. = 164
94 per cent. chloroform	,,	0·15 ,,	8 ,,	+2	−2	+2	−3	+4	mean = 0·155
	,,	0·16 ,,	90 ,,	−5	+13	0	+20	+3	M. W. = 191
100 per cent. chloroform	,,	0·119 ,,	1 hour	+7	+1	+5	−4	+6	mean = 0·122
	,,	0·125 ,,	15 mins.	−10	+6	−13	+9	−25	M. W. = 243

The molecular weight of cinnamic acid in 100 per cent. methyl alcohol has not been determined, but in ethyl alcohol it was found to be 148.

The values for benzoic acid may be slightly vitiated by its relatively considerable vapour pressure at the ordinary temperature. With the molecular weights as ordinates and the percentage of benzene or chloroform as abscissæ, two curves have been plotted which clearly show that a small proportion of alcohol is sufficient to do away with the association. Should this observation prove to be general, it may be of considerable practical importance in those cases where one is restricted to associative solvents because the substance is not sufficiently soluble in the others. A small percentage of a non-associative solvent would not materially affect the solubility, yet it would reduce the molecular weight to its normal value.

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