ON THE NATURE OF THE PROCESS OF OSMOSIS AND OSMOTIC PRESSURE WITH OBSERVATIONS CONCERNING DIALYSIS[1]

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Introduction

A brief but excellent outline of the history of the development of our knowledge of osmosis up to 1877 is given by Pfeffer in his well-known monograph, "Osmotische Untersuchungen." The great importance of osmotic phenomena in physiological processes was clearly recognized as early as 1826 by Dutrochet, and for half a century later osmotic investigations were conducted very largely, though not exclusively, in the interests of physiology. Precipitated membranes were first used by the botanist, Moritz Traube,[2] in 1865, and these were employed by Pfeffer in his researches above mentioned. Special interest in osmosis has developed since 1887, when by using Pfeffer's data of osmotic pressure measurements van't Hoff sought to show that the simple gas laws hold for dilute solutions. Since the latter date so-called semipermeable membranes have been used almost exclusively in osmotic investigations. These membranes usually consisted of ferrocyanide precipitates of some heavy metal, copper ferrocyanide being the favorite precipitate for osmotic work, though the ferrocyanides of zinc and nickel were occasionally employed, as were also a few other precipitates.

In this later work effort in two directions is clearly discernible: (1) Those who have been favorable to van't Hoff's hypothesis of solutions (based on the analogy between gases and solutions), according to which the osmotic pressure, so-called, is due to the bombardment of the semipermeable membrane by the dissolved molecules, have sought either to compare osmotic pressures of aqueous solutions with each other, or to measure directly the osmotic pressure of certain solutions in the hope of securing data to uphold the theory. It is

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[1] Published also in the Transactions of the Wisconsin Academy of Sciences, Arts and Letters, Vol. 15, Part I.

[2] Centralblatt f. medic. Wissenschaften, 1865.

true, however, that considering the vast importance of direct measurements of osmotic pressure for the van't Hoff theory of solutions, but little effort has been made to measure osmotic pressures directly. This has come about very largely because of the attitude taken in the matter by the main adherents of the van't Hoff theory who voiced and continually supported the dogma that the osmotic pressure is necessarily independent of the nature of the membrane if it be semipermeable; and that since it is very difficult to measure osmotic pressures directly, it is better to content one's self with the so-called "indirect" measurements of osmotic pressure, namely, with a computation of the latter from vapor tension, freezing-point or boiling-point observations on solutions, which, be it remembered, involve the assumption that the gas laws hold for solutions. And so we have the rather remarkable situation that direct measurements of osmotic pressure, and indeed the general investigation of osmosis, has not only been neglected by the chief advocates of the gas theory of solutions, but they have in addition actually discouraged work in this direction through the attitude they have taken. They have even claimed to have proven by thermodynamics that the osmotic pressure must be independent of the nature of the membrane provided the latter is semipermeable. The assumptions made in such "proofs," and the fact that there is in reality no such thing as a semipermeable membrane in the strict sense of the word, have been passed over lightly. (2) Quite a different direction in the investigation of osmotic phenomena has been taken by those who have held van't Hoff's conception of the nature of osmotic pressure to be untenable. These men have continually brought forward experiments, of a qualitative nature to be sure, showing that the hypothesis of van't Hoff cannot be held and that no special stress is to be laid upon direct measurements of osmotic pressure, which they have consequently not attempted to make.

In his efforts to measure osmotic pressures directly,

Tammann[1] came to the conclusion that it is not possible to obtain reliable, concordant results by means of the method adopted by Pfeffer,[2] which he consequently abandoned entirely and turned his attention to comparing the osmotic activity of various solutions with one another. Attempts at direct measurements of osmotic pressure have again been taken up recently by H. N. Morse[3] and his coworkers. They have measured the osmotic pressures that are developed when aqueous sugar solutions are separated from water by means of precipitated membranes of copper ferrocyanide. The method they employed is essentially that of Pfeffer, with the exception that they prepared the membranes with the aid of electrolysis. Enough can hardly be said in praise of the care and perseverance exercised by Morse and his assistants in this work, and yet they have neglected a very essential point in their determinations as will appear from considerations given below, and consequently their experiments are not conclusive in establishing, as they suppose, that the gas laws hold fairly well for the osmotic pressures of aqueous sugar solutions, using copper ferrocyanide membranes. Furthermore, attempts to generalize from the data collected by Morse and Frazer on aqueous sugar solutions, as to the behavior of all solutions taking no consideration of the membranes employed, are quite unwarranted. Moreover, while according to Morse and Frazer and also according to Flusin[4] the aqueous sugar solutions show osmotic pressures in approximate conformity to the gas laws, the Earl of Berkeley and E. G. J. Hartley[5] have found materially higher pressures than those deduced from the gas law, even though their membranes,

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[1] Wied. Ann., **34**, 299 (1888). See later attempts by new method, Zeit. phys. Chem., **9**, 97 (1892).

[2] Pfeffer, be it remembered, worked solely in the interests of physiology and for his special purpose his experiments were quite sufficient.

[3] Am. Chem. Jour., **34**, 1 (1905).

[4] Comptes rendus, **132**, 1110 (1901).

[5] Proc. Roy. Soc., **73**, 436 (1904).

which were also prepared with the aid of electrolysis, were admittedly not perfectly tight.

Among the many opponents of the van't Hoff theory of osmosis may be mentioned Lothar Meyer, Raoult, Fitzgerald, Pickering, Quincke, Dieterici, J. Traube, Battelli and Stephanini. The opponents of the van't Hoff idea have generally held that the so-called osmotic pressure is an ordinary hydrostatic pressure brought about by entrance of liquid into the osmotic cell. Concerning the reason for this entrance of additional liquid into the osmotic cell there has, however, been difference of opinion; some holding that it is due to attraction that is essentially chemical in character; others that it is due to capillarity; and still others that it is caused by surface tension. The latter view has lately been prominently brought forth by Traube,[1] whose claim is that "the difference in surface tensions determines the direction and velocity of the osmosis." His idea is that the main direction of osmosis is always toward the liquid having the greater surface tension. Again, Battelli and Stephanini[2] also express the opinion that difference in surface tension is the cause of osmosis. But on the basis of their experimental work, they modify Traube's contention to the effect that the main osmotic current is not always toward the liquid of higher surface tension, but that the process always proceeds in such a direction as to tend to equalize the surface tensions of the liquids on the opposite sides of the septum. Very recently Barlow[3] has also brought forward cases which are not in harmony with the theory of Traube.

In the present investigation the main purpose has been to inquire into the nature of osmosis and osmotic pressure, and to test whether the latter really follows the gas laws. To this end a considerable number of osmotic experiments were performed in which liquids of similar and also of very different

[1] Phil. Mag. [6], 8, 704 (1904).
[2] Atti della Reale Accademia dei Lincei, 14, 3 (1905).
[3] Phil. Mag. [6], 10, 1 (1905).

character were separated from each other by different membranes. In this work observations were taken as to the direction of osmosis with change of membrane, with change of solvent and also with change of solute. The effect of temperature was considered. The degree of permeability of the membranes for various substances was noted, with the result that membranes as semipermeable as any known hitherto were found, which are yet not precipitated membranes. Furthermore it was ascertained *why* the membranes were semipermeable in some cases and not in others. It was consequently possible to foretell for which substances the membranes were permeable and for which substances not permeable. Further, this work has cast light on the process of dialysis. It has been possible to separate different dissolved crystalline substances from each other by dialysis, and also to separate dissolved crystalline from non-crystalline bodies by having the *non-crystalline substances pass through the septum* and the crystalline ones remain behind in solution in the dialyzer. The direct measurements made with the semipermeable membranes employed, moreover, showed that the gas laws do not hold at all in these cases. It was also found that in making direct measurements of osmotic pressures it is necessary to *stir* the liquids separated by the membrane, a very important fact which has been entirely overlooked in all osmotic pressure determinations hitherto made. The necessity of such stirring was really discovered accidentally, as will appear from details given below, after having worked in vain for over a year trying to get reliable, concordant results without stirring. The discovery that agitation of the liquids is essential in osmotic pressure measurements is of paramount importance in deciding as to the nature of the osmotic process.

In the presentation of the experimental work which now follows, the experiments will not be described in the order in which they were actually performed for the reason that greater clearness will be obtained by detailing the results in the light

of the theory which was gradually evolved in the course of the
investigation.

A Typical Case of Osmosis

If chloroform A, Fig. 1, be placed in a glass tube and a
layer of water B be poured upon it, and again a layer of ether
C be carefully poured upon the water, and the whole be allowed
to stand, there will eventually be but two layers A′ and B′,
Fig. 2.   An examination of A′ shows that it consists of chloro-
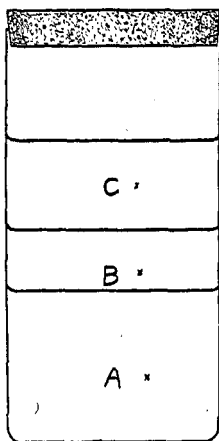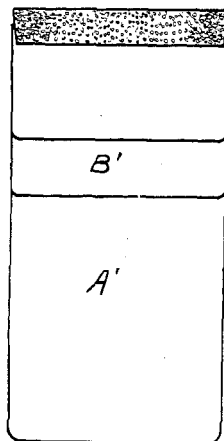

Fig. 1   Fig. 2

form and ether saturated with water, whereas the layer B′
consists of water saturated with ether and chloroform.   In
the change which has taken place, one layer, that of the ether,
has gradually disappeared, and the lower layer has greatly
increased in bulk and lifted the aqueous layer to the top.   The
explanation of this phenomenon is evident.   Ether dissolves
very readily in chloroform, but in water it dissolves much less
readily; again, chloroform and water hardly dissolve each
other at all.   In the arrangement we have in Fig. 1, the
aqueous layer B dissolves ether, and in turn the ethereal
layer C takes up some water.   When the ether has gone into
B until it touches the chloroform layer A, the latter extracts
ether from the aqueous layer B.   Thus the upper part of the
chloroform layer A becomes enriched with ether, whereas

the lower part of the aqueous layer B becomes depleted in ether. The latter depletion is made good by a continuous supply of ether from the upper parts of B, which are in turn supplied with ether from C. Again, the ether in the upper layers of A gradually diffuses into the more distant parts of A. This process of the transportation of the ether in C through B into A proceeds, then, until the supply in C is exhausted. It is to be noted, however, that since chloroform is more soluble in water containing ether than in pure water, the aqueous layer B will take up more chloroform after becoming charged with ether. Thus some of the chloroform is making its way upward into the aqueous layer B, from which it also passes in part into the ethereal layer C.

It is clear then that the ether of layer C is making its way through the aqueous layer B into the chloroform layer A, and that on the other hand the chloroform is passing into the aqueous layer B charged with ether and further into C. Thus we have currents of ether and chloroform going in opposite directions. The movement of the chloroform as to quantity is, however, extremely slight as compared with that of the ether; and so the movement of the latter practically predominates and the ethereal layer is finally absorbed. It must be borne in mind, however, that water, being somewhat more soluble in chloroform charged with ether than in pure chloroform, will to a slight extent go into the layer A as it becomes enriched with ether; and, as has already been remarked, some water also passes into the layer C, for water is somewhat soluble in ether. When the change is complete, we have, as stated above, a lower layer consisting of chloroform and ether saturated with water, and an upper layer of water saturated with ether and chloroform.

The rate at which this process goes on depends on the temperature and upon the pressure, but also upon the thickness of the aqueous layer B and the area of the surface of contact with the ethereal layer C and the chloroform layer A. It is further clear that the process would be hastened if each

of the layers A, B, and C were continually stirred, for by so
doing the slow processes of diffusion would be aided and the
changes in concentration which take place in the layers where
they are in contact with one another would be lessened.

Summed up then, the observed change goes on because
ether is soluble in water, but much more readily soluble in
chloroform, so that the latter is able to extract ether from
the aqueous solution of ether, B. The chloroform-ether
solution in A may be regarded as a solution of chloroform in
ether, especially after a considerable quantity of ether has
accumulated in it; and since but very little chloroform passes
into the aqueous layer B, the latter is practically permeable
only for ether, and therefore this aqueous layer B acts as a
semipermeable septum. It permits ether to pass from C to A,
but allows very little, practically no, chloroform to pass into C.
It is clear further that as A becomes richer and richer in ether,
the tendency for more ether to enter A from B becomes less
and less. Ether dissolves more readily in chloroform than in
water because ether and chloroform have a greater mutual
attraction for each other than have ether and water; it is for
this reason too that chloroform is able to extract ether from
an aqueous solution of the latter. As ether accumulates in
A, however, the power of this layer to extract ether from the
aqueous layer B diminishes, because the attraction or affinity
of chloroform and ether for each other becomes more and
more satisfied. Finally, suppose we prevent the supply of
ether in C from becoming exhausted by adding some as may
be required, a point will be reached where compartment A
has become so rich in ether that the attraction or affinity of
this chloroform-ether solution for additional ether has de-
creased to such an extent that it can no longer extract further
ether from the aqueous layer B. In other words, when the
chloroform solution in ether, A, has become so dilute that its
attraction for additional ether just equals the attraction of
water for ether in the aqueous layer B, the process is arrested.
The point at which this occurs would clearly vary with the
temperature and also with the pressure.

If in Fig. 1 compartment A be filled with carbon bisulphide instead of chloroform, the process would go on as before in a similar manner and for perfectly similar reasons. Indeed, any liquid which in itself does not mix with water, practically speaking, and yet has a greater attraction for ether than has water, would serve in place of the chloroform. The rapidity with which the process proceeds and the final point of equilibrium reached would, however, also be a function of the nature of the substance so employed. If in Fig. 1 the ether in C be replaced by an oil, say olive oil or a hydrocarbon oil, retaining the water in B and chloroform in A, nothing will take place,[1] for these oils are not appreciably soluble in water, that is to say, the attraction or affinity existing between them and water is insufficient to overcome their cohesions to the extent necessary to cause a fusion, a blending, an interpenetration of their masses. Again, if the water in B were replaced by a liquid in which neither ether nor chloroform are appreciably soluble, nothing would take place. Further, if the chloroform A be replaced by a liquid which does not dissolve water and has less attraction for ether than has water, nothing will take place. *It is clear then that the process under consideration proceeds because of the specific nature of the septum B and also that of the two liquids that bathe it.* It should also be emphasized in this connection that while it is essential, as stated above, that the layer B, the water, must be capable of dissolving C, the ether, it is further necessary that this solubility be restricted in character, as it is in fact, otherwise the layer B would not be distinct from C and would become so rich in ether that the boundary lines between A and B would also disappear.

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[1] If olive oil be dissolved in ether and this solution placed in C, whereas water and chloroform are retained in B and A, respectively, the ether would pass through the water into the chloroform, leaving the olive oil behind in C. We have here an illustration of what may be called selective action on part of the membrane (the aqueous septum B) in which property biologists are particularly interested. The explanation is obvious. Water dissolves ether appreciably, but not olive oil, so the latter is left behind.

Returning now to the original experiment Fig. 1 in which ether, water and chloroform are in A, B, and C respectively, let us imagine the aqueous layer B as quasi-solid and also immovable, *i. e.*, attached firmly to the sides of the glass tube, nevertheless otherwise retaining its original properties. This would make A a compartment whose volume remains fixed, and as the ether enters it from B, for reasons already detailed, a hydrostatic pressure would be produced upon the sides, top and bottom of A; and as this pressure develops, it would become more and more difficult for additional ether to enter this compartment. Finally if the walls of this compartment did not give way, a point of maximum pressure would be reached. At this point, at the temperature of the experiment, the affinity of the ether-chloroform solution in A for additional ether is insufficient to extract further ether from the aqueous layer B. In other words, the affinity of water for ether aided by the hydrostatic pressure developed in A (which militates against the ether passing into A) just balances the affinity of the chloroform-ether solution in A for additional ether. And yet the case is after all not quite so simple, for it must be remembered that chloroform is somewhat soluble in water saturated with ether at atmospheric pressure; now this solubility is increased with increase of pressure, so that as the hydrostatic pressure in compartment A increases due to the influx of ether, the outflow of chloroform is continually slightly increasing, which tends, of course, to relieve the pressure. The actual final maximum pressure reached is therefore determined by the relative influx of ether into compartment A and the outflow of chloroform from that compartment. When this outflow is practically nil, or at any rate very slight, we should be dealing with a so-called semipermeable membrane; when the outflow is not a negligible quantity, as in the case of most septa, the final maximum pressure attained is materially influenced thereby.

Now it is easy enough to imagine the aqueous layer B firmly held in place as we have done, but to realize this ex-

perimentally presents great difficulties. It may, however, readily be demonstrated that such hydrostatic pressure is actually produced, without, to be sure, making an attempt to furnish anything more than a qualitative proof that such pressure is really formed. The apparatus used for this purpose is shown in Fig. 3. In this glass tube, D represents mercury, A chloro-
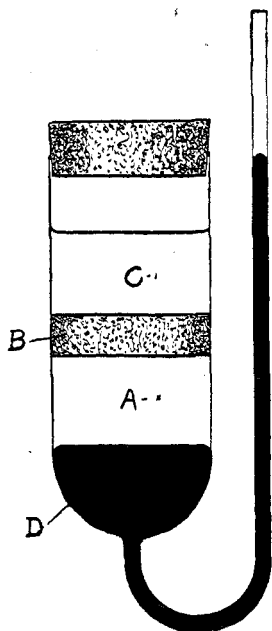

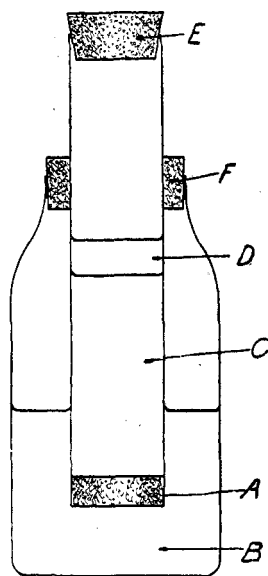Fig. 3   Fig. 4.

form, C ether, and B is a slice of an excellent piece of cork which had been kept under boiling water for some time so as to drive the air out of it and thoroughly inject it with water; during this process much soluble material was also extracted from the cork. The cork thus thoroughly soaked with water was firmly pushed into position. It is of course somewhat difficult to avoid having air bubbles just above and below the cork, but by careful manipulation it is possible to secure the arrangement as shown in Fig. 3. The chloroform and ether used in this case were each first saturated with water, so that they would not unduly rob the cork of its water content,

which was necessarily small enough to begin with. On allow-
ing the apparatus to stand, the mercury rises in the tube as
indicated, showing that pressure is produced on the walls of
A. The mercury rose until the cork either broke or began
to slip upward, the experiment being repeated three times.
Using a cork not soaked in water no pressure was obtained.
It is quite probable that a cork might be so fastened in place
by the aid of mechanical contrivances that an ordinary tube
would give way before the cork would move; but since the
maximum pressure could not be measured in this manner,
the qualitative demonstration of the presence of the pressure
was deemed sufficient. The experiment just described may
be performed also in the form illustrated in Fig. 4, which is
more like the usual arrangement employed in osmotic ex-
periments. In this figure, the liquid B in the bottom of the
bottle is ether; the end of the glass tube is closed with a tight-
fitting slice of cork A saturated with water; in the tube above
the cork is chloroform C; and above the chloroform is water
D. At F there is a cork collar which holds the tube in place.
This collar does not fit perfectly tight, yet it minimizes the
evaporation of the ether. The cork E is rather loosely in-
serted; its purpose is simply to prevent undue evaporation.
This was also the purpose of the layer of water D, which, to
be sure, also kept the chloroform saturated with water. Both
the ether and chloroform used were saturated with water to
begin with as in the previous case. With this arrangement
the layer C increased in bulk, the column rising until the layer
D touched the cork E. The experiment was continued for
two weeks; the cork at A being rather thick caused the change
to progress slowly.[1]

This case of ether, water, chloroform (Fig. 1) has been thus
described in detail because it illustrates all the essential points
to be taken into consideration in the study of the osmotic
process. We have seen what conditions are necessary for the

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[1] Compare in this connection a similar experiment of Nernst: Zeit. phys.
Chem., **6**, 35 (1890).

process to proceed at all, what are the various factors that modify the rate of the change, and what causes the so-called osmotic pressure. It has further been shown under what conditions we get a so-called semipermeable membrane, and it is evident that an absolutely semipermeable membrane exists only in theory. On the basis of his elaborate experimental researches, Quincke[1] has also arrived at this conclusion. He stoutly contends that there really is no such a thing as a semipermeable membrane and that a theory which postulates such cannot be maintained. His words are, "Ich bestreite, dass eine halbdurchlässige Membran existirt. Damit fällt aber auch der osmotische Druck, dessen Theorie die Existenz einer halbdurchlässigen Membran voraussetzt." As stated above, there is in general always an outflow from an osmotic cell as well as an inflow, and when the former is extremely slight as compared with the latter, the membrane is *called* semipermeable; but commonly the outflow is quite sufficient to demand consideration. At any rate, the osmotic pressure is always the resultant of inflow and outflow caused by the attractions that come into play, which attractions are to the mind of the writer the same as what is commonly called chemical affinity, and consequently such so-called osmotic pressures may, under suitable conditions, be very great indeed, while under other conditions they may be quite small. They would, moreover, present considerable variation according to the nature of the substances employed.

No originality is claimed for the ether, water, chloroform experiment, Fig. 1. It occurred to me after a goodly number of the experiments described below had been performed; but in looking over the earlier articles of the rather voluminous literature on the subject of osmosis, I found that in 1854 L'Hermite[2] described the experiment in question. His statements concerning its import and bearing are very clear, though of course he does not speak of semipermeable mem-

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[1] Drude's Ann., 7, 682 (1902).
[2] Comptes rendus, 39, 1177 (1854).

branes and osmotic pressures, for these concepts were at that time quite unknown. A reference to the article of L'Hermite is also made in the bibliography in Lehmann's Molekular-physik.

However, after having L'Hermite's experiment clearly before me, the principles it illustrates soon became the guide in future experimentation, for they enabled me to foretell whether a membrane would be permeable or impermeable for a certain substance under given conditions; and if permeable for several substances, which of these would go through most readily. I was thus enabled to forecast in which direction the main osmotic current would go. These matters were not only of consequence in direct measurements of osmotic pressures, detailed below, but they were also of importance in dialysis as will appear farther on. Again, by demonstrating the nature of the process, it clearly appeared that in determining the maximum osmotic pressure the contents of the osmotic cell must be continually stirred. For, taking the arrangement as given in Fig. 1 and again imagining the aqueous layer B as quasi solid and firmly fixed in place, it is evident that as ether is drawn into compartment A, the liquid in that compartment becomes enriched with ether just where it touches B, and that consequently the osmotic pressure set up in A is not as great as it would be if the liquid in A were continually stirred so as to rapidly distribute the incoming ether throughout the cell and present a fresh surface to the layer B. When stirring is omitted, this work of keeping the contents of B of uniform concentration has to be performed by diffusion, a process which is very slow, and consequently a lower pressure is obtained. It is clear that for similar reasons the contents of B ought in general also to be stirred in attempting to measure the maximum osmotic pressure, as should also the liquid C. But when B is quite thin, as is the case with some membranes, stirring its contents is of less consequence. Furthermore, when practically very little of A enters C (*i. e.*, when B is a so-called semiper-

meable septum) it is obviously not so necessary to stir the
contents of C in osmotic pressure measurements. But the
liquid in the osmotic cell must *always* be stirred, though it is
recognized that in some forms of cells this is far more im-
perative than in others. Attempts to make direct measure-
ments of osmotic pressures without stirring the contents of
the cell are comparable with attempts to make a saturated
solution of a salt by placing an excess of it in a dish, pouring
the solvent upon it and allowing the whole to stand without
agitation. The method of stirring the contents of the osmotic
cell will be described below in connection with the quantitative
measurements of osmotic pressures.

Qualitative Experiments

The following experiments which are largely of a quali-
tative nature were performed in the course of the investiga-
tion in order to determine the influence which the character
of the membrane has upon the permeability of the latter,
and also upon the main direction of the osmotic current.
Unless otherwise stated, the osmometer used was a very
simple one, consisting of an ordinary thistle tube, the mouth
of which was closed with the membrane employed. The
latter was tied on with thread, in which process great care
was used to secure a perfect contact between the glass and
the membrane. To accomplish this a thistle tube was selected
with a flare of about 45° at the mouth. On such a tube the
membranes used could be perfectly securely tied. Very many
evenly applied turns of a stout, moderately fine, white cotton
thread were wound on after the membrane had been carefully
placed in position over the mouth of the tube. This part of
the work required much time, patience and perseverance, as
well as skill and practice. After thus securing the mem-
brane over the mouth of the thistle tube, the latter was filled
with one of the liquids to a point slightly above the bell of the
tube, which was then immersed in a beaker containing the
other liquid. The level of the two liquids was, of course, the
same to begin with.

For convenience in future reference the experiments performed have been numbered. The liquid in the bell of the osmometer will always be called the inner or inside liquid; that in the beaker, the outer or outside liquid.

1. The membrane consisted of sheet rubber, vulcanized caoutchouc, such as is used by dentists in making their "rubber dam." This rubber was very elastic, being almost the pure gum. It could readily be stretched over the osmometer and tied on so as to form a perfect joint, for all folds could be avoided. The inside liquid was a 20 percent aqueous cane sugar solution; the outside liquid was pure water. The experiment ran forty-eight hours. No change took place. The liquids remained at the same level and no sugar passed through the membrane into the water on the outside.

2. A rubber membrane was used as before. The inside liquid consisted of a 20 percent aqueous NaCl solution, the outside liquid of pure water. No change took place, the liquids remaining on the same level and not a trace of salt appearing in the water without. When the outside water was replaced with toluene, the latter caused the rubber to swell, but no salt or water passed into the toluene, neither did the toluene go into the brine. On afterward exposing the membrane to the air, it lost its toluene content and shrank to its former size, remaining throughout quite elastic.

Experiments 1 and 2 show that it is possible to get the joint between rubber and glass perfectly tight. It is perfectly clear that no change took place when water and the aqueous solutions touched the rubber, for the reason that there is no affinity between these liquids and rubber. Thus the first condition necessary for osmosis to take place was lacking, namely, that the membrane must be able to dissolve (*i. e.*, imbibe or take up) one of the liquids that bathe it. When in the second part of experiment 2 the water was replaced by toluene, the latter was taken up by the membrane; but osmosis did not take place because the liquid on the other side, the brine, having no affinity for toluene to speak of was unable to extract toluene from the rubber.

3. The inside liquid was water, the outside liquid 99.5 percent alcohol, the membrane rubber. The liquid rose in the osmometer, showing the main current to be from the alcohol through the rubber to the water. This is what one would expect, for the alcohol is taken up by the rubber and then the water by virtue of its affinity for alcohol extracts the latter from the rubber.

4. This experiment was like No. 3 except that a 20 percent aqueous cane sugar solution was used as the inner liquid. Again the liquid rose in the osmometer, alcohol passing through the rubber into the sugar solution. No sugar, however, was found in the alcohol on the outside. The rise in the osmometer tube was slow, being about 5 cm in five days. The inside diameter of the stem of the thistle tube was about 3.5 mm. The main direction of the current was, of course, such as was to have been expected from what was said in connection with the preceding experiment. No sugar was found in the alcohol outside, for sugar has so little affinity for alcohol, for rubber and for rubber soaked with alcohol that it is not taken up by any of these.

5. The inner liquid was pyridine, the outer liquid water and the membrane parchment. The liquid rose in the osmometer showing the main current to be from the water through the parchment to the pyridine. Some pyridine was also found in the water.

6. The experiment was like No. 5, except that a rubber membrane was used instead of parchment and the water was the inner liquid and the pyridine the outer. The liquid again rose in the osmometer, showing that the main current was in the opposite direction as in the preceding experiment, namely from the pyridine through the rubber to the water. Some water also passed into the pyridine, showing an appreciable minor current.

7. The inside liquid was pyridine, the outside liquid toluene and the membrane parchment. No change took place.

8. This experiment was like No. 7 except that rubber was substituted for parchment. The liquid at once rose in the osmometer, showing the main current to be from the toluene through the rubber to the pyridine. Some pyridine, however, also passed into the toluene.

Rubber readily takes up pyridine, and imbibes toluene still more readily; on the other hand, parchment does not, showing that it has but little affinity for these liquids. It is consequently easy to see why no change occurred in No. 7. When it is further remembered that pyridine and water are consolute liquids, as are also toluene and pyridine, the observations in Nos. 5, 6 and 8 are easily explained. In No. 5 the parchment imbibes water which is then extracted by the pyridine; but since pyridine is soluble in water-soaked parchment, some pyridine also passes into the water outside. In No. 6 the rubber imbibes the pyridine which is then extracted by the water; but as water is somewhat soluble in pyridine-soaked rubber, some of it makes its way into the pyridine without. In No. 8 the fact that toluene is imbibed more readily by rubber than is pyridine again determines the direction of the main current, though in this case, owing to the fact that pyridine has considerable affinity for rubber as well as for toluene, the minor current is of considerable consequence. The cases just considered well illustrate how the nature of the septum and of the liquids that bathe it determines what will actually take place.

In 1898, G. Flusin[1] used carbon disulphide, chloroform, toluene, ether, benzene, xylene, petroleum ether, benzyl chloride, turpentine, petroleum, nitrobenzene, methyl alcohol, ethyl alcohol, and acetic acid, taking these liquids in all possible combinations in pairs and separating them from each other by means of a membrane of vulcanized caoutchouc. He found the main current to be from the liquid which is the more readily imbibed by the rubber, through the septum to the less readily imbibed liquid. Again in 1900[1] he used water,

[1] Comptes rendus, 126, 1497 (1898); 131, 1308 (1900).

methyl alcohol, amyl alcohol, amyl acetate, chloroform, benzene, ether, and ethyl alcohol. He employed hog's bladder as a septum, placing one side of it in contact with ethyl alcohol (the liquid which of those named is, according to him, imbibed least readily) and bathing the other side with each of the other liquids successively. He always found the main current to be in the direction toward the ethyl alcohol and the rate of flow to vary with the amounts of liquid imbibed by the membrane during the first five minutes, which amounts, of course, were determined by independent experiments. I have confirmed all of the results of Flusin where he used rubber membranes. He says nothing, however, about the minor current, which I found to be present in all of these cases to a greater or lesser extent. In other words, the rubber was traversed by both liquids of each pair, though the main direction of the current was quite correctly determined. Flusin shows that the affinity between membrane and liquid is to be measured by the rate with which the latter is imbibed by the former, and not by the total amount of liquid taken up by a given quantity of membrane at the end of a long time, as Tammann[1] contends. Raoult[2] separated methyl alcohol and ether from each other by means of rubber. He always found the direction of the main current to be from the ether through the rubber to the methyl alcohol; and the direction of the main current remained the same, even when the ether was considerably diluted with methyl alcohol. When he substituted a membrane of hog's bladder for the rubber, the direction of the main current was reversed, it being from the methyl alcohol through the septum to the ether. In his article, Raoult has omitted to say anything about the fact that in his experiments there is also a minor current in a direction opposite to that of the major; in other words, that when caoutchouc is the membrane and ether is going into the alcohol there is also some alcohol passing into the ether, and

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[1] Zeit. phys. Chem., 22, 491 (1897).
[2] Compes Rendus, 21, 187 (1895); Zeit. phys. Chem., 17, 737 (1895).

when the bladder is employed there is some ether passing into the alcohol though the main current is that of the alcohol toward the ether.   Raoult was, however, perfectly clear in his own mind with regard to this matter as will appear from a quotation from a letter written by him printed below.

It is hardly necessary to add that in the light of what has already been said above, the results obtained by Raoult and Flusin are exactly such as might have been foreseen.[1]

9. The inner liquid was glacial acetic acid, the outer liquid distilled water and the membrane rubber.   Within five minutes blue litmus paper placed in the water turned red, showing that the acid was passing through the rubber. This was the direction of the main current, which might have been expected, since glacial acetic acid is more readily absorbed by rubber than is water.

10. The inner liquid was a 10 percent solution of acetic acid in water, the outer liquid water, and the membrane rubber. After one and a half hours the blue litmus in the water began to turn red, indicating that in this case too the acid was passing through the rubber.   The direction of the main current then was not altered by diluting the acetic acid considerably with water, which result is in line with what Raoult found in the ether—methyl alcohol experiment referred to above.

11. The inner liquid was a strong solution of trichloracetic acid in water, the outer liquid water and the septum rubber.   But very little acid passed through the rubber into the water.   Hardly any change took place in the twenty hours, during which the experiment was continued.

12. The inside liquid was a solution of trichloracetic acid in benzene, the outside liquid water and the membrane rubber. In this case acid went into the water in very considerable quantity.   This was the direction of the main current.   The experiment was run for twenty hours.

13. The inner liquid was a solution of trichloracetic acid

[1] Compare also remarks by Tammann: Zeit. phys. Chem., 22, 490 (1897).

in water to which considerable benzene had been added, the outer liquid was water and the septum rubber. Very notable quantities of acid passed through the membrane into the water without. The experiment was continued for twenty hours.

The large increase in the amount of trichloracetic acid which passed through the rubber in 12 as compared with 11 is easily explained by the fact that benzene has considerable affinity for trichloracetic acid and also for rubber. In imbibing the benzene therefore large amounts of trichloracetic acid are also absorbed with that hydrocarbon by the rubber. When we dissolve trichloracetic acid in benzene we really unite the acid with the benzene. In this homogeneous liquid, the solution, we have then the acid tied to the benzene; and because of the great affinity of the latter for rubber, the benzene solution of trichloracetic acid, the combination of the acid and the benzene, also has considerable affinity for rubber; and so the acid is also drawn into the rubber because it is united with benzene. To be sure, benzene and acid are not taken up by the rubber in the same proportions in which they occur in the solution, benzene being taken up in relatively larger amounts. This means that the solution is, to a certain extent, decomposed, *i. e.*, altered in concentration, by the rubber. When the latter, soaked with benzene and the acid, is in contact with water, the great affinity between water and the acid again comes into play and by virtue of it acid passes into the water, leaving the benzene behind in the rubber almost completely. Similar considerations hold in No. 13 where a solution of trichloracetic acid, water and benzene is separated from water by a rubber septum, except that here the acid passes through in lesser quantity, and minor amounts of water are undoubtedly also absorbed by the rubber, since in the solution the water is tied on to the benzene and the acid.[1]

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[1] Compare Kahlenberg, "Über das Problem der Lösungen," Chem. Zeitung, 29, No. 81 (1905).

14. The inner liquid consisted of pure water, the outer of o.1 normal solution of $AgNO_3$ in pyridine and the membrane of rubber. The liquid rose rapidly in the osmometer, reaching a height of 25 cm in four hours. The experiment was then stopped and the contents of the cell examined. It was found that pyridine had passed into the water, but no appreciable quantity of nitrate of silver. The entire content of the osmotic cell was evaporated to dryness, the residue extracted with a little water and a drop of nitric acid, and the filtered solution tested with HCl for silver, but none was found.

15. The inner liquid was a o.1 normal $AgNO_3$ solution in pyridine, the outer liquid pure water, and the membrane parchment. The main current was from the water, through the parchment to the $AgNO_3$ solution in pyridine, for the level of the liquid in the osmometer rose to a height of about 18 cm in twenty hours. Water then goes into the cell, forming the main current, but both $AgNO_3$ and pyridine were also found in the water outside, showing a considerable counter-current toward the outer liquid.

16. The inside liquid consisted of o.1 normal $AgNO_3$ solution in water, the outside liquid of o.1 normal $AgNO_3$ solution in pyridine, the membrane being rubber. The main current was from the outer liquid to the inner one, the level rising in the stem of the osmometer. During the night the liquid filled the tube (which was about 32 cm long) entirely and ran over.

17. The outside liquid consisted of toluene, the inside liquid of o.1 normal solution of $AgNO_3$ in pyridine and the membrane of rubber. The liquid rose 22 cm in the osmometer in seventeen hours. The main current consists of the passage of toluene through the septum to the pyridine solution of the $AgNO_3$; however, pyridine was also found in the toluene outside as were mere traces of silver nitrate.

18. This experiment was identical with No. 17 except that a parchment septum was employed. It was continued for four days and no change was observed. It seemed as though a slight lowering of the level of the inner liquid might

have taken place, so the contents of the cell were evaporated to dryness, the residue taken up with water and a drop of nitric acid and tested with HCl for silver, after having been filtered. Only the faintest indication of the presence of silver was thus obtained.

19. The inside liquid was 0.1 normal solution of $AgNO_3$ in pyridine, the outside liquid pyridine and the septum rubber. The liquid rose slowly in the osmometer, indicating the direction of the main current to be from the pyridine through the rubber to the solution. An examination of the outer liquid showed the presence of only a very small amount of nitrate of silver. The experiment was repeated, using a much heavier piece of ordinary gray sheet India rubber as a septum, with the same result. And again it was repeated, using the rubber dam as a membrane once more, but supporting it by tying over the outside of it a piece of muslin. With this arrangement the liquid rose in the stem of the thistle tube to a height of 28.5 cm in eighteen days, remaining there constant for two days, and then receding slightly. The temperature was very nearly 17° throughout the test. The outer liquid was found to contain appreciable amounts of $AgNO_3$, but hardly an estimable quantity. This shows that vulcanized caoutchouc is practically impermeable for $AgNO_3$ under the conditions described; in other words that it is a "semipermeable" membrane.

20. The inner liquid was a 0.05 normal solution of $AgNO_3$ in pyridine, the outer pyridine, and the septum rubber. At 17° C no change whatever was observed after six days. After nineteen days a rise of about 0.5 cm of the liquid in the stem of the osmometer was observed. The outer liquid was then analyzed for silver nitrate. Only traces were found, not an estimable quantity. This shows that the membrane did not leak and that the so-called osmotic pressure of an $AgNO_3$ solution in pyridine which is 0.05 normal is practically nil at 17° C when vulcanized caoutchouc is used as the semipermeable membrane.

21. The inner liquid was a normal solution of $AgNO_3$ in pyridine, the outer liquid pyridine and the membrane rubber. The apparatus was kept at a temperature which varied gradually between —16° and —15° C. At the end of the second day the liquid in the osmometer had risen to a height of 7.2 cm, the temperature being —16°. At the end of the third day the height of the column was 15.6 cm, the temperature being —15°. The membrane was intact and but traces of silver were present in the outer liquid.

22. The inner liquid was a normal solution of $AgNO_3$ in pyridine, the outer liquid pyridine, and the membrane rubber. In this case a piece of common vulcanized rubber about 1 mm thick such as is used on foot-power laboratory bellows was employed. It was supported on each side by pieces of muslin and perforated steel discs, and the whole was then securely screwed to the lower end of an osmotic cell made of steel. The maximum pressure which was read on a closed manometer, using mercury between the air space and the inner liquid, was 14.95 atmospheres at 20° C. The membrane did not "leak," which was evident from the fact that only mere traces of $AgNO_3$ were found in the outer liquid, though the experiment was run for two weeks, the pressure remaining practically constant for five days. This steel osmotic cell consumed considerable time in its construction, and many difficulties had to be overcome in perfecting it and attaching the manometer to it. However, it is unnecessary to enter into a detailed description of the cell, since no special significance will be attached to the single result recorded here, it being given simply to show that a very considerable pressure may be produced by a normal solution of $AgNO_3$ in pyridine when it is separated from pure pyridine by vulcanized caoutchouc at 20°, whereas at —16° (No. 21) the pressure formed is practically insignificant.

Silver nitrate is insoluble in hydrocarbons, which shows that the affinity between that salt and hydrocarbons is slight. Now as caoutchouc is a hydrocarbon substance, the affinity

between it and silver nitrate would be slight. Pyridine has considerable affinity for silver nitrate. It dissolves the salt readily with evolution of a considerable amount of heat. Pyridine is soluble in all porportions in hydrocarbons—is consequently readily imbibed by rubber. When a silver nitrate solution in pyridine is placed in contact with rubber the latter soaks up pyridine, but also some silver nitrate with it, since the pyridine and the salt are bound to each other by mutual attraction. This accounts for the fact that traces of silver nitrate pass into the pyridine when it is separated from a silver nitrate solution in pyridine by means of a rubber septum as in experiments 19, 20, 21 and 22, though the main current is that of the passage of pyridine through the membrane to the solution. Thus the reason why caoutchouc is a "semi-permeable" membrane in these cases is given; and we should expect in all cases in which the solute employed is insoluble in hydrocarbons, like kerosene, benzene, etc., yet is soluble in pyridine, that vulcanized rubber will act as a "semiper-meable" membrane when it is employed in separating pyridine from the pyridine solutions of such solutes. This has been confirmed in the case of cane sugar and lithium chloride which are soluble in pyridine yet insoluble in hydrocarbons. The experiments are given below. Conversely, when a substance is soluble in hydrocarbons as well as in pyridine, that substance will always pass through vulcanized caout-chouc in notable quantities when its solution in pyridine is separated from pure pyridine by means of the caoutchouc septum. Examples of such cases will also be found below. Though experiments 19 to 22 are only quasi-quantitative in character they are already quite sufficient to show that here the osmotic pressure does not follow the gas laws at all. The change of the pressure with temperature is very much greater than proportional to the absolute temperature; and again the pressure varies much more rapidly with change of con-centration of the solute than is required by Boyle's law. Experiment 20 reveals the fact that at room temperature the

osmotic pressure of the 0.05 normal solution of $AgNO_3$ in pyridine is practically nil under the conditions described, while on the basis of the van't Hoff theory the osmotic pressure of this solution ought to be over an atmosphere. We have in No. 20 the case where the solution has been diluted to such a point that its affinity for additional pyridine is practically equal to the affinity between pyridine and the rubber, so that the latter can not be robbed of its pyridine content by the solution, and consequently the liquid in the osmotic cell does not increase in bulk.

The observations made in Nos. 14 and 16 are such as might have been foreseen, considering the fact that water has practically no affinity for rubber; that the latter has considerable affinity for pyridine; that water and pyridine are consolute liquids; and that silver nitrate, though soluble in water and pyridine, is yet not soluble in hydrocarbons and consequently has practically no affinity for rubber. Further, recalling that water is readily taken up by parchment and pyridine and toluene not, and considering these facts in connection with those already mentioned, the data obtained in Nos. 15, 17 and 18 are readily explained.

23. The inside liquid was a 7.06 percent cane sugar solution in pyridine, the outer liquid pyridine and the membrane rubber, supported by muslin tied over it. The liquid rose in the osmometer to a height of 22.7 cm in four days, the height after the second day being 21.8 cm. Sugar had not passed into the outer liquid except in mere traces.

24. This experiment was like No. 23 except that xylene was used as the outer liquid instead of pyridine. The liquid rose to a height of 16.4 cm in four days. Sugar was not present in the outer liquid in appreciable quantities, but pyridine was.

25. The inside liquid was a 1.2 percent solution of sugar in pyridine, the outer liquid pyridine and the membrane rubber supported by muslin. The temperature was kept at 22.°5 C. A rise of the liquid in the osmometer tube was noted

after five minutes. After three hours the column measured 4 cm; after twelve hours about 5 cm. Sugar did not pass through the septum in appreciable amounts. The experiment shows that the solution used is able to produce but a very feeble osmotic pressure.

26. The inner liquid was a 0.125 normal solution of sugar in pyridine, the outer liquid pyridine and the septum rubber supported by muslin. The whole was kept at 0° C. After three days the liquid had risen only 0.5 cm in the osmometer tube; after five days, the rise was but 1.9 cm. The membrane was intact, and practically no sugar had passed into the pyridine without.

27. This experiment was like No. 26 except that a 0.25 normal solution of sugar was used as the inner liquid. The temperature was kept at very nearly —16° C. During the first day the liquid rose to 9.5 cm in the osmometer; on the second day the column measured 13.5 cm; and on the fourth day 17.5 cm. The membrane was intact and only very slight amounts of sugar were present in the outer liquid. The same experiment performed at room temperatures showed a very rapid rise of liquid in the osmometer tube—see pressures measured in the quantitative measurements described below.

28. The inner liquid was a saturated solution of LiCl in pyridine, the outer liquid pyridine and the septum rubber. The liquid rose in the osmometer and LiCl did not pass through the septum into the outer liquid in appreciable quantity.

Experiments 23 to 27 show that vulcanized caoutchouc is a "semipermeable" membrane when it separates sugar solution in pyridine from pure pyridine. The data lead one further to the conclusion that the gas laws do not govern the phenomena, which the measurements to be detailed later confirm. No. 28 shows that when LiCl is used as solute in an otherwise similar experiment, the rubber again acts as a semipermeable septum. The reasons for this behavior have already been discussed in connection with the $AgNO_3$ solutions.

29. The inside liquid was 0.1 normal $AgNO_3$ in pyridine, the outside liquid a saturated solution of cane sugar in pyridine, the membrane being rubber. The level in the osmometer fell, showing the current to be from the $AgNO_3$ solution to that of the sugar. On further examination it was found that $AgNO_3$ had also passed into the sugar solution but in small amount.

30. This experiment was identical with No. 29 except that parchment was used as the septum. The test was continued for three days. No change was observed.

In the light of what has already been said, it is clear that the results in Nos. 29 and 30 are such as might have been anticipated.

31. The inner liquid was a solution of $FeCl_3$ in toluene, the outer toluene, the membrane rubber. The main direction of flow is toward the solution, but $FeCl_3$ also passes through the membrane in considerable quantity, which was to have been expected since this salt is soluble in hydrocarbons. The $FeCl_3$ gradually disintegrates the septum.

32. This experiment was identical with that of No. 31 except that iodine was used as the solute instead of $FeCl_3$. The iodine also passed through the rubber, as was to have been expected; and it disintegrated the septum more rapidly than did the $FeCl_3$. The liquid, however, first rose in the osmometer.

33. The inner liquid was a solution of copper oleate in benzene, the outer benzene and the septum rubber. The liquid in the osmometer rose to a height of 20 cm, showing the main current to be toward the solution; however, large amounts of copper oleate passed through the rubber into the outer benzene. This was to have been expected, since copper oleate is soluble in hydrocarbons.

34. This experiment was identical with No. 33 except that parchment was employed as the septum in place of rubber. No change whatever took place, which was to have been anticipated since none of the ingredients touching the membrane have sufficient affinity for it.

35. This experiment was like No. 33, except that the copper oleate was dissolved in pyridine, and pyridine was used as the outer liquid. Again the main current was toward the solution, but copper oleate passed into the outer pyridine in considerable quantity, which is quite in harmony with the theory advanced.

When we think of a large molecule like that of copper. oleate readily traveling through vulcanized caoutchouc as in No. 35, and that under like conditions cane sugar, $AgNO_3$, and LiCl do not pass through that septum, it certainly must convince us that the membrane does not act as a sieve. Again No. 34 shows that parchment is not a "porous" material as is so commonly assumed from osmotic experiments with aqueous solutions in which it is employed as septum.

36. The inner liquid was a strong solution of sodium oleate in water, the outer liquid water and the septum rubber. No change occurred.

37. The experiment was like 36 except that parchment was employed as the septum. In this case sodium oleate was found in the outer water, though the inner liquid showed slight increase in bulk.

Sodium oleate, though soluble, in water is insoluble in hydrocarbons; bearing this fact in mind, the results in Nos. 36 and 37 are readily explained.

38. The inner liquid consisted of a normal solution of naphthalene in pyridine, the outer liquid was pyridine and the membrane rubber. Practically no change in level occurred, but large quantities of naphthalene passed into the pyridine without.

39. The inner liquid was a normal solution of camphor in pyridine, the outer pyridine and the septum rubber. Practically no change in level occurred, but considerable amounts of camphor appeared in the outer liquid.

40. The inner liquid was a saturated solution of camphor in 99.5 percent alcohol, the outer liquid 99.5 percent alcohol and the septum rubber. After half an hour a slight lowering

of the level of the liquid in the osmometer was noted; it continued to go down for three days, when the experiment was stopped.   Much camphor had passed into the alcohol without.

41. The inner liquid was a saturated solution of camphor in toluene, the outer liquid toluene and the membrane rubber. The liquid at once rose rapidly in the osmometer.   In nine hours it reached a height of 32 cm.   It continued to rise for three days, the duration of the experiment.   Large quantities of camphor had passed through the septum into the outer toluene.   Camphor is very soluble in toluene.

That naphthalene and camphor should pass through rubber was to have been expected, Nos. 38 to 41, since these substances are very soluble in hydrocarbons.   In No. 40 the main current is from the solution of camphor in alcohol to the alcohol, while in 41 the main current is from the toluene to the camphor solution in toluene.   This occasions no surprise when it is borne in mind that toluene is imbibed much more rapidly and more copiously by rubber than is alcohol, and that an alcoholic solution of camphor is imbibed by rubber more rapidly than is alcohol.   Again, remembering that it is the relative rate of inflow and outflow which determines whether the bulk of the liquid in the osmotic cell will change or not under given conditions, the results in 38 and 39 are readily explained.

42. In the osmometer was placed a solid block of camphor in form of a cube which weighed 2 grams; the outer liquid was 99.5 percent alcohol, and the membrane rubber.   The osmometer was immersed in the liquid so that the membrane was slightly below (about 0.5 cm) the surface of the liquid. The arrangement is shown in Fig. 5.   After five minutes there seemed the least evidence that the camphor was being attacked, but even after four hours, there was but little further change.   Since alcohol is not very readily imbibed by rubber this occasioned no surprise.

43. This experiment was identical with No. 42, except

that toluene was used instead of alcohol. Plain evidence
that the camphor was dissolving appeared in three minutes.
In forty minutes the solid camphor had all disappeared and
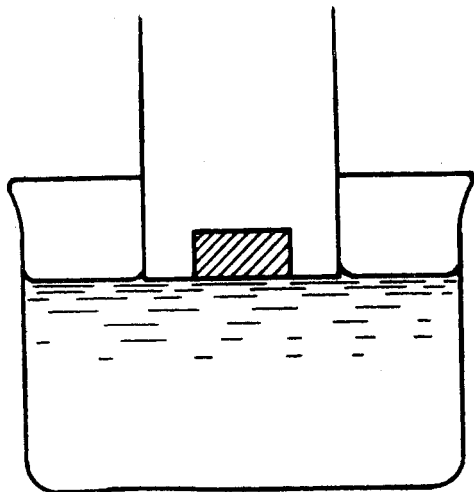was found in very large quantities in the outer liquid. The

Fig. 5

membrane became much distended, bulging downward. The
level of the liquid was alike in and outside after four hours,
it having risen slightly on the inside.

44. This experiment was like No. 42 except that xylene
was employed instead of alcohol. The observations were
practically identical with those of No. 43 where toluene was
employed, which might have been expected.

45. This experiment was also like No. 42 except that
pyridine was employed instead of alcohol. After four minutes
it was evident that the camphor was being attacked. A very
thin layer of liquid, less than 1 mm thick, appeared on the
upper side of the rubber. In four hours all the camphor
had gone through the rubber into the pyridine, leaving a
depth of solution of only about 1 mm on the upper side of the
membrane. During the process the membrane became some-
what distended and bulged upward toward the camphor.

46. In this case the arrangement was again like in No.
42, except that CCl_4 was employed instead of alcohol. After

about four minutes it was evident that the block of camphor was beginning to disappear. In forty-three minutes the whole block was gone, having passed through the rubber into the CCl_4, leaving on the upper side of the membrane a camphor solution less than a millimeter deep. The membrane became distended and bulged upward. After four hours, the liquid on the upper side of the membrane was from 1 to 2 mm deep.

47. This experiment was also like No. 42 except that CS_2 was used as the liquid instead of alcohol. After four minutes it was clearly evident that the block of camphor was being attacked. After thirteen minutes a thin layer of liquid was visible on the upper side of the rubber. After forty-five minutes all solid camphor had disappeared, having passed through the rubber into the CS_2, leaving on the upper side of the membrane a solution about 3 to 4 mm deep. After four hours the membrane appeared very much distended, bulging downward, the liquids in and outside being on a level.

48. In this case a cube of paraffine of rather high melting-point (70°) was separated from 99.5 percent alcohol by means of a rubber septum, the arrangement being as described in No. 42. After twenty-four hours the lower corners and edges of the paraffine cube appeared slightly rounded. No liquid was visible on the upper side of the rubber, however. After three days the large bulk of the paraffine was still intact, though it was distinctly evident that the substance was slowly passing through the rubber septum into the alcohol beneath, without any liquid layer appearing on the upper side of the membrane.

49. This experiment was identical with the preceding one, No. 48, except that toluene was used instead of alcohol. In this case solution gradually accumulated on the upper side of the rubber, though paraffine passed through into the toluene on the outside. After twenty-four hours only about one-eighth of the paraffine was left undissolved and the liquid on the inside was practically on a level with that on the outside. Much paraffine was found in the outer liquid.

50. In this case the cube of paraffine was separated from pyridine by means of rubber, the arrangement being as described in connection with No. 42. The observations were practically the same as when alcohol was employed, No. 48.

51. The experiment was identical with the preceding one No. 50, except that CCl_4 was used instead of pyridine. After twenty-four hours about three-fourths of the paraffine was still left in the solid state; it floated on the layer of liquid which had formed on the upper side of the rubber. Considerable paraffine had gone through the septum into the CCl_4 below. The membrane was much enlarged and bulged downward. After two days, all the paraffine had dissolved and the liquids in and outside were nearly on a level.

52. About 2 grams of dry powdered $AgNO_3$ was placed on the upper side of a rubber membrane, the lower side being bathed by pyridine. The arrangement was as pictured in Fig. 5, the powdered $AgNO_3$, which was spread out over the surface of the membrane, taking the place of the block represented in the figure. The experiment then was the same as No. 45 except that the $AgNO_3$ was used in place of camphor. After seven hours no liquid was visible on the upper side of the membrane. Pyridine had, however, passed into the silver nitrate and formed a solid addition product with it. No appreciable amount of $AgNO_3$ had passed into the pyridine without. After twenty-four hours all the $AgNO_3$ had dissolved and the liquid in the osmometer had risen to a height of about 1.5 cm and continued to rise. After four days the experiment was stopped and the outer liquid examined for $AgNO_3$. It was, however, found to be present only in mere traces. This shows that vulcanized caoutchouc is indeed a good "semipermeable" membrane in this case.

Considering experiments Nos. 42 to 52 in which solids were separated from liquids by means of rubber septa, it is evident that whether the solid will pass through the membrane or not depends on the nature of the solid, the membrane and the liquid employed. Furthermore, if the sub-

stance composing the solid does make its way through the septum, the fact as to whether the action is accompanied with an accumulation of liquid on that side of the septum occupied by the solid or not is clearly determined by the rate with which the solution formed is absorbed by the membrane (which is determined by the mutual attraction or affinity of the saturated solution and the membrane for each other) and also by the rate with which the pure solvent is imbibed from the other side.

Now it is well known that camphor dissolves very readily in hydrocarbons and consequently has considerable affinity for rubber, and we should therefore expect it to pass through the latter when it is employed as an osmotic membrane. An alcoholic solution of camphor is more readily imbibed by rubber than is pure alcohol, and so it occasions no surprise when in No. 42 we find the block of camphor slowly making its way through the rubber septum into the alcohol, and without the appearance of liquid on the side occupied by the camphor. The action is slow because alcohol is not imbibed rapidly or copiously and because the septum holds on to the strong camphor solution very tenaciously, so that only a small portion of the camphor thus saturating the rubber is washed out of the latter by the alcohol on the other side.

When the same experiment is performed using a hydrocarbon as the liquid instead of alcohol, Nos. 43 and 44, the action goes on very much more rapidly on account of the great affinity between rubber and the hydrocarbon or a camphor solution in a hydrocarbon. The strong camphor solution is so greedily absorbed by the rubber that but little liquid appears on the upper side of the membrane while the solid camphor lasts, and it is as though the solid camphor were passing through the rubber septum by mere contact with it. The process reminds one strikingly of the manner in which solid food placed in the alimentary canal is digested and absorbed. Here the presence of the food in contact with the walls of the tract excites the flow of the digestive juices toward

the solids; the latter are acted upon and the resulting liquid is absorbed by the walls of the canal. In our experiments the camphor in contact with the rubber saturated with a hydrocarbon excites a flow of hydrocarbon toward it. The hydrocarbon acts on the camphor "dissolving" it, and the resulting solution is then so rapidly absorbed by the septum as to leave no liquid on the side occupied by the camphor.

When as in No. 45 pyridine is used instead of a hydrocarbon, the camphor is still absorbed, but not as rapidly, for pyridine is not taken up by rubber as readily or as copiously as are hydrocarbons; neither has camphor so great an affinity for pyridine as for hydrocarbons. On the other hand, camphor very rapidly disappears when CCl_4 or CS_2 (Nos. 46 and 47) are employed, for these substances have great affinity for rubber and also for camphor.

When paraffine instead of camphor is separated from alcohol, toluene, pyridine or carbon tetrachloride by means of rubber, Nos. 48 to 51, the action is in all cases slower, which fact is readily comprehended when it is borne in mind that camphor dissolves more readily in the liquids named than does paraffine.

Finally in No. 52, where solid silver nitrate is separated from pyridine by rubber, we have an illustration of a typical case in which the liquid accumulates very greatly on the upper side of the membrane. Here the solute has very little affinity for the rubber, and so the solution of the salt practically does not get into the septum on account of the fact that pure pyridine is more readily imbibed and silver nitrate is difficultly soluble in rubber soaked with pyridine, that is to say, in a hydrocarbon diluted with pyridine. If a block of cane sugar or one of chloride of lithium were separated from pyridine by means of a rubber septum, the action would be similar to that observed in the case of silver nitrate, No. 52. The same would be true if any solid which is soluble in pyridine yet not soluble in hydrocarbons were separated from pure pyridine by means of a rubber membrane. It would be

interesting to test this in the case of more substances which are insoluble in hydrocarbons and yet are soluble in pyridine, but the number of such substances is rather limited, for it must be remembered that pyridine is itself nearly a hydrocarbon in character and is consolute with hydrocarbons.

Qualitative Tests with Animal and Vegetable Membranes

A number of qualitative tests were made with membranes of organic origin. It was thought best to place the results of these experiments on record here, though it is contemplated to take up the whole matter of the action of organic membranes separately at some later date.

Various animal membranes were tested as to their permeability for sodium chloride, urea and cane sugar. The membranes were stretched over square wooden frames quite loosely so as to form bags or pockets into which one liquid was placed; these bags were then suspended in the outer liquids in such a manner that only the lower sagging part, and not the upper edges were in contact with the outer liquids. As membranes to be tested were selected the pericardium, diaphragm, small intestine, large intestine, stomach, aorta, urinary bladder and gall cyst of a young ox. The animal was perfectly sound and normal and about three years old. The membranes were used soon after the animal had been killed. On the upper side of each membrane was placed an aqueous solution containing 23.4 grams of sodium chloride, 40 grams of urea and 342 grams of cane sugar in 2000 cc, while the lower side of the membrane was immersed in pure water, the arrangement being as already described. It was found that in case of all of the membranes mentioned the sodium chloride passed through more rapidly than the urea and sugar, which fact was established by examining the outer liquid from time to time during the first four hours. After twenty-four hours, besides much salt very considerable quantities of urea and cane sugar had gone through all the membranes. A special test made by separating water from

an aqueous solution of sodium sulphate by means of the stomach membrane, showed that the latter is permeated but slightly by sodium sulphate, for the amounts of the latter salt in the outer liquid were but small.

The vegetable septa employed consisted of the rinds of California oranges and grape fruit and Florida grape fruit. The grape fruit, also called shaddock, is the fruit of *Citrus decumana*. In each case the fruit was carefully cut in two transversely with a sharp knife, so that the halves after careful removal of the pulp formed two cups. Each half rind was filled to about half of its capacity with the liquid to be tested and then suspended in pure water so that the latter was about on a level with the liquid in the rind. The suspension of the rind was accomplished by means of fine aluminum wire run through small holes pricked through the upper edges of the rind. Each experiment was continued for twenty-four hours, unless otherwise stated. It was found to be impracticable to continue the experiments much longer, for the rinds after being immersed in water for a considerable time undergo alteration, becoming soft and losing their waxy outer coating.

With the arrangement as just described and employing water as the outer liquid and an aqueous solution as the inner liquid, it was found that sodium chloride readily passes through orange skins, but sodium sulphate very much less readily. Indeed, only traces of the latter salt were found in the outer liquid even when strong solutions were employed. Again, urea readily goes through the orange rinds, but sugar passes through only in very small amounts. When an aqueous solution of potassium alum was used it was found that a slight amount of potassium sulphate appeared in the outer water, but no aluminum sulphate, showing that the latter ingredient is left behind during the time of the experiment at least.

In the upper half of the rind of a Florida grape fruit was placed 100 cc of a solution containing 10 grams sodium chloride plus 10 grams of sodium sulphate. The rind so charged was

suspended in distilled water as above described. The outer water had a volume of 500 cc. Tests of the outer liquid showed that the NaCl was passing through much faster than the Na$_2$SO$_4$. This experiment was run for seven days; the rind did not seem to be altered much.

The lower half of the rind of a California grape fruit containing 70 cc of an aqueous solution which contained 10 grams of NaCl plus 10 grams of sugar in 100 cc, was suspended in a dish in 300 cc of water. It was found that the sugar passed through the rind much more slowly than the salt. The experiment was continued for seven days.

A similar experiment in which 80 cc of an aqueous solution containing 10 grams sugar plus 10 grams urea in 100 cc was placed in the upper half of the rind of a California grape fruit suspended in a dish containing 400 cc water, yielded the result that both urea and sugar pass through the rind, but the latter more slowly. After twenty-four hours sugar may be detected in the outer liquid with Fehling's solution. The urea acts on the rind, thickening and hardening it. Much urea is thus retained in the rind, also considerable amounts of sugar. These facts were determined by an examination made after the experiment had run for seven days.

To 70 cc of a saturated solution of boric acid in water 10 grams of sugar were added. This solution was placed in the upper half of the rind of a California grape fruit, the outside being bathed by water. The experiment was continued for five days, the rind remaining intact and practically unaltered during this time. Only traces of boric acid passed through the rind. Sugar passed through slowly, but at the end of five days it was found in the outer liquid in considerable quantity.

It was found, further, that in dilute aqueous solutions H$_2$SO$_4$, HCl and HNO$_3$ readily pass through the skins of grape fruit, but the rinds are much altered by the acids, appearing shrunken and darkened in color. Citric acid passes through less rapidly than the mineral acids mentioned. It is apparently retained to a considerable extent in the rind.

The experiments made with the rinds of grape fruit were also repeated with the skins of California oranges, with practically the same results.

Quantitative Measurements of Osmotic Pressures

The quantitative measurements of osmotic pressures were made with so-called semipermeable membranes, that is to say, with membranes through which the solvent passes so much more readily than the solute, that the amount of the latter which goes through the septum is practically a negligible quantity. From what has been said above, it appears that the latter quantity is never absolutely nil, and that consequently there is really no such a thing as a semipermeable membrane, strictly speaking.

Now as has been intimated, the qualitative experiments above detailed enable one to foretell when a membrane will permit the solvent to go through so much more readily than the solute that the amount of the latter which traverses the membrane is so slight that the septum may be called semipermeable. From the ether, water, chloroform experiment, already described as a typical case of osmosis, it appears that the ether makes its way through the water into the chloroform because (1) ether is soluble in water and (2) chloroform has much more affinity for ether than has water, so that ether is extracted from the water layer by the chloroform; on the other hand, the water does not permit chloroform to pass into it and into the ether beyond to an appreciable extent, because chloroform is so very slightly soluble in water even when the latter is impregnated with ether.

Holding these things in mind let us look for the proper solvent and solute to employ with rubber as the membrane so that the latter shall be semipermeable. It must first be remembered that rubber (vulcanized caoutchouc) is practically a hydrocarbon. The rubber employed was of excellent quality and was almost the pure gum. On analysis it was found to contain 0.38 percent ash, and a Carius determination

yielded 0.30 percent chlorine and 0.95 percent sulphur. Before the analysis was made the sample was wiped superficially, washed with distilled water, dried with filter-paper and finally left in a desiccator over strong sulphuric acid for twenty-four hours. It is evident that in order to pass through a rubber membrane a substance must be taken up by the rubber, the rubber must imbibe the substance; in other words, the substance must be soluble in rubber.[1] Again the liquid bathing the other side of the rubber must be capable of extracting the imbibed substance from the rubber, thus completing the transference. On the other hand, those substances which are not soluble in rubber, *i. e.*, are not taken up by the rubber, will obviously not pass through the latter. And so what is required is a solvent which will readily be taken up by rubber, without, however, disintegrating the same, and a solution of such a character that the solute shall not be soluble in rubber. The less affinity the solute has for rubber the better, for then when the solution is brought into contact with the rubber the latter will imbibe practically only solvent to the exclusion of solute, thus leaving the solution slightly more concentrated, that is to say, making a partial separation of solvent and solute.

In casting about for a suitable solvent very many substances were tried. It was, of course, desirable to secure a solvent that was not too volatile at ordinary temperatures or too obnoxious. In the course of this work it soon became evident that water, alcohols and, in general, compounds containing considerable hydroxyl, relatively speaking, are not suitable for they are not taken up readily enough by rubber nor in sufficient quantity. On the other hand many compounds, like hydrocarbons, their halogen substitution products, carbon disulphide, ether, etc., though taken up readily by rubber and in considerable quantity, gradually act upon the latter to such an extent as to form with it a very soft,

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[1] The act of such solution or imbibition is really mutual; *i. e.*, the rubber attracts the substance in question, and the latter in turn attracts the rubber.

sticky mass, or even a liquid, a combination or solution then of such mechanical properties as to be entirely unsuitable for quantitative osmotic experiments. After trying a large number of liquids, pyridine was finally taken as being the most suitable for the purpose in hand. From its very nature pyridine is a substance which would perhaps be expected to fulfil the requirements. Its high carbon and hydrogen content make pyridine almost a hydrocarbon; indeed, it dissolves in hydrocarbons in all proportions. Since rubber is a hydrocarbon, we should expect it to imbibe pyridine readily. It was found that pyridine is imbibed by rubber, increasing the bulk of the latter somewhat to be sure, but without otherwise materially altering the mechanical properties of the rubber. Indeed, I found that vulcanized caoutchouc may even be boiled in pyridine for hours, in which case there is a slight amount of material extracted from the rubber, giving the liquid a brownish color; but the rubber is not disintegrated or affected materially otherwise. The rubber used as membranes in the actual quantitative measurements was in fact thus extracted with boiling hot pyridine. After such treatment, rubber, when dried, has practically all of its original properties; it is perhaps a little easier to rupture it by stretching it hard. It might at first be somewhat surprising that pyridine does not disintegrate rubber more. However, while pyridine is closely akin to hydrocarbons and consolute with them, it must be borne in mind that water, which has but little affinity for hydrocarbons, also is consolute with pyridine. Pyridine is then a rather unique substance, and it is hardly surprising that it should be imbibed by rubber sufficiently for the purpose in hand without unduly disintegrating it. Direct experiment showed that at room temperature (about 20° C) 100 grams of the vulcanized caoutchouc used imbibed 144.42 grams of pyridine in twenty-four hours, while the amount imbibed in seventeen days was 145.17 grams.

A suitable solute would be one that is soluble in pyridine yet insoluble in hydrocarbons. For instance, a substance soluble in petroleum or benzene would in general also be

soluble in pyridine, but it would also be soluble in rubber
(a hydrocarbon) and hence would pass through the latter.
Thus oleic acid, the oleates of the heavy metals, ferric chloride,
naphthalene, camphor are soluble in hydrocarbons, are con-
sequently readily taken up by rubber, and when dissolved
in pyridine pass through the rubber when the latter in an
osmotic experiment separates the solution from pure pyridine.
Because of the peculiar nature of pyridine already alluded to
above, this liquid dissolves a goodly number of substances
which are insoluble in hydrocarbons.   The solubility of such
substances in pyridine is, to be sure, rather limited as to quantity
as a rule.   So cane sugar, silver nitrate, lithium chloride are
insoluble in hydrocarbons and yet reasonably soluble in
pyridine.   One would consequently expect that when solu-
tions of either of these substances in pyridine be separated
from pure pyridine by means of a rubber septum, practically
none of the solute would pass through the rubber; in other
words, the latter would be practically impermeable for sugar,
silver nitrate and lithium chloride.   Now this is actually
what was found in the qualitative tests described above.
These substances pass through rubber in extremely slight
quantities which are quite comparable with the amounts of
cane sugar that pass through the much studied copper ferro-
cyanide membrane, when it separates water from an aqueous
sugar solution.   However, on account of the fact that sugar
has a high carbon and hydrogen content, one would expect
it to have more affinity for a hydrocarbon than either silver
nitrate or lithium chloride, and that consequently it would
pass through rubber a little more readily than these salts.
Experiment has also shown that this is actually the case,
though, as stated above, the amount of sugar which passes
through the rubber membrane is quite small.

The quantitative measurements of osmotic pressures
were then made by using solutions of cane sugar, lithium
chloride, and silver nitrate in pyridine, these solutions being
separated in each case from pure pyridine by means of a mem-

brane of vulcanized caoutchouc previously treated with boiling hot pyridine so as to extract any soluble ingredients. It was not the purpose of the quantitative measurements of osmotic pressures to produce and measure enormous pressures, though as was shown above in No. 22 a pressure of approximately fifteen atmospheres was actually measured in the case of a normal solution of silver nitrate in pyridine. The efforts were rather directed toward determining with a sufficient degree of accuracy moderate pressures, using different concentrations of the solutions employed at several different temperatures.

The osmotic cells were made entirely of glass, excepting. of course, the surface actually closed by the membrane itself,
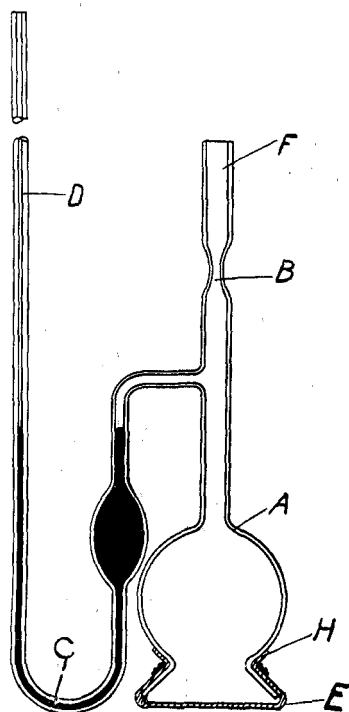

Fig. 6

The different parts of the cells were fused together so as to form one piece, thus avoiding cemented joints of any kind. Fig. 6 shows how these cells were made. To a stout, care-

fully-made thistle tube having a flare of about 45° at E a T was attached, the tube being provided with a bulb and bent as shown in the figure, C. To C was fused a manometer tube D having a bore of about 0.5 mm; this tube was made as long as the experiment required. The small bulb and bent part of the tube C contained mercury. At B the tube was somewhat contracted as shown, and after putting the required amount of pure, clean mercury into the apparatus and filling the rest of it with the solution to be tested through the orifice F by means of a capillary funnel tube, the apparatus was carefully heated at B by means of a small flame and finally drawn off, leaving the whole securely sealed. With practice this part of the operation may be so performed that practically no air bubble remains in the apparatus after the tube has been drawn off at B.

Before placing the mercury and the solution into the cell, however, the membrane must be securely put into place. It is first of all essential that the opening of the bell of the thistle tube E be as nearly circular as possible, and that the points on the outer edge of the orifice lie in very nearly the same plane. The rubber membrane consisted of a high quality of sheet rubber as is used by dentists: Its ash, sulphur and chlorine content have already been given above, and it has also been stated that the material was extracted with hot pyridine before using it. The rubber so prepared was carefully tied over the orifice at E. In this process it was stretched only moderately so as not to thin it unduly.[1] In tying the membrane on, the rubber was always stretched to such an extent, however, that no folds whatever remained where it touched the glass. With proper care it is possible to get a smooth surface of rubber to rest snugly against the surface of the glass. The rubber was finally securely fastened into place by carefully winding the whole surface from H to E smoothly and closely with moderately fine thread. When

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[1] When finally in place, the thickness of the membrane was only a small fraction of a millimeter.

these precautions are observed one hardly ever fails to get a
perfectly tight joint between the glass and the rubber, which
is so all-essential.

The next step consisted of supporting the membrane so
that it would withstand pressure. To accomplish this there
was first tied over the membrane a piece of smooth, soft yet
strong muslin. This cloth was drawn tightly over the mem-
brane, and securely tied on by winding moderately fine yet
strong thread over it smoothly and evenly from H to E. It
is of course impossible to get rid of folds in the cloth where it
is tied on the surface H to E, but it is quite possible to dis-
tribute these folds fairly evenly around the circumference,
in such a manner that the cloth where it actually touches the
rubber on the mouth of the thistle tube and just at the edge at
E, lies perfectly smoothly and snugly against the surface of
the membrane giving it proper support. After this a circular
perforated disc of stout sheet steel made of proper size so as
just to cover the lower end of the thistle tube was placed on
the muslin covering the rubber; and this disc was then securely
held in place by tying over it very firmly another piece of
strong muslin by means of stout thread evenly and tightly
wound on as in the previous cases. Thus there was the
rubber tied on the glass, then the muslin snugly covering
and supporting the rubber, then the steel disc sieve pressing
against and supporting the muslin, and finally the outer layer
of muslin firmly holding the disc in the proper position. The
perforations in the disc were about 1 mm in diameter and
the disc itself was about 0.5 mm thick. By observing closely
the precautions here laid down, cells were practically always
obtained without fail which were perfectly tight, rigid and
capable of withstanding pressures up to the point of bursting
the glass bell of the thistle tube. Furthermore, on taking
such an apparatus apart even after experiments that had
continued for weeks, the membrane was found to be intact
and in perfect condition. Experiments demonstrating that
such membranes do not leak have already been given above,

Nos. 1 and 2. We have here then a simple, direct and certain method of preparing so-called semipermeable membranes for osmotic pressure measurements, which are yet not precipitated membranes; and furthermore we know *why* the membranes are semipermeable for the solutions that come into question.

After the membrane has been put into place as described, the apparatus is charged with the required amount of mercury and then with the solution to be tested, the tube being drawn off at B before the small flame of a blowpipe so as to leave no air in the apparatus. The latter is then placed in a large vessel containing the pure solvent, and the rise of the liquid in the manometer tube is observed from time to time, a pair of sensitive thermometers graduated to 0.1° being placed in the solvent near the osmometer to indicate the temperature. The apparatus was set up in a basement room, whose temperature changed but slightly and only very gradually during the course of the experiments. It is highly essential that the temperature be kept as constant as possible during the experiments and that sudden fluctuations be avoided. From what has been said it is evident that the experiments were finally set up in much the same way in which Pfeffer performed his tests, only in this case additional care was taken to cover up the dish so as to minimize evaporation and to protect the surface of the pyridine from the moisture of the air. All measurements were made with the open manometer and the height of the mercury column was estimated to within 1 mm in each case. It was found to be quite needless to measure more closely than this, for the results of separate duplicate experiments showed greater variations as a rule.

I will first give the results of the experiments performed by using the method just described, which method, though it is the usual one, had to be modified later in one important particular in order to secure reliable results. The individual experiments are numbered consecutively with those preceding so as to facilitate future reference to them.

53. The liquid in the osmometer was a solution of cane sugar in pyridine containing one-fourth of a gram-molecule per liter of the solution. The outer liquid was pure pyridine. The experiment was run in triplicate, that is, three separate individual tests were made with the same solution. The temperature in each case was 17°.5 C. (*a*) In the first of these experiments the pressure came up slowly, remaining nearly constant after the second day. The experiment was nevertheless allowed to go on for nine days when the pressure was finally measured and found to be 186.2 cm at 17°.5 C. Before discontinuing the experiment, the whole of the outer vessel was packed in melting ice for ten hours. The mercury column became constant at 125 cm after three hours and remained there for the remaining seven hours. The temperature was then permitted to rise slowly and after three days the mercury column was 159.5 cm high, the temperature being 16°.4. When the whole had finally reached the temperature 17.5, the mercury column was again 186.0 cm high. This then would seem to be pretty good evidence that the maximum pressure had indeed been reached. During the operation care was taken not to disturb the apparatus by jarring it in any way. The outer liquid was found to contain traces of sugar, but the exact amount was not determined. (*b*) In the second independent yet perfectly similar experiment, the pressure also rose gradually, changing but slightly after the second day. The temperature was kept at 17°.5 C, and at the end of eleven days the column of mercury measured 155.6 cm. This experiment was then allowed to run for four days longer. At eight in the morning of the fourteenth day the mercury column measured 166.4 cm at 16°.4 C, while at five in the afternoon of the fifteenth day it measured 166.7 cm at 16°.0 C. As in the previous case, care was taken not to jar the apparatus during the experiment. In this case, too, traces of sugar were found in the outer liquid. (*c*) In a third similar experiment the pressure also increased but little after the second day. The experiment was stopped at the end of

four days in this case, when the mercury column was 107.4 cm high, the temperature being 17°.5 C. Only traces of sugar were found by testing the outer liquid.

It will be noted that the highest pressure was observed in (*a*). In this experiment the pressure came up more rapidly than in the other two cases, accomplishing 115 cm in the first twenty-four hours. The discussion of the causes of the discrepancies in the results of (*a*), (*b*) and (*c*) will be left until a little later.

54. This experiment was performed in duplicate. The arrangement was exactly like that in No. 53 except that the liquid in the osmometer consisted of a solution of cane sugar in pyridine containing one-eighth of a gram-molecule per liter of the solution. (*a*) The pressure rose slowly, increasing but slightly after forty-eight hours. On the sixth day the mercury column measured 62.4 cm, the temperature being 17°.5 C. The whole was then surrounded with melting ice, and after two hours the mercury column measured 0.2 cm; at the end of ten hours the pressure was 0.6 cm. The temperature then gradually rose during the night as the ice disappeared. At 14°.5 C the column measured 48.8 cm and at 17°.5 C it again came up to 62.0 cm, nearly where it was before the chilling process. In this case the experiment was left set up for five days longer, when the column measured but 43.6 cm at 18° C. Sugar was found to be present in the outer liquid in small amount. (*b*) This was a duplicate of (*a*). The observations made were practically the same as in (*a*) except that the pressures were different. The chilling process with ice was omitted in this case. After two days the pressure increased but slightly. On the third day it was measured carefully and found to be 52.8 cm at 17°.5 C. During the next two days the temperature fell very gradually to 14°.5 C and the column then measured 42.5 cm. The temperature then rose gradually to 18° C during the succeeding three days, when the pressure was 46.3 cm.

55. In this experiment the inner liquid was a solution

of cane sugar in pyridine containing 0.25 gram-molecule per liter of solution, while the outer liquid was a solution of cane sugar in pyridine containing 0.125 gram-molecule per liter of solution. The pressure rose slowly, the mercury column reaching a height of 137.5 cm at 16°.8 C. By far the most of this was accomplished during the first two days. The final measurement just given was taken after thirty days. The experiment was then left undisturbed for twenty-six days longer. The pressure began to diminish gradually and finally measured only 89 cm, when the experiment was discontinued. The membrane when examined at the end of this time was to all appearances intact and but slightly changed, if at all.

56. Two experiments were made with solutions of cane sugar containing 0.25 gram-molecule of cane sugar per liter of solution in pyridine as the inner liquid, and pure pyridine as the outer liquid, employing in this case, however, a common thick sheet rubber—such as is used on the ordinary foot-power laboratory bellows—in place of the finer vulcanized caoutchouc used in the other experiments. The experiments were conducted side by side as duplicates of each other. The pressure rose gradually, the mercury column reaching a height of 43.0 cm in one case and 39.5 cm in the other at 22° C. The rubber was found to be much softened when examined at the end of ten days, the duration of the experiments. The maximum pressure was practically reached after forty-eight hours. The pressure diminished gradually after seven days. Small amounts of sugar were found in the outer liquid, though the exact amount was not determined.

From the results just detailed it is evident that the methods employed are not capable of yielding concordant values. Though only attempts to measure osmotic pressures of sugar solutions in pyridine have been described, similar experiments were made using lithium chloride and silver nitrate solutions in pyridine. In these cases the results were no more concordant than in those in which sugar was solute.

At first it was thought that the difficulty lay in the membrane itself, the initial experiments having been performed by using the sheet rubber without further treatment; but actual tests showed that whether the rubber was previously extracted with boiling hot pyridine or not made no perceptible difference in the results. It will be noted that one set of experiments was made, using a common thick sheet rubber (No. 56). In this set the results were very different from those obtained with the thin rubber of high grade (No. 53), and yet the duplicates did not differ from each other more than when thin rubber was used. It was also determined by several trials that the non-concordance of the results of duplicate experiments could not be laid to the fact that in some cases the rubber was stretched rather more than in others. It was not to be expected, of course, that the maximum pressure would be reached in the same time in two experiments that were similar, for the areas of the surfaces of the membranes and their thickness were not exactly the same. It might further be possible that the differences in pressure observed in the experiments that were duplicates of each other occurred because slightly different amounts of sugar passed through the different membranes; in other words, that there was more leakage of solute in one case than in the other. Such leakage or lack of semipermeability would operate to diminish the osmotic pressure in two ways, (1) by directly letting material out of the cell as the pressure rises, and (2) by increasing the amount of solute in the outer liquid and so weakening the cause which creates the pressure. It is quite true that in all cases small quantities of sugar passed through the membranes, and that these were perhaps not always exactly the same. The qualitative tests made, however, always showed that the quantity which had passed through was very small and far below the amount required to produce a noticeable osmotic pressure with the apparatus employed during the time of the experiments. It will be recalled that a 1.2 percent solution of sugar in pyridine yields practically

no osmotic pressure (No. 25) and that the same is true
of a 0.05 normal solution of silver nitrate in pyridine at room
temperature (No. 20). Furthermore, when two similarly
charged osmometers were set in one and the same outer vessel
filled with pyridine, they nevertheless in general failed to
indicate identical pressures. All this led me to the con-
clusion that the non-concordance of the pressures measured
could not be due to leaks, defects or various degrees of "semi-
permeability" of the membranes.[1]

I confess that I was about at my wits' end to understand
why such duplicate experiments made as nearly as possible
the same in every way should yet yield results that were not
more concordant. In all, some seventy independent trials
had been made, in which great care had been used to get the
experiments alike, but to no avail. Yet the membranes
were not defective. One day after measuring carefully the
height of the mercury column in one of the experiments
which had been running for two weeks and in which the
pressure had changed inappreciably for several days, I
happened to brush against the apparatus in such a way as to

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[1] Measurements of the electrical resistance of the membranes were also
made which further established this fact. Placing on each side of the mem-
brane of an osmotic cell, such as was employed in the pressure measurements,
a circular platinum electrode about 2.5 cm. in diameter, so that the planes of
the electrodes were parallel to that of the membrane, and that the metallic sur-
faces were close to the membrane without actually touching it, the cell was
filled with an aqueous saturated solution of NaCl and the same solution was
used as the outer liquid. The electrodes were thus immersed in the saturated
NaCl solution and the membrane separated them from each other. The elec-
trical resistance between the plates was measured by means of the Kohlrausch
method; but it was found to be so great that it was not possible to estimate it
accurately, being upwards of 70,000 ohms. Various rubber membranes tested
in this manner gave results of the same order of magnitude. When the same
experiment was performed, using a parchment membrane, the edges of which
protruded so that they did not dip into the brine, the resistance measured was
less than an ohm. Using the same arrangement with a rubber membrane and
a normal solution of silver nitrate in pyridine as the liquid on each side, the re-
sistance was over 90,000 ohms, and remained the same for four days, when the
experiment was discontinued. A small hole pricked through the membrane
with a needle in the latter case caused the resistance to drop to 450 ohms.

jar it thoroughly without, however, upsetting it or otherwise modifying it in any way. Some minutes later when I chanced to look at the apparatus, I noticed that the level of the mercury, which had been practically constant, had risen over 2 cm. higher. The apparatus was then shaken repeatedly from time to time, seizing it with an insulating cloth so as not to alter the temperature, with the result that each time the pressure rose somewhat higher. The explanation of this was, of course, perfectly obvious at once. The pressure is produced by the entrance of solvent into the osmotic cell, consequently right on the inner side of the membrane the solution becomes more dilute than at other points in the interior of the cell. If the cell is left undisturbed the very slow processes of diffusion seek to equalize the strength of the solution in the cell, but clearly shaking the apparatus, or, better yet, stirring the interior content of the cell, would at once accomplish what it would take diffusion processes a very long time to do, even though they be aided somewhat by gravity, owing to the form of the osmotic cell. And it was moreover perfectly evident, too, that to shake the osmometer, filled as it was with considerable pressure on, would not thoroughly mix the contents of the osmotic cell. It is clear that with a more dilute solution in immediate contact with the inner side of the membrane than is in the rest of the osmotic cell the maximum osmotic pressure can not be attained. Furthermore, as in cells slightly different in form when left perfectly at rest the dilute layer in contact with the inner side of the membrane would in general not disappear at the same rate by diffusion and disturbances due to gravity and difference of density of the layers, concordant results could not be expected in duplicate experiments, however carefully performed, without stirring the contents of the osmotic cell. *In all direct measurements of osmotic pressures which have for their aim the determination of the maximum pressure attainable in a given case, it is consequently necessary to stir the interior contents of the osmotic cell continually while the measurement*

*is being made, in order that the concentration of the contents of
the cell may remain uniform and a layer of maximum concen-
tration be kept in immediate contact with the inner side of the
septum.* Again, since there really is no such thing as a semi-
permeable membrane in the strict sense of the word—which
fact has already been emphasized above—it is evident that
some of the inner content of the cell, be it ever so slight, is
making its way through the membrane into the outer liquid.
Thus right next to the membrane on the side bathed by the
outer liquid, the septum is really not in contact with the
pure solvent—the outer liquid—but rather with a *solution*
more or less dilute. When the apparatus is at rest, the slow
diffusion processes, aided by gravity perchance, tend to
keep the outer liquid of uniform concentration; but these
agencies clearly can not be relied upon to keep pure solvent
in contact with the outer surface of the membrane in osmotic
pressure measurements. Indeed, when the surface of the
membrane is not smooth and presents considerable area to
the outer liquid, a film of liquid is apt to adhere tenaciously
to the outer surface of the septum, in spite of the effects of
diffusion. In the usual osmotic experiments using aqueous
sugar solutions in a cell made by precipitating copper ferro-
cyanide on the inner side of an unglazed porcelain cup, the
slight amount of sugar that passes through very likely lingers
very tenaciously in the pores of the cup just outside of the
actual membrane, forming there a film of solution of such
strength that its effect upon the osmotic pressure is not a
negligible quantity. At least its effect can not be assumed
to be negligible without further experimental work. Nor
would stirring the outer liquid in such a case as this be apt to
remove the difficulty. In the osmotic cells described above
where thin rubber membranes supported by cloth and per-
forated steel discs were used, the effect in question is no
doubt less than in the walls of a porous cup, but it is by no
means negligible. Here the cloth and the disc hinder diffusion,
and it is very necessary to stir the outer liquid thoroughly

and continuously in making the osmotic pressure measurements.

I would like to emphasize here once more then that it is very essential to stir the contents of the osmotic cell and also the outer liquid continuously in any attempt to measure directly the maximum osmotic pressure that may be produced in a given case; and that since in all past experiments this has been entirely neglected, the results of such experiments can not be considered as final and conclusive. In reality, as has been pointed out above in connection with the ether, water, chloroform experiment of L'Hermite, the membrane itself ought also to be stirred during the process. This is of course less necessary when the septum is quite thin than when it is thick. It should be borne in mind, however, that even stirring the contents of the cell and the outer liquid simultaneously can never entirely keep the concentration of the liquid layers in immediate contact with the two sides of the septum exactly the same as the concentration of the liquids further away from the membrane; yet in many cases this may be accomplished with a fair degree of approximation. Moreover, by using the stirring process, the osmotic pressures may be measured fairly approximately even when the amount of material passing out of the cell is not negligible; in other words, when the membrane is not semipermeable.

The apparatus devised for stirring the contents of the cell and also the outer liquid simultaneously during the measurement of osmotic pressures is pictured in Fig. 7 in diagrammatic form. In the figure, the beaker B of a capacity of 1000 cc or more, contains the outer liquid. The latter is stirred by means of the stirrer F, which is moved up and down by the motion of the crank C. In the experiments performed it was admissible to make this stirrer of iron, for this is not attacked by pyridine. F consisted then of a bright, stout iron wire bent in ring form. Just above the cork closing the beaker, this stirrer F was jointed so that it would not need

so large an opening in the cork in which to move up and down. A thermometer is placed in the liquid to register the temperature. The whole apparatus is set in a constant temperature room, or the beaker B is immersed in a bath of constant temperature, not shown in the figure. The osmotic cell S is made exactly as heretofore described, except that before tying on the membrane, the stirrer is inserted into the apparatus through the opening in the bell of the thistle tube. This stirrer consists of a perforated disc of light sheet iron fastened by riveting and a drop of solder, to a sufficiently stout, yet flexible, iron wire, the upper end of which carries a lug of soft iron soldered on, as shown in the figure. In order that the perforated disc at the lower end of this stirrer might not pound on the delicate membrane and injure it, prongs of wire were soldered on the main vertical wire of the stirrer; and after the latter had been introduced into the osmotic cell, these prongs were bent outward in such a way that they would strike the side of the bell of the thistle tube (see figure) as the stirrer moved downward, thus allowing the perforated disc to come close to the membrane without actually touching it. These prongs, of course, do not interfere with the upward movement of the stirrer. The soft iron lug at the upper end of the stirrer had a longitudinal groove (not shown in the figure) filed into it to facilitate the introduction of the liquid into the cell. After the glass part of the osmotic cell had been blown in one piece, the iron stirrer was introduced and the prongs bent into the required position; the membrane was then tied on and supported with cloth and steel disc as heretofore described. The proper quantity of mercury was then introduced and finally the cell was filled with the solution. A fine long funnel tube was employed in introducing the mercury and the solution into the osmotic cell. The upper end of the osmotic cell, through which the cell had been filled, was then drawn off before a blowpipe flame, as already described, so that practically no air remained in the cell after it was sealed. The osmotic cell was

mounted in the beaker as indicated in Fig. 7, the cork closing the cell securely, leaving only a little play for the stirrer F.

Over the sealed end of the osmotic cell is placed the solenoid M; and by making and breaking the current in M, the stirrer in the osmotic cell is moved up and down. By means of the wires LL the small electric motor G is connected with a number of storage batteries; the latter are not shown in the figure. The motor G turns the wheel W, through the agency of a belt, and thus operates the crank C which moves the stirrer F. Now the wheel W is made of hard rubber and on it are fastened two small brass plates PP which are connected with each other by a wire; mounted on separate supports, independent of the wheel W, are the two brass brushes DD, which make contact with PP. These brushes DD are connected with the source of current and the solenoid M by means of wires as shown in the figure. As the wheel W turns and the brushes DD come into contact with the brass plates PP on the wheel, the current in the solenoid M is established, the soft iron lug is attracted and the stirrer in the osmotic cell moved upward only to be dropped again as soon as W has turned far enough to destroy the electrical connection.[1] Thus both the outer liquid and that in the cell are stirred continuously. R is a resistance to regulate the current in the solenoid. It was found that in order to get good steady motion the hard rubber wheel W was too light. This defect was remedied by boring holes A through the wheel near its edge all around the circumference, and filling these with lead. On the same axis with W was another wheel (not represented in the figure) of the same size and weight, which served to balance the apparatus and at the same time to operate the stirrers of a second osmotic experiment like that shown in the figure. Thus osmotic experiments could be performed in

[1] The arrangement was such that the slight heating effect produced by the current in passing through the solenoid was negligible, for the readings of the manometer did not change perceptibly after the current had been turned off and sufficient time allowed for any difference in temperature to become equalized.

duplicate, using but one motor. The arrangement for making and breaking the current in the solenoids of course did not require duplication, since the same current could be sent through both coils in series.

With this new apparatus the osmotic pressures of 0.125 normal LiCl solution in pyridine and also of 0.125 solution of cane sugar in pyridine were measured, using vulcanized caoutchouc as the membrane and pure pyridine as the outer liquid. The 0.125 normal solutions were selected rather than the 0.25 normal, because the latter yielded a rather higher pressure than could be conveniently estimated with an open manometer. The preliminary results (above recorded) obtained with 0.25 normal sugar solutions without shaking do not indicate this, for the highest pressure observed was below 200 cm; but it was found that by stirring, this pressure could be about doubled.

With the stirring apparatus described, Fig. 7, it, of course, takes much more time to set up each individual experiment, for the arrangement is much more complicated. The necessity of stirring in osmotic experiments was only found out after a long series of preliminary tests made in the old-fashioned way without stirring, and so during the time left only a limited number of tests could be carried out. Working with pyridine, moreover, has a very depressing effect on the nervous system, it being impossible to keep the air in the laboratory entirely free from it. The effect appears to be cumulative in character, for one's system seems to become more and more sensitive to the substance. For this reason I felt constrained not to prolong the work with pyridine unduly. It will be remembered that I have carried on experiments with pyridine continuously for about two years, and off and on for a much longer time. During the investigations I have at times found it necessary to counteract the depressing effects of pyridine by taking small doses of strychnine.

The results of the experiments performed with the stirring apparatus will now be given. It need hardly be stated again
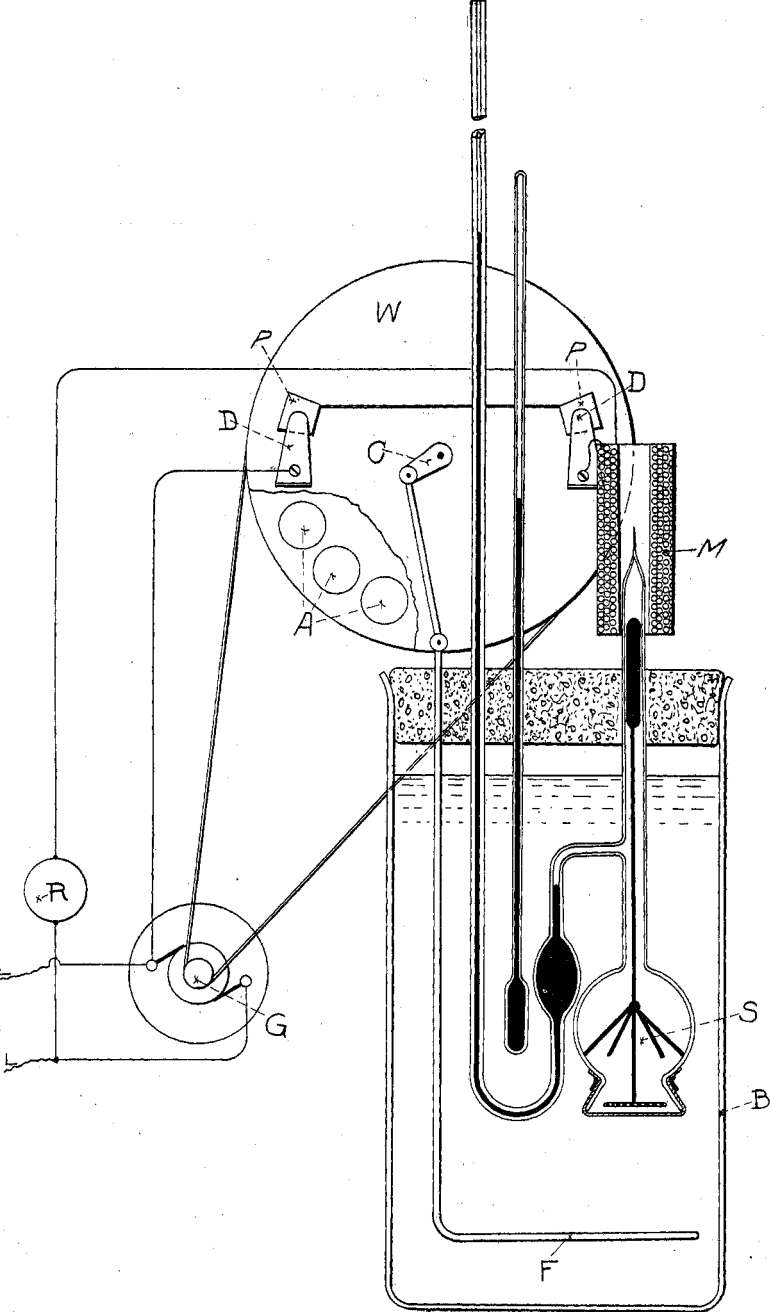
Fig. 7

that the LiCl and the sugar were dry and of a high degree of purity, as was also the pyridine.

57. The inner liquid was 0.125 normal solution of LiCl in pyridine and the outer liquid pure pyridine. It required 46 cc to fill the cell. The volume of the outer liquid was 600 cc. The temperature was 19°.0, and the experiment was run for three days with constant stirring. The maximum height which the mercury column reached was 51.2 cm at 19°.0 C, corrected. This height was practically attained during the first twenty-four hours. At the end of the experiment, the whole of the outer liquid was evaporated to dryness and the LiCl in the residue estimated. It was found that the 600 cc of outer liquid contained 0.0130 gram of LiCl, which shows definitely to what extent the solute has actually passed into the outer liquid.

In the light of what has been said in the preceding pages, it is evident that a determination of the exact amount of solute present in the outer liquid at the time when the maximum pressure is attained is an essential part of all final osmotic pressure measurements, yet such estimations have hitherto always been omitted even in experiments in which great care has been bestowed upon other details.

58. This experiment was exactly like the preceding one (No. 57) except that the outer liquid consisted of 1200 cc of pyridine instead of 600 cc and the temperatures were as indicated below. The experiment was continued for twenty-seven days, at the end of which time an examination showed the membrane to be perfectly intact. The entire outer liquid was finally evaporated to dryness and the LiCl determined in the residue. It was found that the 1200 cc of the liquid contained but 0.0267 gram of LiCl. The pressure rose slowly, the mercury column measuring over 50 cm after the first day. On the sixth day the mercury column measured 51.5 cm, the temperature being 24°.0. On the twelfth day the mercury column measured 53.2 cm, the temperature being 20°.95; on the fourteenth day, 54.9 cm, the temperature

being 21°.96; on the fifteenth day 54.2 cm, the temperature
being 19°.6. The beaker containing the outer liquid was then
packed in melting ice. The temperature sank to 2°.0 and
was kept there for twelve hours. After two hours of thus
cooling, the mercury column was only 9.0 cm high and re-
mained there without change for the remaining ten hours.
The ice was allowed to melt gradually for the next twelve
hours. When the temperature had reached 21°.4 C the
mercury column measured 56.1 cm; this was on the seven-
teenth day. During the next three days the outer beaker
was again kept surrounded with melting ice. It was difficult
to keep the temperature of the apparatus perfectly constant
during all this time. It gradually sank to 2°.2 and finally
to 1°.6. When the temperature had reached 1°.6 the pressure
indicated by the manometer was 2.9 cm and remained con-
stant for six hours. The temperature was then gradually
raised, and at 20°.5 the mercury column reached a height of
53.0 cm, where it remained constant for twelve hours. The
outer beaker was then surrounded with a bath of a tem-
perature of 36° C, the change to that temperature being made
gradually, which, of course, was also done in the preceding
cases where the temperature of the bath was radically altered.
At 36° the height of the mercury column became constant at 101.0
cm and remained so for about half a day, when the tempera-
ture of the bath was gradually raised to 58°.7 and kept there.
At this temperature the mercury column rose to a height of
128.3 cm, where it remained practically constant for two
hours. The temperature was then gradually permitted to
fall, and at 25°.5 C the column in the manometer finally
registered 51.9 cm on the last day of the experiment. It was
after all this that the entire outer liquid was evaporated to
dryness and the amount of LiCl in the residue determined
with the result already recorded. The discussion of the
results of this experiment will be deferred until after the next
two experiments have been described.

59. The inner liquid was a solution of sugar in pyridine

containing 0.125 gram-molecule per liter. The outer liquid was pure pyridine and the septum vulcanized caoutchouc. The experiment was run with constant stirring for three days, the temperature being kept constant at 20° C. The maximum pressure reached was 98.3 cm, nearly the whole of which was attained during the first day. On concluding the experiment the whole of the outer liquid consisting of 400 cc was evaporated to dryness; the residue was taken up with water, and the sugar determined with Fehling's solution, after inverting with HCl. It was found that the 400 cc contained 0.1149 gram of sugar.

60. This experiment was as nearly as possible a duplicate of the preceding one (No. 59). On the fifth day the mercury in the manometer reached a height of 91.8 cm, the temperature having gradually gone up to 21° C. In this case too the pressure increased but little after the second day. On the morning of the seventh day the pressure was 94.0 cm, the temperature being 21°.95 C; in the evening of the same day 95.5 cm at 22°.15. On the eighth day the outer beaker was packed in melting ice, the temperature in the beaker being 2°.0 C. During this time the mercury in the manometer registered practically no pressure, or at best only a few millimeters. The ice was then permitted to melt gradually, and on the ninth day the pressure registered 92.0 cm at 19°.4 C. The temperature was then slowly raised to 46° C, where it was kept for twelve hours. The pressure became constant after about three hours at 114.2 cm and remained there for nine hours. The experiment was then discontinued. The whole of the outer liquid consisting of 1200 cc was then evaporated to dryness, and the sugar was taken up with water, inverted with HCl and determined with Fehling's solution. The result was that in the 1200 cc 0.2205 gram of cane sugar was found.

Taking into consideration the pressures developed while the apparatus is kept nearly at a constant temperature, we find that according to No. 57 the osmotic pressure of the 0.125

normal solution of LiCl is 51.2 cm at 19°.0, and according to
No. 58 it is 54.2 cm at 19°.6. Again, according to No. 59 the
osmotic pressure of a 0.125 normal sugar solution is 98.3 cm
at 20°.0, while according to No. 60 it is 91.8 cm at 21°.0.
Even in these cases the agreement of the duplicates leaves
much to be desired, for the differences in pressure observed
can hardly be due to the slight differences in temperature.
They are more likely due to individual differences in the mem-
branes used, and to the fact that even with constant stirring,
it was not quite possible to keep the liquids in immediate
contact with the membrane of perfectly uniform concentra-
tion on each side. These difficulties have already been dis-
cussed at length above. There can be no doubt, however,
that the results obtained are approximately the osmotic
pressures of the solutions in question, under the conditions
of the experiments.

The effect of stirring is clearly shown by a comparison of
experiment No. 54 where the highest osmotic pressure of a
0.125 normal sugar solution was found to be 62.4 cm at 17°.5
without stirring, and the result recorded in No. 59, where with
stirring the osmotic pressure was found to be 98.3 cm at 20°.0.

Taking the highest values found, namely 54.2 cm for 0.125
normal LiCl solution at 19°.6 and 98.3 cm for 0.125 normal
sugar solution at 20°.0, we note (1) *that the electrolyte
gives by far the lower pressure,* and (2) that neither the LiCl
nor the sugar give anywhere near the pressure called for by
the gas laws, according to which a 0.125 normal sugar solution
ought to give a pressure of approximately three atmospheres
(228 cm Hg) at 20°. Further, it will be recalled that a 1.2
percent solution of sugar yielded practically no osmotic
pressure at 0°, whereas according to the gas laws it ought to
have produced about 0.8 of an atmosphere. And again,
0.05 normal solution of $AgNO_3$ yielded no osmotic pressure,
whereas according to the gas laws it ought to have produced
over an atmosphere. Further, the changes of pressure above
recorded as caused by changes of temperature are so very

much greater than they would be if they were proportional to the absolute temperature that additional comment seems quite superfluous. The osmotic pressures here investigated, then, do not follow the gas laws at all. Again, the electrolyte LiCl yields a much lower pressure than the non-electrolyte, sugar, which is exactly the opposite of what the theory of electrolytic dissociation requires.

Observations Concerning Dialysis

When both cane sugar and copper oleate are dissolved together in pyridine and the solution is separated from pure pyridine by means of a vulcanized caoutchouc membrane, the copper oleate passes through the septum and the sugar remains behind. This is what one would expect from what has been said above. But here we have a case where a crystalline body, the sugar, is separated from a non-crystalline substance, the copper oleate, by dialysis in which process the non-crystalline or colloid body passes through the septum and the crystalloid remains behind. Again, when camphor and sugar are together dissolved in pyridine and the solution is separated from the solvent by means of a rubber septum, the camphor passes through and the sugar remains behind, which might have been anticipated. Here we have a case in which crystalloids are separated from each other by dialysis.

In fact it is clear that in general any substance which is soluble in both hydrocarbons and in pyridine may be separated from sugar by dialysis, when the pyridine solution of it and the sugar is separated from the pure solvent by a rubber septum. In such cases the sugar will always remain behind in the dialyzer and the other substance will pass through whether it be crystalline or non-crystalline. Any other substance soluble in pyridine but not soluble in hydrocarbons, may in general be substituted for sugar. Thus the rôle of the nature of the membrane in the process of dialysis is demonstrated. The current view that crystalloids always pass through membranes more readily than colloids is evidently untenable, it has been shown that just the opposite may occur,

and that even crystalloids may be separated from each other by dialysis when the proper septum is chosen. *Whether substances can be separated by dialysis or not does not depend at all upon their crystalline or non-crystalline nature as is so commonly supposed, but upon their affinity for the septum employed.* After what has been said above, it is evident that stirring the liquids hastens dialysis.[1]

Several experiments in addition to those here described have been performed, but as I hope to continue the experimental work on dialysis their presentation will be reserved for a later communication.

General Remarks

The conclusion reached above that the process of osmosis depends upon selective solubility (in other words, upon the affinities involved) is in agreement with what Overton[2] has found in his physiological studies. The importance of the recognition of the true nature of osmotic processes for progress in physiology can hardly be overestimated.

From the time of Dutrochet all investigators who worked on osmosis experimentally with different membranes and various liquids have been impressed with the important rôle of the nature of the membrane in determining whether osmosis would occur at all or not, and if so, in what direction. The following quotation taken from the article of L'Hermite, cited above, shows how clearly he had grasped the situation: "Je pense avoir démontré par la discussion des expériences de mes devanciers et des miennes, que l'endosmose n'est point le resultat d'une force particulière, mais de l'affinité elle-même en étendant l'acceptation de ce mot a l'attraction capillaire qui en est le premier degré." I should also like to quote the opinion of Raoult, which he voiced in a letter written

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[1] Since the above was written it came to my notice that in 1848 Jolly, Liebig's Ann., **68**, 6 (1848), refers to a case where he shook the dialyzer to hasten the process.

[2] Vierteljahrsschr. d. naturforsch. Ges. in Zürich, **44**, 88 (1899). See also the discussion in Chap. 5 of Höber's Physik. Chem. d. Zelle u. Gewebe, Leipzig (1902). Compare also Livingston, "The Rôle of Diffusion and Osmotic Pressure in Plants," Chicago (1903).

January 7, 1897, to Prof. W. D. Bancroft, and which through the latter's kindness I am able to present here. This quotation, which requires no further comment, gives everything contained in the letter relative to the osmotic process.

"La question de l'osmose, que beaucoup croient résolue par des formules mathématiques fondées sur des hypothèses commence à peine à être posée. Mes expériences auxquelles vous faites allusion, prouvent qu'i ly a certainement des diaphragmes *actifs*. Existe-t-il également des diaphragmes *passifs*, comme pour les gaz? Pour le moment tout le mond paraît le croire, sur la foi de van't Hoff; mais pour mon compte, je n'en ai jamais pu trouver un seul.

"Si je n'ai pas continué mes publications sur ce suject, c'est que j'ai rencontré de très grandes difficultés pour mesurer les pressions osmotiques avec des diaphragmes mous. Existe-t-il, d'ailleurs, une veritable pression osmotique? Je n'en suis pas sûr. Il arrive certainement toujours une pression pour laquelle le mouvement osmotique semble s'arrêter; mais j'ai lieu de croire qu'elle correspond au moment où la quantité de liquide qui passe dans un sens par *osmose*, est égale à celle qui passe en sens opposé par *filtration*.

"La question est intéressante et fort délicate. Aussi, verrais-je avec un très grand plaisir d'autres expérimentateurs s'engager dans cette voie."

Again, very recently Barlow[1] working in the laboratory of J. J. Thomson has re-emphasized the fact that the osmotic current is caused by the mutual potential energy of solution of the liquids and that the direction of osmosis is conditioned by the character of the membrane.

Precipitated membranes, like those of copper ferrocyanide, etc., are hydrates, that is, they contain more or less water. When such a membrane is used to separate water from an aqueous solution, the latter abstracts water from the septum—the hydrate—which again takes up water from the side bathed by the pure solvent. The affinity of the solution

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[1] l. c.

for additional solvent must be sufficient to extract some water from the membrane in order that an osmotic pressure may be produced. If in addition the solute has considerable affinity for the septum, copper ferrocyanide for example, as many of the salts of the alkali metals are known to have, for instance, the solute will pass through to a notable extent; if on the other hand, the solute has very little affinity for the septum, as is the case with cane sugar, the membrane will allow but very small quantities to pass through, and hence will be "semipermeable." It is perfectly clear, too, that, in general, different precipitated membranes would lose part of their water with different degrees of readiness, and hence in quantitative measurements of osmotic pressures different results would be obtained when different precipitated membranes are used. This is shown to be true by the experiments of Pfeffer[1] who found that when a copper ferrocyanide membrane was used a 1 percent sugar solution yielded an osmotic pressure of 51.0 cm at 14°.2; when a Prussian blue septum was employed the pressure was 38.7 cm at 13°.9; and when a calcium phosphate membrane was used the pressure was 36.1 cm at 15°.2. In all three cases the sugar which passed through the septa was insignificant according to his determinations. While the results of Pfeffer are not final as determinations of the maximum osmotic pressures, inasmuch as he did not stir the liquids while measuring the pressures, the experiments nevertheless serve to show that the pressures developed with the different septa are by no means the same. If one were to compute the molecular weight of sugar from the osmotic pressures which a 1 percent aqueous solution of it develops when copper ferrocyanide, Prussian blue and calcium phosphate are used as membranes respectively, different values would obviously be obtained, that is, the conclusion would be reached that the molecular weight of sugar in one and the same solution varies in different cases, which is obviously absurd. The experimental facts

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[1] "Osmotische Untersuchungen."

are, of course, readily explained by what has been said above.

Further, when precipitated membranes are used and the osmotic process goes on very rapidly, it generally occurs that the solution robs the precipitated hydrate of water faster than the latter is taken up from the pure water bathing the other side of the septum. In such cases the membrane develops ruptures through which the solution oozes out of the cell, hence the necessity of the usual practice of adding the "membrane formers" to the liquids on each side of the membrane to repair such leaks. It is obvious that in any osmotic experiment the composition of the septum is always in a state of change, though the extent of this may be slight in some cases. Here lies one of the chief difficulties of measuring osmotic pressures (which are equilibrium pressures) with soft diaphragms to which Raoult alludes.

It must be borne in mind that the application of the gas laws, either in simple or modified form, to dilute solutions is based upon the experiments which Pfeffer made with copper ferrocyanide membranes, and which Morse and Frazer have recently sought to verify. But these experiments have all been made without stirring and with but one membrane, and hence are not final. Furthermore, the osmotic pressures of sugar solutions in pyridine, using vulcanized caoutchouc as the semipermeable membrane, show definitely that the gas laws do not obtain here at all. In the face of the experimental facts which we now have as showing the nature of the osmotic process and the magnitude of the osmotic pressures under different conditions, the general, indiscriminate application of the gas laws in their simple or somewhat modified form to all dilute solutions, and even to some that are not dilute, as now in vogue, can not be too greatly deplored. To speak of the osmotic pressure of any isolated solution without specifying what membrane separates it from what other liquid is nonsense,[1] in the light of the facts here presented. And further, to assume that solutes are polymerized

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[1] Compare also views expressed by Van Laar, Chemisch Weekblad, **2**, 1–16 (1905).

or dissociated in dilute solutions because the osmotic pressures developed by the latter in given cases happen to deviate from values computed from the gas laws is evidently equally unjustifiable practice.

Summary

In this paper it has been shown that whether osmosis will take place in a given case or not depends upon the specific nature of the septum and the liquids that bathe it; and if osmosis does occur, these factors also determine the direction of the main current and the magnitude of the pressure developed. The motive force in osmotic processes lies in the specific attractions or affinities between the liquids used, and also those between the latter and the septum employed. These attractions or affinities have also at times been termed the potential energy of solution, etc., they are to the mind of the writer essentially the same as what is commonly termed chemical affinity.

It has been emphasized that osmotic pressures are equilibrium pressures, and that in osmotic processes there is always a current in both directions, though the main current may in specific cases be so much stronger than the minor that the latter almost sinks into insignificance. In such cases the septum employed is termed "semipermeable."

Vulcanized caoutchouc has been found to be a "semipermeable" membrane when it separates pyridine solutions of silver nitrate, lithium chloride, and cane sugar from the pure solvent.

The necessity of stirring the contents of the osmotic cell and also the outer liquid during osmotic pressure measurements has been pointed out, and a new apparatus for measuring osmotic pressures accordingly has been devised.

The results of the osmotic pressure measurements show that the gas laws do not hold; and it has consequently been pointed out that the latter cannot serve as a basis for a satisfactory theory of solutions.

The advantage of stirring in processes of dialysis has been indicated; and it has been shown that whether substances pass through membranes or not does not depend upon their colloidal or crystalloidal character, but solely upon their affinity for the membrane employed and for the liquids that bathe it.

In conclusion I desire to thank Messrs. F. L. Shinn, J. H. Mathews, Wm. Marquette and H. E. Eggers for assistance which they have kindly rendered me from time to time in the experimental part of the work.

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