OSMOTIC STUDIES

(Reply to Ernst Cohen and J. W. Commelin)

BY LOUIS KAHLENBERG

Two years ago I presented in the pages of this Journal¹ an article entitled "On the Nature of the Process of Osmosis and Osmotic Pressure with Observations Concerning Dialysis," in which the results of an extensive series of experimental investigations of both qualitative and quantitative nature were detailed. As the outcome of this work, it was shown that whether osmosis will take place or not in a given case depends upon the specific nature of the septum employed 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. It was furthermore 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 sinks almost into insignificance. In such cases the septum is termed "semipermeable." Vulcanized caoutchouc was found to be a "semipermeable" membrane when it separates pyridine solutions of either silver nitrate, lithium chloride or cane sugar from the pure solvent. The necessity of stirring the contents of the osmotic cell and also the outer liquid during the osmotic pressure measurements was pointed out, and a new apparatus for measuring osmotic pressures accordingly was devised. The results of the osmotic pressure measurements showed that the gas laws do not hold for the solutions studied, and it was consequently pointed out

¹ Jour. Phys. Chem., **10**, 141-209 (1906); also Trans. Wisconsin Academy of Sciences, Arts and Letters, Vol. **15**, Part **1**.

that these laws cannot serve as a basis for a satisfactory theory of solutions.

Immediately after the appearance of this paper Ernst Cohen, director of the van't Hoff laboratory at Utrecht, apparently alarmed at the danger threatening the van't Hoff theory of solutions, published a short notice in the *Chemisch Weekblad*¹ cautioning the public to accept with reserve what he chose to term my far-reaching conclusions. In this note he omits consideration of all my work except the quantitative measurements of osmotic pressures made with solutions of sugar, lithium chloride, and silver nitrate in pyridine, employing a vulcanized caoutchouc membrane, and using pure pyridine as the outer liquid. It will be recalled that the osmotic pressures measured in these cases are far below those calculated according to the gas laws. Mr. Cohen calls attention in his article to the well-known facts that cane sugar may act as a weak acid, that pyridine is a base, that silver nitrate forms addition products with pyridine, and adds that the latter might also act on lithium chloride. In this connection the reference that Mr. Cohen makes to his own work and that of Kullgren in 1901 as demonstrating that cane sugar has weak acidic properties is quite superfluous, for the existence of sucrates, like the sucrate of lime for instance, has been known for a long time. That cane sugar does not form an addition product with pyridine was shown in this laboratory by G. M. Wilcox.² Furthermore, that silver nitrate forms with pyridine the compounds $\text{AgNO}_3 \cdot 6\text{C}_5\text{H}_5\text{N}$, $\text{AgNO}_3 \cdot 3\text{C}_5\text{H}_5\text{N}$ and $\text{AgNO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ has recently been further investigated here³ in connection with a study of the equilibrium in the system silver nitrate pyridine. Again, according to researches made in this laboratory,⁴ lithium chloride forms with pyridine the compounds

¹ *Chemisch Weekblad*, Amsterdam, **3**, 290 (1906).

² *Jour. Phys. Chem.*, **5**, 589 (1901).

³ Kahlenberg and Brewer: *Jour. Phys. Chem.*, **12**, 283-289 (1908).

⁴ Kahlenberg and Krauskopf: *Jour. Am. Chem. Soc.*, **30**, 1104-1115 (1908).

$\text{LiCl} \cdot 2\text{C}_5\text{H}_5\text{N}$ and $\text{LiCl} \cdot \text{C}_5\text{H}_5\text{N}$. It is, of course, perfectly clear that even if the existence of such addition products in the solutions be assumed, this would not alter the number of dissolved molecules contained in a given volume of solution, though it would increase the size of the dissolved molecule and diminish the number of molecules of solvent accordingly. In solutions like eighth-normal, however, the relative number of solute and solvent molecules would vary but slightly. It is quite evident that the osmotic pressures I observed in the case of the solutions of cane sugar, lithium chloride, and silver nitrate cannot be harmonized with the gas laws by making use of the fact that the last two compounds mentioned are capable of forming addition products with pyridine as above detailed.

This Mr. Cohen appears to have recognized himself, for in his next article, which he published jointly with J. W. Commelin,¹ no explanations of observed osmotic pressures are made on the basis of such possible interactions of solvent and solute.

The fifty-two pages of the paper of Cohen and Commelin present: an introduction of two pages; a review of previous work done in measuring osmotic pressures covering twenty-six pages, of which about eleven pages are devoted to a consideration of my quantitative measurements of osmotic pressure; a description of the authors' own apparatus, methods and preparations used, occupying sixteen pages; three pages devoted to the results of their own measurements; four pages on the influence of water; and finally about half a page giving the summation of the conclusions reached.

The brief introduction is intended to impress upon the mind of the reader the great importance of the van't Hoff theory of dilute solutions, and to duly caution all not to pronounce against that theory "auf Grund einer geringen Anzahl unter sich wenig übereinstimmender Versuche." It is stated that Pfeffer's osmotic pressure measurements are

¹ Zeit. phys. Chem., **64**, 1-52 (1908).

simply used by van't Hoff as corroborations of his computations, and that the real basis of the latter's theory lies not in the osmotic pressure measurements, but rather in the determination of those magnitudes that of necessity are quantitatively related to osmotic pressure, namely: (a) isotonic coefficients; (b) lowering of the freezing point; (c) lowering of the vapor tension; (d) elevation of the boiling point; (e) change of solubility of gases with pressure; (f) partition coefficients. Then follows the remarkable statement that the large amount of material that has been gathered concerning the constants just mentioned would be worthless to him alone, who denies that these are necessarily related to osmotic pressure. This position I would regard as absurd and quite untenable in the light of experimental facts to which I have called attention in my paper. No one would deny the value of the constants above mentioned under (a) to (f), but it must be denied that they are of necessity related to actual osmotic pressures (that is, pressures that are experimentally measured by means of so-called semipermeable membranes) in any such way as required by the theory of solutions of van't Hoff. I submit that I have shown conclusively by the numerous qualitative experiments (which Mr. Cohen apparently disdains even to discuss) that the specific nature of the membrane and the liquids that bathe it determines whether osmosis will take place or not, and in what direction. It is shown in that paper how to proceed to find substances for which vulcanized caoutchouc is "semipermeable," and it is definitely established upon an experimental basis that the "semipermeability" of a membrane depends upon its selective action. Later in their paper (p. 27) Cohen and Commelin graciously concede that the discovery of vulcanized caoutchouc as a "semipermeable" membrane is of importance as it opens the way to find additional septa of this kind, but they entirely underrate the vastly more important point, that there is really no such thing as a semipermeable membrane, that *osmosis always goes on in both directions, if at all, and that it is only in the few limiting cases when the osmosis*

in one direction by far outweighs that in the other, that we have a so-called semipermeable membrane. A clear recognition of this robs direct osmotic pressure measurements of practically all the importance that has hitherto been accorded them as a foundation for a theory of solutions. On page 27 Cohen and Commelin unearth the following from the reply of van't Hoff¹ to Lothar Meyer: "Wiederum haben wir die im Grunde zwecklose Frage: Was übt den osmotischen Druck aus? Wirklich, wie schon betont, ich kümmere mich schliesslich nur um dessen Grösse; da er sich mit dem Gasdruck gleich gezeigt hat, ist man geneigt, an einen ähnlichen Mechanismus wie bei Gasen beim Zustandekommen zu denken. Wen dies aber auf falsche Wege führt der lasse den Gedanken an Mechanismus einfach fort." Again in this connection they cite from van't Hoff's Vorlesungen:² "Es sei betont, dass jede Vorstellung den man sich über den Mechanismus des Entstehens vom osmotischen Drucke oder der Wirkung der semipermeablen Membran macht, ohne Einfluss auf die weitere Entwicklung ist. Die Frage also, ob der Druck vom gelösten Stoff herrührt, kann ganz ausser Spiel bleiben; ebenso diejenige, ob derselbe auf Stoss oder Anziehung begründet ist. Auch die Wirkung der Membran, es sei als Sieb, es sei durch vorübergehende Absorption ist einerlei." As ardent defenders of the van't Hoff ideas they boldly declare on p. 27: "Diejenigen die es sich zur Aufgabe machen, van't Hoff's Auffassung über den osmotischen Druck zu bestreiten, kämpfen gegen Windmühlen;" and on p. 2 of the introduction they state that the time for countenancing the contention that the osmotic pressure is not of necessity related to the constants (a) to (f) above mentioned, "wäre aber erst dann gekommen, wenn der Versuch gemacht würde, die für jeden Spezialfall auf thermodynamischer Basis fussenden Beweise zu widerlegen."

It is a well-known dodge of the thermodynamicists to

¹ Zeit. phys. Chem., 6, 485 (1892).

² Vorlesungen Ueber theoretische und physikalische Chemie, Braunschweig (1899), 2 Heft, S. 24.

claim that they are not concerned with the mechanism of osmosis and with that which produces osmotic pressure, for they simply require to know the magnitude of the latter in order to proceed with their computations. Right here lies the strength, but also the great weakness of thermodynamic methods. *What we want to know above all things is what causes osmosis and osmotic pressure in order to put us into position to discuss more intelligently the results of osmotic experiments, and to determine to what extent such results are actually useful in forming a true basis for a tenable theory of solutions.* But in any case, the thermodynamicists are concerned with the magnitude of osmotic pressure when so-called semipermeable membranes are employed. We note with what haste they lay hold of such results as those obtained with aqueous sugar solutions and copper ferrocyanide membranes by Morse and Frazer, which show an approximate agreement with the requirements of the gas laws, and how they pass lightly over the results of Berkeley and Hartley, who obtained much higher pressures than the gas laws require. It is consequently of importance to them that my own work with vulcanized caoutchouc membranes has yielded results that are entirely out of harmony with the gas laws.

Now while with aqueous solutions and a copper ferrocyanide membrane osmotic pressures may apparently in a number of cases, like cane sugar, glucose, amygdaline, anti-pyrine, salicine and mannite, be obtained which approximate to the requirements of the gas laws; it is equally true, that when we use other membranes and other solutions, osmotic pressures may be obtained that do not conform to the requirements of the gas laws at all. Indeed it would seem probable that the results obtained with cane sugar solutions and copper ferrocyanide membranes are rather a curious exception than an example of the usual osmotic behavior of substances. The "osmotic pressure" as usually used in thermodynamical computations concerning solutions is an hypothetical magnitude which has no counterpart in actual

osmotic phenomena, for the pressure is assumed to be quite independent of the nature of the membrane as long as the latter is "semipermeable," and experiment shows conclusively that this assumption cannot possibly be maintained.

The sixteen pages which Cohen and Commelin devote to a review of osmotic pressure measurements contain facts well known to all and consequently need no further consideration here.

In the eleven pages devoted to a discussion of my paper, Cohen and Commelin describe the method of experimental investigation adopted by me and seek to show that the results of my experiments do not warrant the conclusion that the osmotic pressures observed do not follow the gas laws. Furthermore, they try to make out that my results show that whether the contents of the osmometer and the outer liquid are stirred or not does not affect the osmotic pressure. In their discussion of my results they present three tables in which the numerical data I have collected experimentally are used. These tables are here reproduced and numbered as in their article.

TABLE 3

No. of experiment	Solute	Concentration	Temperature	Osmotic pressure
19	AgNO ₃	0.1 normal	17°	28.5 cm
20	"	0.05 normal	17°	0.5 "
21	"	normal	—16°	15.6 "
22	"	normal	20°	14.95 atm.
23	cane sugar	0.02 normal	—	22.7 cm
25	"	0.0035 normal	22° .5	5 "
26	"	0.125 normal	0°	1.9 "
27	"	0.25 normal	—16°	17.5 "
28	LiCl	saturated	—	Pressure not given

Except in Experiment 22, the pressures are represented in centimeters of the particular solution employed. In Experiment 22, a closed mercury manometer was used, the mercury being of course in contact with the solution of silver nitrate in pyridine. To this Cohen and Commelin object,

calling attention to the fact that thus silver amalgam forms at the point of contact. While there is an interaction where the mercury touches the silver nitrate pyridine solution, this is slight for the cross-section of the manometer tube is small and the action goes on very slowly; furthermore, in the interaction the equivalent solute content of the solution remains the same. I should like further to call attention to the fact that in my paper I distinctly make the following statement in connection with Experiment 22 (l. c., p. 164): "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 silver nitrate 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." By means of the remark that in No. 22 silver amalgam is formed, Cohen and Commelin apparently seek to divert the reader's attention from the main issue, for they state in this connection: "Bereits in den in obiger tabellarischer Uebersicht zusammengestellten qualitativen Versuchen glaubt Kahlenberg, den überzeugenden Beweis erblicken zu dürfen für den Satz, dass die Gesetze verdünnter Gase hier nicht gelten;" and then they cite the following from my paper: "Though Experiments 19 to 22 are only quasi quantitative in character, they are already sufficient to show that here the osmotic pressure does not follow the gas laws at all." Now I submit that this latter conclusion is correct, and is precisely the one that any unbiased mind will reach on carefully regarding the data compiled in Table 3, in spite of the opinion of Cohen and Commelin to the contrary.

Cohen and Commelin further present the following compilation of the data that I have collected:

TABLE 4
Experiments without stirring

No. of experiment	Solute	Concentration	Temperature	Osmotic pressure in cm Hg
53 ^a	cane sugar	0.25 norm.	17° 5	186.2
			0° 0	125.0
			16° 4	159.5
			17° 5	186.0
53 ^b	"	0.25 norm.	17° 5	155.6
			16° 4	166.4
			16° 0	166.7
53 ^c	"	0.25 norm.	17° 5	107.4
54 ^a	"	0.125 norm.	17° 5	62.4
			0° 0	0.2
			0° 0	0.6 (8 hrs. later)
			14° 5	48.8
			17° 5	62.0
			18° 0	43.6
54 ^b	"	0.125 norm.	17° 5	52.8
			14° 5	42.5
			18° 0	46.3
		0.25 ¹ norm.		
55	"	0.125 norm.	16° 8	137.5
56 ^{a2}	"	0.25 norm.	22° 0	43.0
56 ^{b2}	"	0.25 norm.	22° 0	39.5

TABLE 5
Experiments with stirring

No. of experiment	Solute	Concentration	Temperature	Osmotic pressure in cm Hg
57	LiCl	0.125 norm.	19° 0	51.2
58	"	0.125 norm.	21° 96	54.9
			2° 0	9.0
			21° 4	56.1
			1° 6	2.9
			20° 5	53.0
			36° 0	101.0
			58° 7	128.3
			25° 5	51.9
59	cane sugar	0.125 norm.	20° 0	98.3
60	"	0.125 norm.	22° 15	95.5
			2° 0	±0.0
			46° 0	114.2

¹ The inner liquid was 0.25 normal, while the outer liquid consisted of a 0.125 normal solution.

² In No. 56, thick rubber membranes were used.

Now Cohen and Commelin propose to discuss the data in Tables 4 and 5 to ascertain whether these results show that stirring the liquids in contact with the membrane is necessary in osmotic pressure measurements. They say: "Zur Beantwortung dieser Frage wollen wir die Abweichungen vom Mittel in Parallelversuchen berechnen (Tabelle 6)." They present the following table, which, as will be noted, is compiled from Tables 4 and 5:

TABLE 6

No. of experiment	Mode of experiment	Maximum pressure	Mean pressure	Deviation from mean. Percent
I	53 ^a Without stirring	186.0	153.4	21.0
	53 ^b " "	166.7		9.0
	53 ^c " "	107.4		30.0
II	54 ^a " "	62.4	57.6	8
	54 ^b " "	52.8		
III	56 ^a " "	43.0	41.2	4
	56 ^b " "	39.5		
IV	57 With stirring	51.2	53.0	3.5
	58 " "	54.9		
V	59 " "	98.3	96.9	1.5
	60 " "	95.5		
VI	54 ^a Without stirring	62.4	77.2	—19
	54 ^b " "	52.8		—32
	59 With stirring	98.3		27
	60 " "	95.5		24

Concerning Table 6, Cohen and Commelin then continue as follows: "Aus Tabelle 6 ergibt sich nun Folgendes: 1. Dass die Abweichungen in Parallelversuchen, die ohne Rühren ausgeführt werden (III) nicht grösser zu sein brauchen, als in Parallelversuchen mit Rühren (IV), so dass der Einfluss des Rührens hier gar nicht bewiesen ist. 2. Dass die Abweichungen zwischen vergleichbaren Versuchen, die einerseits mit Rühren, anderseits ohne Rühren ausgeführt sind, nicht grösser sind als die, welche vorkommen können in Versuchen, die alle ohne Rühren (I) ausgeführt wurden. Es

scheint uns demnach wenig konsequent, wenn Kahlenberg diese Abweichungen in den zwei Fällen auf Rechnung entgegengesetzter Ursachen bringt und sie in (I) einer ungenügenden Mischung der verschiedenen Flüssigkeitsschichten im Osmometer zuschreibt, in (VI) aber einer durch Rühren verbesserten Durchmischung. Streng genommen ist hiermit schon nachgewiesen, dass Kahlenberg nicht das Recht hatte, die Ergebnisse der vier Versuche 57-60 (denn nach seiner eignen Aussage sind nur diese als entscheidend zu betrachten) als ein genügendes Argument zu betrachten für seinen Schluss, dass die einfachen Gasgesetze nicht für verdünnte Lösungen gelten. Er scheint dann auch, vielleicht ganz unbewusst, die Schwäche seiner Beweisführung selbst gefühlt zu haben. Denn obwohl er sich einerseits, wie wir gesehen haben, sehr kategorisch über den Wert aller früheren Versuche die ohne Rühren ausgeführt wurden, äussert, zaudert er nicht, an mehreren Stellen seiner betreffenden Abhandlung selbst qualitative Versuche wie Nr. 20 und 25 (Tabelle 3) zur Stütze seiner Darlegungen heranzuziehen." I have quoted Cohen and Commelin thus in full, in order that their exact attitude may be understood and no injustice be done them in pointing out the fallacy of their position.

In the first place (I) in Table 6 represents an early set of results obtained with a 0.25 normal sugar solution, whereas all the other results with sugar solutions in Table 6 were obtained with solutions of half that strength. Results in (I) can consequently not be compared with others of the table. Again, results (III) in Table 6 were obtained with a thick rubber membrane of entirely different quality than that used in the other experiments detailed in the table, consequently group (III) is not comparable with the other results. Now again, Experiments 57 and 58, namely Group IV, Table 6, were conducted with lithium chloride as solute, whereas all the others in the table were carried out with sugar as solute; the results of Group IV are consequently not to be compared with the others in Table 6. We have left then solely for legitimate comparison Groups II and V of Table 6, which

are gathered in Group VI, Table 6. It will be noted on looking at Table 6, Group VI, that the results without stirring are *very* much lower than those with stirring, the former being less than two-thirds of the value of the latter. Now Cohen and Commelin take the mean of the results with and without stirring in Group VI and compute (in the last column of the table) the deviation from this mean and compare these deviations from the mean with those of Group I, with which, as stated above, they are not comparable at all. Moreover, *the argument that stirring is necessary in quantitative osmotic pressure measurements is not that fairly concordant results might not be obtained without stirring, as Cohen and Commelin seem to think, but rather that, in carefully executed, perfectly comparable experiments, stirring always yields higher pressures.*

Any one comparing the results I have obtained with stirring and without stirring in the case of the 0.125 normal sugar solutions (Nos. 54*a* and 54*b* with 59 and 60) must certainly admit that stirring greatly increases the osmotic pressure developed. To compute the mean of the results of these four experiments and to argue for the deviation of the individual results on either side of such mean that the effect of stirring is nil is obviously absurd. Nor do I base the fact that it is necessary to stir in seeking to measure maximum osmotic pressures entirely upon the results of Group VI, Table 6, for in numerous other cases after I had accidentally discovered the effect that jarring the apparatus had in increasing the osmotic pressure, I assured myself that after the pressure had apparently become constant, stirring or even shaking would cause the pressure to increase further. I desire to emphasize that I consider this fact quite indisputable, for since the publication of my paper numerous other experiments on osmosis in this laboratory have confirmed this fact, which, moreover, one would naturally expect to find from the considerations laid down in my paper concerning the nature of the process of osmosis.

I have never used Nos. 20 and 25, Table 3, as an argu-

ment in discussing the effect of stirring in osmotic pressure measurements. But I have used and do still use these as a most powerful argument against the contention that the gas laws hold for osmotic pressures of dilute solutions. Moreover, *all the results in Table 3 are an unanswerable argument against the tenet that the gas laws hold in osmotic experiments.* In fact I consider all the qualitative and quasi quantitative experiments that I have made and described in my paper as a powerful argument against the contention that the gas laws regulate osmotic pressure. My references to these qualitative and quasi quantitative experiments are consequently not made because of an unconscious realization of the weakness of the argument presented by the quantitative measurements, as Cohen and Commelin pretend, but rather with the full realization that, as I have stated in my original article, the results in Table 3 "are already quite sufficient to show that here the osmotic pressure does not follow the gas laws at all." The soundness of this position I cheerfully leave to the judgment of others. Indeed, after the publication of my paper, many men of prominence, among them no less a one than the late Professor H. W. Bakhuizen-Roozeboom of Amsterdam, expressed themselves to me in writing as to the correctness of my position. We are, moreover, at present engaged in this laboratory in determining the lowest concentrations of various solutions that will still develop an osmotic pressure that is appreciable at all. This work has already yielded an abundance of further results showing that stirring is quite necessary and that the gas laws do not govern here at all. In due time the results of these labors will be published. On account of its nature, the work requires considerable time.

On pages 25 and 26 of their article Cohen and Commelin try to make out that in testing the effect of temperature on osmotic pressure my osmometer acted mainly as a thermometer, that the experiments were not run long enough, and that the reason that the osmotic pressures were found

to be nil¹ at low temperatures was because the membranes were not supported from above and consequently bulged, that is, were convex upward. In answer to this I wish to call attention to the fact that these gentlemen have performed experiments only at 25°, and that consequently what they say might have happened, or did happen, in my experiments at lower temperatures are merely conjectures. It is therefore quite unnecessary to go into the details of their considerations here; suffice it to say, they are entirely untenable; but I wish to state that in no case could there have been any bulging inward of the membrane of my osmometer, for the membrane was always under slight pressure from within outward. Moreover, I wish to call special attention to the fact that the stretched rubber membrane over the mouth of the osmometer does not yield and bulge inward, "beim geringsten Ueberdruck," as Cohen and Commelin state; in fact it takes quite an appreciable pressure to cause such a tense membrane to bulge inward so as to cause a notable effect on the osmometer, of which I have recently assured myself experimentally.

But to settle the whole matter as to whether the 0.125 normal sugar solution actually gives practically no osmotic pressure as found before, I chose the best method, namely renewed experiment. I prepared a 0.125 normal sugar solution and with it performed three independent osmotic experiments at 0°. The substances and the procedure were practically those described in my previous paper. The solution, the pyridine used as outer liquid, and the apparatus were first each separately chilled to 0° by means of ice in a cold cellar, care being taken to guard the liquids and interior of the apparatus from moisture. The osmometers were quickly filled and the apparatus quickly set up. All was done practically at 0° and the apparatus was kept at 0° by means of a large amount of chopped ice. Thus the possibility of ther-

¹ The osmotic pressures at zero and below were by no means always nil as Cohen and Commelin pretend. Compare for instance Table 3, results at 0° and at -16°.

metric effect was completely eliminated.¹ In two of these experiments (*a* and *b*) the membranes employed were of the same manufacture as those used in my previous quantitative measurements; in the other case (*c*) a thinner vulcanized caoutchouc membrane of excellent quality, but of different manufacture, was employed. In setting up the experiments care was taken to have the level of the liquid in the stem of the simple osmometer employed slightly above that of the outer liquid to begin with, so that there could be no possibility of the membrane becoming convex inward. Moreover, to doubly safeguard that such bulging did not happen, a simple contrivance was introduced into the osmometer, which would indicate any upward convexity of the membrane if it occurred. This contrivance consisted of a small, very light weight, perforated sheet iron disc to which was soldered a long iron wire. The disc rested on about the center of the membrane, and the wire passed upward into the stem of the osmometer, on which by means of a mark the position of the upper end of the wire was sharply located. During the experiments not the slightest inward convexity of the membranes was observed, for the end of the wire, which was slightly bent so as to form a pointer, always rested on the same mark. Mercury manometers were not used, for they were quite unnecessary, the pressures being so slight. In (*a*) and (*b*) the maximum pressures in cm of the osmometer liquid were 7 and 9 cm, respectively, while in (*c*) where a membrane of different quality was used, a maximum pressure of 23 cm was obtained. These pressures developed within the first ten hours, and remained practically constant for about three days. During the fourth day they began to diminish slowly, showing that the maximum had been reached. After four days the experiments were discontinued.

¹ It would seem quite superfluous to add here that thermometric effects were also guarded against in all my previous experiments. Every one who has worked with osmotic apparatus in quantitative osmotic pressure measurements knows that due care must be taken to avoid thermometric effects of the osmometer.

The outer liquids showed the presence of only traces of sugar; the exact amounts were not determined. From these experiments it is evident then that the osmotic pressure of 0.125 normal sugar solutions at 0° is very slight indeed, which practically confirms my previous experiments, No. 54a and 60, and demonstrates that the explanations of Cohen and Commelin are untenable. To Mr. W. G. Wilcox, who assisted me in carrying out these experiments, I take this opportunity to extend my thanks.

A careful scrutiny of the various results I have previously obtained at different concentrations and at different temperatures will lead any unbiased person to the conclusion that the gas laws do not regulate the osmotic pressures observed. Moreover, as stated above, we are at present measuring the minimum concentrations at which various solutions show any appreciable osmotic pressure whatever, and this work is being carried on at different temperatures. The results indicate that the osmotic pressures are not governed by the gas laws at all.

Having thus shown that the objections of Cohen and Commelin to my experiments and conclusions are worthless, let us turn our attention to their own attempts to measure osmotic pressures. They chose cane sugar as solute and pyridine as solvent, using a rubber membrane as I did. They seem to have had difficulty in securing good vulcanized caoutchouc, which in America is available at practically every dentist's office. At Mr. Cohen's request I sent him a piece of the rubber I had used. They constructed an apparatus similar to mine, but were unable to get concordant results from similar experiments, without, however, being able to find a reason for such discrepancies. They discuss the possibility that in their experiments the membrane was not thoroughly imbibed with pyridine while being tied on the osmometer, that the tension of the membranes was different in different cases, that the cloth used might have stretched, that the temperature was not the same throughout the apparatus, that the electric stirrer moved through too small a

distance, and that water might have gotten into the apparatus. They then proceed to construct another apparatus calculated to obviate these difficulties. They make the cell of iron; fasten the glass manometer into it with glycerine-litharge cement; put the membrane into place by pressing it unstretched against the flange bottom of the cell, using a large metal ring and bolts. They further cement a glass tube into another iron tube attached to the cell in order to be able to work the electric stirrer, and place the whole cell into another cylindrical glass vessel fitted with a sheet iron cover through which pass a thermometer, the stem of a calcium chloride tube, the stem of a Witt stirrer and the manometer tube. They seek to get all these joints absolutely tight, and then further seek to secure the sheet iron cover to the glass cylinder by attaching to the latter a circular trough of sheet iron, into which the cover is laid and secured by means of a mercury joint, over which, since it is to be used under some pressure, they put a cement consisting of a mixture of pitch and wax. And thus they claim to secure an absolutely tight apparatus which can be completely immersed in the water of a thermostat; to use their own language, "In dieser Weise lässt sich das äussere Gefäss samt Deckel in das Wasser des Thermostaten bringen ohne dass Gefahr besteht, dass auch nur die geringste Spur Wasser in den Apparat dringt." On p. 41 they reiterate practically the same statement. But one looks in vain in their paper as to how they determined that this remarkable apparatus with its many so perfectly made joints was tested to make sure that it could be kept under water for days at a time without having the least trace of water enter into it. The test they used with the bicycle pump to determine whether the inner cell was tight seems to me also quite inadequate. Further, they test the inner and outer liquid with a polariscope, a procedure which might do for the strong solutions used in the osmometer cell, but which is worthless in testing the outer liquid, which is so dilute that in a 50 cm. tube the rotation is only a few hundredths of one degree (see p. 45 of

their paper) and consequently lies almost within the limits of experimental error. It is precisely for this reason that I did not employ a polariscope (which to be sure is, to use their language, "sehr bequem") and took the trouble to evaporate the entire outer liquid to dryness, invert the sugar and determine its amount with Fehling's solution.

Considering now the results of Cohen and Commelin, we find that they are given in their Tables 11 and 14 as follows:

FROM TABLES 11

Concentration	Pressure in cm Hg		Theoretical osmotic pressure from Table 12
	I	II	
0.025 norm.	10.3	6.2	—
0.025 "	17.9	12.3	46.48 cm Hg
0.05 "	34.7	41.2	92.96 " "
0.05 "	35.3	22.5	—
0.10 "	82.3	67.1	185.92 " "
0.10 "	50.8	71.9	—

All work was done at 25° C., and in Table 11 without stirring.

TABLE 14

Membrane	Maximum osmotic pressure in cm Hg at 25°. Solutions are 0.1 normal	
	Without stirring	With stirring
"Cofferdam"	47.8	63.2
	71.7	50.1
From Kahlenberg.....	65.4	75.6
	54.2	46.4

The values in Table 14 are the only ones obtained without and with stirring.

From Table 11 it appears at once that the results are not concordant in the parallel experiments, which fact Cohen and Commelin also point out, without, however, being able to ascribe a reason therefore. Furthermore, in Table 14

parallel results do not agree, and just half of them are higher with stirring, and the other half are higher without stirring. The authors conclude that they have not measured equilibrium pressures in any of these cases and that the effect of stirring is nil. Cohen and Commelin finally devote four pages to the influence of water in their experiments, surely a timely topic considering the many jointed apparatus they use immersed completely in the water of a thermostat. The experiments with water will not be discussed here, for the authors promise to look into the matter further. They state that the fact that their pyridine boiled between 115° and 117° showed that it contained some water. Now the truth is that the addition of water to pyridine lowers the boiling point; and the high and slightly rising boiling point which dry pyridine shows on distilling it, is due to the presence of slight amounts of higher boiling homologues, notably picoline, which the pyridine contains.

In their final summation, Cohen and Commelin state that their critical study of my experiments shows that I had no right to doubt the validity of the gas laws as applied to osmotic pressures on the basis of my experiments, a position which, as I have pointed out in the present paper, cannot be maintained, for all my experiments show conclusively that the osmotic pressures do not follow the gas laws. And what about the osmotic pressures which Cohen and Commelin themselves present as the results of their own measurements! Are not these all far below what the gas laws require, poorly concordant though they be? And then Cohen and Commelin boldly assert that they have constructed a new apparatus in which the errors attached to my experiments were circumvented. But let any unbiased critic regard the results they have obtained with this "improved" apparatus. I take it that these speak powerfully against the claims they make for it. My osmotic cell and manometer attached were together made of but one piece of glass; there were no cemented joints whatever used in any part of the apparatus. This is to be considered as far superior to the apparatus of

Cohen and Commelin, which contains joints that, as every careful experimenter knows, are well-nigh impossible to secure perfectly. Again, they use a ground glass joint to attach their manometer to the glass tube that is cemented into the cell, as stated above, and they grease this ground glass joint and seek to secure it further by tying it in place with string. It is needless to remind the reader that pyridine is an excellent solvent for grease. Further, by keeping the temperature constant by means of a constant temperature room, instead of immersing the whole apparatus into an aqueous thermostat, I avoided the danger of getting water into the apparatus. Again, whether the membrane is stretched to a somewhat different degree in different experiments or not makes no difference, of which fact I assured myself early in my researches (see p. 190 of my paper). I desire to add here too that whether the membrane is first soaked in pyridine before tying it on or not, makes no difference. In all my experiments the membrane was stretched moderately tight so that no folds were encountered in making the joint between glass and rubber and no wrinkles occurred when the rubber was later soaked in pyridine. The cloth was always tightly stretched on dry, and then when it became wet with pyridine it shrank on still more securely. A yielding of the strong cloth used in the slight pressures measured was not to be feared. The work of Cohen and Commelin of attaching the membrane to the osmometer in the cumbersome way they adopt is quite unnecessary; it is also to be observed that the rubber jammed between the metal ring and the base of their osmometer also acts somewhat in the osmosis, and this part of the membrane is certainly always under different strain in different experiments, for it is obviously quite impossible to tighten the bolts used alike in different experiments. Furthermore, I should like to state here that in my Experiment No. 20 where a steel cell was used, the membrane was attached to the cell in much the same way as that adopted by Cohen and Commelin.

With their apparatus which is thus open to serious ob-

jections, Cohen and Commelin have in two series of experiments made with and without stirring, Table XIV, been unable to confirm the fact that when the experiments are conducted with stirring higher results are always reached; on the other hand, they have also clearly been unable to demonstrate the contrary. The Witt stirrer, which they used, is inefficient; the hollow space under the osmotic cell due to the projection of the heavy iron ring, makes thorough mixing of the outer liquid increasingly difficult. Furthermore, the cloth they use to support the membrane from above by retaining the solution operates greatly against keeping a solution of proper concentration in contact with the upper side of the membrane, which is obviously of prime importance. Again, their inner stirrer had simply a disc at the lower end and no lateral prongs as in my apparatus.

Summary

In summing up the situation then, Cohen and Commelin have failed to show that stirring is unnecessary in measuring maximum osmotic pressures. Their apparatus has failed to yield concordant results and it can consequently not be regarded as an improvement on the one I used, as they claim. If anything, the results Cohen and Commelin present are additional evidence demonstrating that the gas laws do not hold for osmotic pressures in the cases investigated.

In consideration of all the facts presented, there is no reason whatever for modifying the conclusions I have reached in my previous paper.

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