A Study of the Semi-Permeable Membranes of Zinc Ferrocyanide and of Copper Cobalticyanide.

Dissertation.

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INTRODUCTION.

Ten years ago it was discovered in this laboratory[1] that semi-permeable membranes could be deposited very satisfactorily by means of the electrolytic method. Several membranes which were deposited at that time by this process proved to be quite active. When tested by the methods then available, they appeared to be quite promising. However,none of them with the exception of the previously well known copper ferro cyanide membrane were extensively investigated. In fact no thorough investigation was possible until the problem of producing satisfactory porous cells had been solved. Later, when the problem had been satisfactorily worked out the supply of good cells was too limited to justify the sacrifice of any of them for the investigation of membranes of unproved excellence. Recently, however the supply of cells reached the point where a portion of them could be devoted to this purpose. Hence the investigation of a number of the membranes which were then electrolytically deposited has been resumed. The investigation that was undertaken by the author was that of zinc ferro cyanide.

1. Amer. Chem. Jour. 26, 80.

Tammann was the first to observe that this substance is osmotically active. His work along this line was limited to the ferrocyanides of copper and zinc. He used the so-called optical method which consisted in allowing a drop of copper or zinc sulphate to fall into a solution of potassium ferrocyanide. This drop is immediately surrounded by a film of copper or zinc ferrocyanide. The passage of water through this film is always, of course from the more dilute to the more concentrated solution. Hence the drop will swell or shrink according as the solution within it is more or less dilute than the solution which surrounds it. Thus by observing the currents about the drop Tammann was able to determine the relative concentrations of the two solutions.

The earliest investigations of the electrolytically deposited zinc ferro cyanide membrane was made in this laboratory by B.F. Carver[1] in 1903. After showing that this membrane could be deposited electrolytically by the method of Morse & Horn[2] Carver studied its osmotic activity measured in terms of the rate of endosmose. This was determined by measuring the amount of solution delivered from a cell in which the membrane was deposited. In some cases he measured the pressure developed by attaching an open manometer to the cell. However, it has been shown on many occasions that it is impossible to measure correctly osmotic pressure with cells such as were available

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1. B.F. Carver Dissertation Johns Hopkins Univ. 1903.
2. Amer. Chem. Jour. 26, 80.

at the time when Carver did his work. Consequently, it must be remembered that experiments of this nature merely indicate the osmotic activity at low pressures, and do not in the least indicate its power to withstand higher pressures.

Three years later W.L. Kennon[1] took up the study of the zinc ferro cyanide membrane. And although Kennon did his work with better cells he did not carry his investigation far enough to determine whether the failure to obtain satisfactory results was due exclusively to a defective membrane or in part to defective cells. Kennon speaks of the zinc ferro cyanide membrane in the following language. " However, the membranes deposited under the conditions employed in this work seem unsuitable for the measurement of high osmotic pressures.----- The results obtained hardly seem capable of explanation on any other basis than that the membrane does not adhere firmly to the cell wall.-- Again, the ease with which the membrane could be detached from the cell by simple agitation with water is a further indication of the imperfect manner in which it is attached to the cell wall. --- It might therefore be concluded that zinc ferro cyanide deposited under the conditions employed in this work, cannot be deposited on the rather dense walls of the cells used, in a form suitable for the measurement of high osmotic pressures." In as much as since Kennon's time

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1. W.L. Kennon Dissertation Johns Hopkins Univ. 1906

the cells have been improved in many ways it was suggested that

the author resume the investigation of the zinc ferro cyanide membrane, to ascertain with greater certainty whether it is suitable for the measurement of osmotic pressure.

Zinc ferro cyanide, $Zn_2 Fe(CN)_6 3H_2O$, is formed as a heavy, white, gelatinous precipitate when aquous solutions of zinc sulphate and potassium ferro cyanide are mixed. It is insoluble in water and little soluble in the dilute mineral acids. It is however soluble in the caustic alkalis.

The type of cell used in this investigation was that now commonly in use in this laboratory, which was described in the American Chemical Journal Vol. 45 page 111. Before depositing a membrane in a cell it is necessary to remove all the air enclosed in the minute pores of the cell wall. This was done in the usual manner by electrical endosmose with a .005 normal solution of lithium sulphate. The cell was surrounded by an anode and contained within a cathode, both electrodes being of platinum. At intervals the electrolysis was stopped and the solutions on the exterior and interior of the cell were thoroughly mixed. When it was considered that the air had been entirely removed, the cell was taken out emptied and rinsed with water. The cell was then soaked for a time in distilled water. Afterwards the minute quantity of electrolyte still remaining within the cell wall was removed by continuing the electrolysis with the use of distilled water.

When the resistance has become equivalent to the resistance of distilled water the cell is considered as ready for the deposition of the membrane.

In the deposition of the membrane the cell, surrounded by a metallic cylinder which serves as an anode, is placed in a glass vessel. Within the cell is a platinum cylinder which serves as the cathode. The cell is closed by a rubber stopper through which pass an overflow tube, a funnel which reaches nearly to the bottom of the cell and the wire leading to the cathode. After closing the circuit the appropriate solutions are poured simultaneously into the cell and into the vessel in which the cell is placed.

In this investigation of the zinc ferro cyanide membrane two cells designated Znl and Zn ll were used. And although the work with these two cells was carried on simultaneously and under exactly the same conditions the conduct of each will be considered separately.

Experimental Part

Cell Zn I

Cell Zn I was subjected to electrical endosmose with a .005 normal solution of lithium sulphate for a period of four and one quarter hours, during which time 59c.c. of the lithium sulphate solution passed from the exterior to the interior of the cell. A 109 volt current was used for this purpose. The resistance offered by the cell with the electrolyte was

approximately 10,000 ohms. After the air had been completely

removed in the manner described, the solution of the electrolyte was replaced by distilled water and the electrolysis continued with frequent renewal of the water. The removing of the electrolyte required about forty hours. During this time the resistance rose uniformallyfrom 7,100 ohms to 39,600 ohms, at which point it remained practically constant. The conductivity having become constant, it was considered that the electrolyte was entirely removed from the wall of the cell. The preliminary work of removing the air and after that the electrolyte from the cell wall extended over a period of twelve days.

The deposition of the zinc ferro cyanide membrane in cell Zn I was commenced on Oct.26. The method of its deposition and development was essentially the same as the method already described. The cell, surrounded by an anode of zinc and containing within it a cathode of platinum was placed in a glass vessel. Within the cell was placed a solution of potassium ferrocyanide and in the glass containing the cell was placed a solution of zinc sulphate. The zinc sulphate and potassium ferrocyanide solutions used in this connection were one tenth osmotically normal, due allowance being made for the dissociation of the two salts. In using potassium ferrocyanide in the electrolytic deposition of the ferrocyanide membranes,potassium hydroxide is always formed by a decomposition of the potassium ferrocyanide. Consequently, in order to prevent decomposition of the zinc ferro cyanide membrane, by the potassium hydroxide formed, a very

frequent renewing of the potassium ferro cyanide solution is necessary. In this work the solution within the cell was renewed at intervals of three minutes. The resistance of the membrane was determined once in six minutes.

Perhaps the best manner in which a brief history of the initial deposition of the membrane can be given is by means of a table. In this table simply a statement of the length of the time deposition and of the maximum resistance obtained during that period will be given.

Oct.	26	3.06 P.M. _ 4.42 P.M.	maximum	resistance	28,590	ohms
	27	10.51A.M. - 12.28P.M.	"	"	37,883	"
		3.05 PM - 4.55 P.M.	"	"	54,285	"
	28	3.00 P.M. - 4.10 P.M.	"	"	38,000	"
	31	11.33 A.M. - 12.37P.M.	"	"	37,666	"
		2.48 P.M. - 4.29 P.M.	"	"	41,851	"
Nov.	1	2.45 P.M. - 4.35 P.M.	"	"	34,242	"
	2	11.45 A.M. - 12.43 P.M.	"	"	46.818	"
		2.25 P.M. - 4.30 P.M.	"	"	59,210	"
	3	11.08 A.M. - 12.31 P.M.	"	"	58,947	"
	9	10.45 A.M. - 12.11 P.M.	"	"	62,111	"
		3.12 P.M. - 4.36 P.M.	"	"	74,666	"
	10	11.12 A.M. - 12.32 P.M.	"	"	83.571	"
	14	11.07 A.M. - 12.03 P.M.	"	"	70,000	"
		3.11 P.M. - 4.32 P.M.	"	"	93,750	"
	22	11.15 A.M. - 12.34 P.M.	"	"	84,630	"
	29	10.47 A.M. - 12.15 P.M.	"	"	84,630	"

It was noticed that in each instance during the first few minutes of membrane deposition the resistance increased very rapidly. Also it was noted that the longer the period of soaking of the membrane in pure water, the lower the initial resistance and the more rapid the rise of the resistance during the first five or ten minutes of membrane deposition. It has been suggested that this rapid rise in the resistance of the membrane may be due to the membrane assuming, while being soaked in water in the absence of an electrolyte, a more colloidal state. Then when the electrolytes, in subsequent strengthening of the membrane are brought by the current in close proximity to the membrane a much denser packing of the membrane results. If this is the true explanation of the phenomena, then it is easy to see why a long soaking is followed by a greater and quicker rise in resistance than is a shorter period of soaking.

Another interesting feature of this membrane was the appearance, during the deposition, of patches of membrane of unusual thickness. These were formed generally at the point where the glazed and unglazed interior portions of the cell met. The first appearance of these patches was on Nov. 1. At that time the cell had been subjected to the membrane forming process for four days. These patches were carefully removed by rubbing the interior cell wall at the point where they were formed with a soft cloth. The only result following their removal which was noted was a subsequent slight increase in the resistance of the membrane. Again two days later there were noticed other

patches similar to the first in approximately the same position. These were not removed at this time and the only apparent difference between the membrane in cell Zn I and cell Zn II which did not have any patches at this time was perhaps a slightly lower resistance. And there is no direct evidence that even this difference was caused by these patches. About a week later the patches were again removed in the manner already described. Two weeks later patches appeared in both cells at the junction of the glazed and unglazed portions. These were not removed and the cell was set up for measurement with the patches on the interior wall. After the cell was taken down the patches did not appear as large, and never appeared to increase in size although the cell was set up for measurement and also subjected to the membrane forming process repeatedly after this time. There are several possible explanations for the formation of these patches. However,in spite of that fact, it would be difficult to satisfactorily explain why these should occur.

Experiment I

Cell ZnI was set up for the first measurement at 3.05 Nov. 29. Its resistance was 84,630 ohms. A weight normal cane sugar solution was used. The sugar solution was made osmotically normal with respect to potassium ferro cyanide, while the solution surrounding the cell was made one hundredth normal with respect to zinc sulphate. The cell was set up at twenty-five degrees, which is the temperature at which the membrane was deposited.

The initial rise of the mercury in the manometer was watched very closely, and rate of rise was as follows:-

3.05 P.M. mercury at 0
3.16 P.M. " had risen 62.0 mm.
3.23 P.M. " " " 111.0 "
3.33 P.M. " " " 181.0 "
3.39 P.M. " " " 222.0 "
3.45 P.M. " " " 256.0 "
3.55 P.M. " " " 305.0 "
4.05 P.M. " " " 336.0 "
4.16 P.M. " " " 354.0 "
4.27 P.M. " " " 361.0 "
4.34 P.M. " " " 365.0 "

The total length of the original nitrogen column in the manometer was 445.43 m.m. Since the rise of the mercury column was apparently perfectly continuous there was either no leakage of the membrane or the increase in the osmotic pressure was more rapid than the leakage. Otherwise there would have been either a halt in the ascent of the miniscus or a positive falling of the same. Also, as will be noted in this brief table, the rise of the mercury was very rapid. Which indicates, as has previous work with this membrane, that it is very active.

After these preliminary observations the cell was placed in a constant temperature bath. The pressure continued to rise uniformly until 1 P.M. Nov. 30 at which time it reached 3.39 atmospheres, the maximum pressure which was obtained for this experiment. The pressure of the normal solution of cane sugar is known from other work to be 27.05 atmospheres at this temperature.

The pressure then began to slowly fall being at 5 P.M. 3.36 atmospheres, at 10 P.M. 3.33 atmospheres, and at 10 A.M. the next morning 3.28 atmospheres. From the constant decrease in pressure it was evident that there was a leakage of the membrane. Consequently the cell was taken down. The sugar solution taken from the cell was of a blue tinge and so dark that it was impossible to read its rotation in the saccharimeter. However there must have been a loss in rotation for the solution was undoubtly diluted.

On taking down, the cell was placed in a saturated solution of thymol and allowed to soak for forty-eight hours. On Dec. 4 the cell was again subjected to the membrane forming process. The resistance at first was very low being only 17,833 ohms. However the resistance gradually rose until it reached 82,307 ohms. The cell was then again soaked in a saturated thymol solution. On Dec. 5 the membrane was reinforced, the resistance being at the start 27,894 ohms, at the end of five minutes it had risen to 46,087 ohms and from that point the resistance gradually rose to 116,000 ohms. On Dec.6 the membrane was once more reinforced, this time for a period of an hour, its maximum resistance for this period being 116,000 ohms.

Experiment II

Cell Zn I was again set up at 4 P.M. Dec. 6. Its resistance was 116,000 ohms. As in the previous experiment a weight normal cane sugar solution was used. Also hundredth normal solutions of zinc sulphate and potassium ferrocyanide

were used as membrane menders. The pressure rose uniformly, though less rapidly than in the former experiment, until 10 A.M. Dec. 7 at which time it was 1.52 atmospheres. The pressure then fell constantly for twenty-four hours, after which time the cell was taken down. The solution taken from the cell was too cloudy to read the rotation in the saccharimeter. The precipitate which rendered the solution cloudy was extremely slow in subsiding so that even after two days it was not practical to determine the rotation of the solution. However considering the low pressure the dilution must have quite large. The cell was soaked in saturated thymol solution for two days, after which the membrane was again reinforced. The initial resistance after the soaking was 53,250 ohms which gradually rose to 106,500 ohms... The cell was then soaked for two weeks, when the membrane was again reinforced, the maximum resistance now being 100,000 ohms.

Experiment III

Cell ZnI was set up on Jan. 4 at 4 P.M. The resistance was 100,000 ohms. A weight normal sugar solution was used, with hundredth normal solutions of zinc sulphate and potassium ferro cyanide as membrane menders. The mercury rose slowly until 9 P.M. but not far enough to come within the range of the telescope on the cathetometer. At 9 A.M. the following morning the mercury had dropped to atmospheric pressure and it did not rise again although the cell remained in the bath for forty-eight hours longer. The cell was then taken down. The loss in rotation showed that there had been considerable dilution and consequently considerable leaking of the membrane. After soaking for two days the membrane was again reinforced. The resistance at the start

was 14,705 ohms and gradually rose to 83,384 ohms.

Experiment IV

Cell ZnI was set up on Jan. 13 at 12.00. Weight normal sugar solutions and hundredth normal solutions of zinc sulphate and potassium ferro cyanide as membrane menders were used. The final resistance was 83,384 ohms. The cell was in the bath for three days and at no time could any rise in the mercury be perceived. Consequently there was no pressure developed. On taking down the cell the solution showed a large loss in rotation indicating a considerable dilution.

Cell ZnII

Since the deposition of the zinc ferro cyanide membrane in cell ZnII was essentially the same as in the case of cell ZnI only a brief statement of the preliminary work need be given. A .005 normal solution of lithium sulphate was used for the removal of the air. The endosmose was 121cc in four hours, with a maximum resistance of 8,384 ohms. In the removal of the electrolyte from the cell wall which required approximately forty hours a maximum resistance of 56,000 ohms was obtained. In reporting in connection with the deposition of the membrane in cell ZnII, simply a statement of the length of each period of membrane deposition and of the maximum resistance obtained during that period will be given in tabular form.

Oct. 26	3,06 P.M. - 4,42 P.M.	maximum	resistance	28,375 ohms
27	10.51 A.M. - 12.28 P.M.	"	"	37,833 "
	3.05 P.M. - 4.55 P.M.	"	"	54,285 "
28	3.00 P.M. - 4.10 P.M.	"	"	38,000 "

Oct. 31	11.33 A.M. - 12.37 P.M.	maximum	resistance	37,666 ohms
	2.48 P.M. - 4.29 P.M.	"	"	41,851 "
Nov. 1	2.54 P.M. - 4.35 P.M.	"	"	30,542 "
2	11.45 A.M. - 12.43 P.M.	"	"	56,500 "
	2.25 P.M. - 4.30 P.M.	"	"	75,333 "
3	11.08 A.M. - 12.30 P.M.	"	"	74,666 "
9	10.45 A.M. - 12.11 P.M.	"	"	58,947 "
	3.12 P.M. - 4.36 P.M.	"	"	74,666 "
10	11.12 A.M. - 12.32 P.M.	"	"	65,000 "
14	11.07 A.M. - 12.03 P.M.	"	"	70,000 "
29	10.47 A.M. - 12.15 P.M.	"	"	73,333 "

Experiment I

Cell ZnII was set up for the first measurement Nov. 29 at 3.00 P.M. A weight normal cane sugar solution was used, with hundredth normal solutions of zinc sulphate and potassium ferro cyanide as membrane menders. The resistance was 73,333 ohms. In all of the work with cell ZnII the temperature was 25°. The record of the initial use of mercury in the manometer is as follows:

3.11 P.M.	mercury at o				
3.21 P.M.	"	had	risen	22m.m.	
3.33 P.M.	"	"	"	56.0	m.m.
3.45 P.M.	"	"	"	86.0	"
3.55 P.M.	"	"	"	115.0	"
4.05 P.M.	"	"	"	139.0	"
4.16 P.M.	"	"	"	162.0	"
4.26 P.M.	"	"	"	183.0	"

The total length of the original nitrogen column in the manometer was 497.52 m.m. Since the rise in pressure was continuous there could have been either no break in the membrane or the leakage was slower than the increase in osmotic pressure. In this case as in the first experiment with cell ZnI it was shown that fresh zinc ferro cyanide is a very active membrane. During the observations noted in the above table the cell was in a constant temperature bath while the manometer was exposed to the temperature of the room which was somewhat lower. After placing the cell in the larger bath the pressure rose until 10 P.M. at which time it was 4.49 atmospheres, the maximum pressure for this experiment. The pressure, then commenced to drop. It fell constantly for thirty-six hours at the end of which time the cell was taken down. The solution taken from the cell was of a greenish blue color and too cloudy to permit a determination of its rotation. There must however have been a decided loss in concentration. The cell was soaked out and the membrane reinforced in the manner heretofore described, the maximum resistance obtained being 98,636 ohms.

Experiment II

Cell ZnII was again set up on Dec. 13 at 11.30 A.M. with a weight normal solution of cane sugar. Hundredth normal solutions of zinc sulphate and potassium ferro cyanide were used as membrane menders. The resistance at this time was 98,636 ohms. The mercury rose about an inch in the manometer and remained there for two days, after which the cell was taken down. The solution from the cell showed a large loss in rotation which indicates that there was a considerable leakage of the membrane.

Since the membrane developed very little pressure and the solution from the cell showed a greenish blue color it appeared probable that the membrane had been infected by penicillium. It had been well established in the work on the copper ferro cyanide membrane that penicillium not only ruins a membrane containing nitrogen but that it also produces a greenish blue color in solutions containing potassium ferro cyanide. On this account it was thought best to give the cell a short treatment with some very powerful disinfectant. Consequently on Dec. 17 the cell was subjected for a period of twenty minutes to concentrated fumes of hydrocyanic acid.

This work was carried out under a hood provided with a good draft. The neck of a bell-jar which fitted tightly to a glass plate was closed with a three hole rubber stopper. Two delivery tubes passed through two of these holes. These were connected with wash bottles. By applying suction to one of these wash bottles the bell-jar could be filled with a saturated water vapor. This atmosphere of saturated water vapor was necessary in order that the membrane should not become dry and thereby useless. Also by means of suction the bell-jar could be flushed out before opening and thus all danger from any excess of hydrocyanic acid fumes could be avoided. Through the third hole in the rubber stopper was passed a dropping funnel. By means of this funnel acid could be slowly added to a beaker, within the bell-jar, which contained crystals of potassium cyanide. After this treatment with hydrocyanic acid fumes the membran e in cell ZnII was reinforced in the usual manner, with a maximum

resistance of 62,222 ohms. This cell was set up on Jan. 4 as was also cell ZnI which had not been treated with hydrocyanic acid fumes. A comparison of the records of the two cells, in both of which the greenish blue color had appeared, and but one of which had been treated with hydrocyanic acid fumes, shows that even a thorough disinfection did not suffice to greatly improve the membrane.

Experiment III

Cell ZnII was set up at 4 P.M. Jan 4, its resistance being 62,222 ohms. A weight normal sugar solution and hundredth normal solutions of zinc sulphate and potassium ferro cyanide as membrane menders were used. At 4.35 the mercury in the manometer had risen about an inch. At 9.30 P.M. the mercury was apparently in the same position. At 9 A.M. the following morning the mercury had dropped to atmospheric pressure and remained there for two days, after which the cell was taken down. The solution taken from the cell showed, as would be expected, a very considerable dilution. However it did not exhibit the greenish blue color proving that the treatment with hydrocyanic acid fumes in all probability had killed the penicillium.

It was concluded that it was useless to experiment further with the zinc ferro cyanide membranes. And it was suggested to the author that an attempt be made to remove this membrane and to substitute it by one of proved excellence. The membrane selected for this purpose was the nickel ferro cyanide membrane. The cells containing the zinc ferro cyanide membrane had been

demonstrated to be thoroughly useless for the measurement of osmotic pressure. But it was not certain that the failures hitherto recorded were due entirely to the menbrane. In other words it remained to be proved whether the cells were or were not of good quality,

This suggestion was carried out and the results obtained were quite gratifying. The method of removing the zinc ferro cyanide membrane is taken up in detail later in this paper and so only reference to it will be made here. The arrangements for the deposition of the nickel membrane were the same as those already described except that an anode of nickel was used and the cell was immersed in a solution of tenth normal nickel sulphate. The deposition of the nickel ferro cyanide membranes in both cells was commenced on Mar. 16. The record of the deposition of this membrane in cells ZnI and ZnII which will be hereafter designated Ni_8 & Ni_7 respectively, is seen in the following table. This table will give simply a statement of the lengths of the periods of membrane deposition and of the maximum resistance obtained during each period.

					Cell Ni_7		Cell Ni_8	
ar. 16	11.55 A.M.- 12.30 P.M.	maximum	resistance		7,957	ohms	5,850	ohms
18	11.35 A.M.- 12.10 P.M.	"	"		16,133	"	20,166	"
20	11.50 A.M.- 12.20 P.M.	"	"		21,454	"	17,353	"
21	10.30 A.M.- 11.23 A.M.	"	"		27,143	"	18,387	"
22	11.30 A.M.- 12.08 P.M.	"	"		36,000	"	26,666	
	2.20 P.M.- 3.30 P.M.	"	"		37,333	"	28,000	"
27	2.00 P.M.- 3.18 P.M.	"	"		38,333	"	28,750	"
30	11.25 A.M.- 12.22 P.M.	"	"		54,272	"	36,773	"

Apr. 1	11.45 A.M.- 12.15 P.M.	maximum resistance	57,000	ohms	38,000	ohms
5	11.25 A.M.- 12.17 P.M.	" "	52,376	"	30,000	"
7	2.05 P.M.- 3.25 P.M.	" "	61,111	"	44,000	"
12	2.30 P.M.- 3.22 P.M.	" "	61,111	"	47,817	"
28	10.25 A.M.- 11.50 A.M.	" "	66,475	"	56,500	"

Since these two cells were set up for measurements alternately it perhaps will be well to consider the conduct of each seperately.

Experiment I

Cell Ni_7

Cell Ni_7 was set up for the first measurement on April 28 at 30°. A weight normal solution was used, the usual quantity of membrane menders also being added. The resistance of the cell at this time was 66,475 ohms. The rise of the mercury in the manometer was closely watched. It rose apparently without a single halt, which indicates that either there was no leaking of the membrane or the leakage, if there was such, was less than the increase of the osmotic pressure. The rate at which the pressure increased was phenomenal. At 3 P.M. or after a period of three hours the osmotic pressure was over twenty-four atmospheres, the pressure having started at atmospheric pressure. At 9 P.M. the pressure had risen to over twenty-five atmospheres. At 9 A.M. the following morning the pressure developed was 25.608 atmospheres which was the maximum pressure for this experiment. The true osmotic pressure of cane sugar solution at this temperature and concentration of solution is known from other work to be 27.223 atmospheres. So rapid a rise from atmospheric to nearly full osmotic pressure in so short a time is unusual.

After this maximum pressure had been obtained the pressure fell uniformly for two days at the end of which time the pressure was 24.598 atmospheres. The cell was then taken down and placed in a thymol solution. The solution taken from the cell showed some loss in rotation. On May 2 the membrane was reinforced for one and one-half hours during which time the maximum resistance was 57,000 ohms.

Experiment II

Cell Ni_7 was set up on May 2 at 30°. A weight normal sugar solution was used, with hundredth normal solutions of nickel sulphate and potassium ferrocyanide added as membrane menders. The pressure rose to 24.089 atmospheres during the first five hours. At 9 A.M. on the following morning the pressure had risen to 24.26 atmospheres which was the maximum pressure for this experiment. The pressure remained constant for two days at the end of which time the cell was taken down and placed to soak in a thymol solution. The solution taken from the cell showed some loss in rotation. On May 6 the membrane was reinforced for one hour, the maximum resistance being 44,333 ohms. On May 8 the membrane was again reinforced, the resistance being in this case 73,333 ohms.

EXPERIMENT III

Cell Ni_7 was set up for measurement on May 8. A weight normal sugar solution was used. Hundredth normal solutions of nickel sulphate and of potassium ferro cyanide were added as membrane menders. At 8 P.M. or eight hours after setting

up the pressure was 32.06 atmospheres. At 10 A.M. the following morning the pressure had risen to 32.24 atmospheres. The pressure of thiry-two atmospheres is above that which is known to be normal for the solution at 30°.

The explanation of the over pressure is to be found in the conditions previous to the placing of the cell in the bath. There are two conditions which lead to the development of surplus pressure in the cell. In the first place it occurs whenever the solution at the time of the setting up of the cell is at a temperature lower than that of the bath in which the cell is finally placed. The solution, in this case, on being warmed up to the temperature of the bath expands and produces a mechanical pressure which may with the already developed osmotic pressure exceed the true osmotic pressure of the solution. Whenever this occurs water should be discharged from the solution through the membrane resulting in a slight concentration of the solution. But the water does not instantaneously pass through the membrane, hence there is for an indefinite time an over pressure upon the cell contents. The second cause is of a similar nature. The temperature of the mercury in the manometer is usually somewhat lower than that of the bath and this also expands on warming up and may give a surplus pressure, if the placing of the cell in the bath is delayed for purposes of observation until a considerable osmotic pressure has already been developed.

Cell Ni_8

EXPERIMENT I

Cell Ni_8 was set up for the initial measurement on May 5 at 30°. Its resistance was 63,333 ohms. A weight normal sugar solution was used, the usual quantities of membrane menders also being present. The rise of pressure was even more rapid than in the case of cell Ni_7. The pressure rose in one and one quarter hours to approximately 29 atmospheres. The pressure fell for two days at the end of which time it was 10.98 atmospheres The cell was then taken down and placed in a thymol solution. The solution taken from the cell showed a considerable loss in rotation, indicating that the membrane though more active initially was less strong than that in the other cell.

The work of developing the nickel membranes was not carried to the point at which they were able to maintain the maximum osmotic pressure of concentrated solutions for an indefinite time. Their further work was undertaken by others. Enough was done however to show beyond question that the general failure of the zinc ferro cyanide membranes could not be due to imperfect cells.

CONCLUSIONS.

The results of this investigation show, 1. That the zinc ferro cyanide membrane may be easily deposited by the electrolytic method.

2. That the membrane while fresh is quite active and able to sustain very moderate pressures.

3. That the membrane rapidly deteriorates with age, so that the pressures attained on each succeeding experiment are lower than in the preceeding one.

4. That the membrane after deposition tends to become granular. This tendency is evidenced by the fact that the solutions when removed from the cell are always cloudy in consequence of the presence of suspended zinc ferro cyanide, which has been detached from the cell wall. There can no longer be any doubt that the zinc ferro cyanide membrane is wholly unsuited to the measurement of osmotic pressure.

THE SEMIPERMEABLE MEMBRANEof COPPER COBALTI CYANIDE.

One of the many different electrolitically deposited substances which have been examined in this laboratory in regard to their osmotic activity is copper cobalti cyanide. In 1903 Carver made a preliminary investigation of the osmotic activity of this substance. It was shown by him that under the conditions of his work the copper cobalti cyanide membrane was probably less active than those of the zinc and nickelferro cyanides. He employed potters cells of considerable porosity and therefore was unable to obtain pressures of any considerable magnitude. Still he attempted to measure the relative osmotic pressures obtained in the case of various membranes, by determining the height to which the solution would rise in an open manometer. He also measured the overflow for periods of several days. Thus conclusions drawn from his work may not be entirely conclusive.

Three years later when far more perfect cells were obtainable a second investigation of the copper cobalti cyanide membrane was carried out by E.J.Hoffman. In the introduction to the discussion of this membrane Hoffman points out a fact which cannot be too strongly emphasized. In this connection it will be well to give the author's exact words. "It should be noted that many failures to make direct measurements of osmotic pressure have been due, not to the membrane, but to the faulty character of the cell wall in which, or upon which, the membrane was deposited. The importance of keeping this distinction clearly in mind can not be urged too strongly, for many conclusions reached concerning osmotic pressure and its measurement may be entirely erroneous for no other reason than that the cell wall did not provide sufficient support for the membrane." The above caution applies with special force to all early work upon electrolytically deposited membranes, where potters' cells were of a necessity used. Hoffman used a cell for the deposition of his copper cobalti cyanide membrane in which there had previously been one of zinc ferro cyanide. And his unsatisfactory results may have been due to this cause, as will be shown hereafter. It was therefore suggested that the author resume the investigation with entirely fresh cells.

Copper cobalti cyanide, a precipitate the composition of which is supposed to be Cu_2 Co_2 $(CN)_{12}$, is formed when an aqueous solution of potassium cobalti cyanide is treated with a

solution of copper sulphate. The precipitate, which is of a

turquoise blue color is insoluble in water and acids, but it is soluble in ammonium hydroxide. It is also acted upon by potassium hydroxide, forming a green color which becomes darker and finally takes on the black appearance characteristic of cupric oxide. During the deposition of the copper cobalti cyanide membrane by the electrolytic method potassium hydroxide is formed. In order to prevent this from decomposing the membrane a quantity of acetic acid equivalent to the potassium is added to the cobalti cyanide solution. In other respects the method employed in depositing the membrane was the same as that employed in the case of the copper ferro cyanide membrane. That is, the anode was of copper and the cathode of platinum. The solutions were osmotically of tenth normal concentrations. In the investigation of copper cobalti cyanide as a possible membrane for the measurement of osmotic pressure two cells, Co_1 and Co_4 were used. Both cells were new, that is no membrane had been previously deposited in them. Since the preparing of these cells for the deposition of the membrane, and later the deposition of the membrane, was not carried simultaneously the history of each of the two cells will be given seperately.

EXPERIMENTAL PART.

Cell Co_1

The preliminary work of preparing cell Co_1 for the deposition of the copper cobalti cyanide membrane was commenced on Jan. 9. The cell was first allowed to soak in a .005 normal

lithium sulphate solution for a few hours. On Jan. 10 the cell was subjected to the action of the current for two hours. During this time 32cc of the liquid passed through the cell wall. The resistance rose from 5,250 ohms to 35,000 ohms, during this time. The cell was then soaked some days in water. After which it was placed, on Jan. 17-18, in distilled water and the electrolysis continued, with frequent renewal of the distilled water. When the electrolyte had been completely removed from the cell it was considered to be ready for the deposition of the membrane. The resistance at the beginning of the deposition was 18,181 ohms. This however soon dropped to 6,644 ohms, but during the next hour and a half it rose slowly to 12,500 ohms. The subsequent conduct of the cell is given in the table below. It is to be understood that whenever the deposition of the membrane was suspended it was placed in soak in a solution of thymol.

Jan.	25	10.25 A.M.- 12.47 P.M.	maximum	resistance	17,000	ohms.
		2.20 P.M.- 4.40P.M.	"	"	19,833	"
	26	10.37 A.M.- 12.15 P.M.	"	"	24,777	"
	27	10.45 A.M.- 12.46 P.M.	"	"	24,333	"
	28	1o.25 A.M.- 12.40 P.M.	"	"	27,630	"
	30	10.05 A.M.- 12.35 P.M.	"	"	30,790	"
		2.40 P.M.- 4.44 P.M.	"	"	33,428	"
	31	10.20 A.M.- 12.45 P.M.	"	"	37, 666	"
		2.13 P.M.- 4.44 P.M.	"	"	38,000	"
Feb.	1	10.17 A.M.- 12.44 P.M.	"	"	44,170	"
		2.15 P.M.- 4.36 P.M.	"	"	47.200	"
	2	9.58 A.M.- 12.43 P.M.	"	"	47,500	"
	3	10.07 A.M.- 11.44 A.M.	"	"	46,660	"

Feb. 4	9.57 A.M.- 12.37 P.M.	maximum	resistance	46,500	ohms
6	3.10 P.M.- 4.30 P.M.	"	"	41,200	"
7	11.20 A.M.- 12.15 P.M.	"	"	46,000	"

When the above records were compared with those of the deposition of the copper ferro cyanide membrane it was seen that the conduct of these two membranes was quite similar.

Experiment I

Cell Co_1 was set up for the first measurement on Feb 7 at 4.15 P.M. A weight normal sugar solution being used. Also hundredth normal solutions of copper sulphate and potassium cobalti cyanide were used as membrane menders. The temperature was 15°. Its resistance was 46,000 ohms. At 9 P.M. the solution had developed an osmotic pressure of .769 atmospheres. The pressure continued to increase slowly but uniformly until 4.30 P.M. on Feb. 8 at which time the pressure was 1.71 atmospheres, which was the maximum pressure for this experiment. It then rose slowly and uniformly until the cell was taken down at 9 A.M. on Feb. 10. At this time the pressure was 1.28 atmospheres. The solution taken from the cell showed a decided loss in rotation, which of course indicated a dilution. Subsequently the membrane was reinforced on six successive days, namely, Feb. 13, 14, 15, 17, 18, 20 & 21 on which days the maximum pressures were 49,565 ohms, 41,429 ohms, 38,000 ohms, 49,130 ohms, 54,500 ohms, 50,000 ohms respectively. The total time utilized in the above mentioned membrane reinforcement was twenty-one hours.

Experiment II

Cell Co$_1$ was set up on Feb. 23 at 12.15 P.M. with a weight normal cane solution. The mercury in the manometer rose steadily until 9 P.M. when a pressure of 5.28 atmospheres was reached. At 10 A.M. the following morning it had fallen to 4.20 atmospheres, at 12.30 P.M. it was 3.93 atmospheres. At 5 P.M. it had again risen to 5.538 atmospheres but at 8 P.M. fell to 5.198 atmospheres. At 9.30 A.M. the following morning the pressure had risen to 7.52 atmospheres. From this time the pressure rose steadily until 5.00 P.M. Feb. 27 when it had reached 8.54 atmospheres. However the next morning at 10.00 A.M. the pressure developed was 8. 56 atmospheres. From this time the pressure rose steadily until 9.00 A.M. on Mar. 3 when it was 9.17 atmospheres. At 12.30 P.M. the same day it had fallen to 9.12 atmospheres. From this point the pressure still again increased until 12.30 Mar. 4 when it was 9.22 atmospheres. At 5.00 P.M. the pressure had fallen to 9.21 atmospheres. From this time the pressure gradually rose until 10.00 A.M. on Mar. 8 when the pressure was 9.697 atmospheres which was the maximum for this experiment. At this time the cell was taken down and soaked in a thymol solution for four days. On Mar. 12 the membrane was reinforced for a period of one and one half hours the maximum resistance being 26,219 ohms. On Mar. 13 the process was repeated this time developing a resistance of 21,800 ohms. The resistance of the cell on the following day after being subjected to the membrane forming process for a period of five hours was 34,062 ohms. The maximum resistance on Mar. 15 after the membrane had

been reinforced for a period of three hours was 29,460 ohms. Before the cell was set up on Mar. 24 the membrane was reinforced for a period of two hours the maximum resistance for that time being 37,667 ohms.

Experiment III

Cell Co_1 was set up Mar. 24 at 12.30 P.M. with a weight normal cane sugar solution. Also the usual solutions of membrane menders were used. At 9.00 A.M. on Mar. 25 there was an osmotic pressure of 1.39 atmospheres. The pressure increased gradually for twenty-four hours at which time it was 2.49 atmospheres. During the next twenty-four hours the pressure increased to 18.16 atmospheres. From this time 9.00 A.M. on Mar. 27 the pressure rose very gradually until Apr. 11 when it had reached 24.59 atmospheres, which was the maximum attained in this experiment. This pressure was maintained for two days when the cell was opened. The cell was then put to soak in a thymol solution of the usual concentration. In this experiment the pressure with one exception increased uniformly, and without a break in the membrane so far as could be observed, from the time that it was set up until it was taken down which was for a period of eighteen days. This is a decided contrast to the previous experiment in which the membrane broke at least six times in a period of eleven days, which indicates that the membrane was very much strengthened in the second case. When this cell was opened the solution was found to have lost decidedly in rotation, showing that the membrane had at some period leaked.

This was the last complete experiment with the Co_1 cell. It

was set up again after the usual soaking and reinforcing of the membrane, but when the pressure had reached about twenty-three atmospheres circumstances made the discontinuance of the experiment necessary.

Cell Co_4

As has already been noted cell Co_4 was also a new cell. The preliminary work of removing the air from the cell wall was carried out in the manner already described. This required approximately six hours, during which time 61c c of the lithium sulphate solution passed through the cell wall and the resistance rose from 3,562 ohms to 56,000 ohms. Several hours were required to completely remove the electrolyte from the cell.

On Feb. 8 the deposition of the copper cobalticyanide membrane in cell Co_4 was commenced. A brief history of this process can be best given in the form of a table, which will contain simply a statement of the length of the period of deposition and the maximum resistance obtained during that period.

Feb	8	11.00 A.M.- 12.42 P.M.	maximum	resistance	22,400	ohms.
		2.40 P.M.- 4.43 P.M.	"	"	34,000	"
	9	1o.35 A.M.- 12.40 P.M.	"	"	65,294	"
	10	11.00 A.M.- 12.20 P.M.	"	"	80,000	"
	11	10.50 A.M.- 12.45 P.M.	"	"	98,333	"
	13	10.14 A.M.- 12.20 P.M.	"	"	162,857	"
		2.50 P.M.- 4.40 P.M.	"	"	162,857	"

Feb. 14	10.19 A.M.- 12.37 P.M.	maximum resistance	145,000 ohms
	2.27 P.M.- 4.42 P.M.	" "	145,000 "
15	10.50 A.M.- 11.40 A.M.	" "	114,000 "

It will be noticed on comparing the above records with those for cell Co_1 that the resistance rose much faster in the latter case than in the former. The explanation for this may perhaps be that there was a difference in the porosity of the cell walls. However later work showed the membranes in both cells to be quite satisfactory.

Experiment I

Cell Co_4 was set up Feb. 15 at 12.00 M. with a weight normal sugar solution, the temperature being 15°. The final resistance of the membrane was 114,000 ohms. The mercury in the manometer, so far as it was observed, rose continuously. At 9 P.M. the solution had developed a pressure of 5.95 atmospheres. The following morning at 9 A.M. it was 7.01 atmospheres, which was the maximum developed during this experiment. After this time the pressure fell slowly for forty-eight hours at which time the cell was opened, the pressure then being 3.60 atmospheres. The cell was then soaked in thymol solution for two days, after which the membrane was reinforced on three successive days. The maximum resistances obtained were 15,571 ohms, 13,750 ohms, & 110,000 ohms respectively.

Experiment II

Cell Co_4 was set up on Feb 23 at 12.15 P.M. with a weight normal sugar solution. The final resistance of the

of the membrane was 110,000 ohms. At 9 P.M. the membrane had developed a pressure of 5.323 atmospheres. The pressure at 10.00 A.M. the following day had dropped to 3.15 atmospheres. Subsequently it rose gradually for forty eight hours at the expiration of which time it was 12.10 atmospheres. The pressure then fell to 11.84 atmospheres, after which it rose again very uniformly for eleven days to 20.64 atmospheres. The cell was then taken down and placed to soak in the usual thymol solution. The solution taken from the cell was somewhat diluted as shown by its loss in rotation. After the membrane had been soaked in the thymol solution for a period of three days it was reinforced in the usual manner on four successive days, the maximum resistances for these periods being 66,875 ohms, 90,835 ohms, 109,000 ohms & 109,000 ohms respectively.

Experiment III

Cell Co_4 was set up Mar.15 with a weight normal sugar solution. The resistance of the membrane being 109,000 ohms. The pressure developed at 8 P.M. was 1.17 atmospheres. The following morning at 9 A.M. the pressure had risen to 8.32 atmospheres. During the next three hours it increased to 12.60 atmospheres. At 5.00 P.M. the pressure was 17.23 atmospheres. From this time the pressure rose uniformly for eight days, at the end of which time it was 25.29 atmospheres. After it had remained practically constant at that point for three days the cell was taken down and placed in a thymol solution. After the cell had soaked in the thymol solutionfor two days the membrane was again reinforced at three seperate periods the total time of which was three and a half hours. During this

time the maximum resistance obtained was 95,833 ohms.

Experiment IV

On Apr. 20 at 12.00 M. cell Co_4 was set up for the fouth time with weight normal cane sugar solution. At first the pressure rose slowly being at 10.00 A.M. the following morning only 1.04 atmospheres.. Seven hours later it was only 1.50 atmospheres. During the following day the pressure rose from 3.69 atmospheres at 9.00 A.M. to 6.87 atmospheres at 5 P.M. However during the following night it rose from a pressure of 6.87 atmospheres to one of 24.02 atmospheres. During the two days following it rose slowly but uniformly to 26.516 atmospheres. This being the maximum pressure obtained during the experiment. Also it was the maximum pressure obtained during the investigation of the copper cobalti cyanide membrane. The pressure obtained from a large number of experiments with other membranes, at this temperature and concentration of solution, has been shown to be 27.223 atmospheres The solution taken from the cell showed some loss in rotation. The leakage of the membrane probably occured during the early part of the experiment when the increase in the osmotic pressure was very slow.

Conclusions.

In this investigation of the copper cobalticyanide membrane it has been shown that although it is not as active at first, as the nickel ferro cyanide membrane, it however promises to be very satisfactory. This membrane appears to be quite similar in its behavior to the copper ferrocyanide membrane. In the initial deposition of both membranes it has

been found that the rise in resistance of the membrane is very much slower than in the case of zinc and nickel ferro cyanides. However this rise, in the case of both the cobalti and ferro cyanides of copper is very uniform. Also this membrane like that of the copper ferro cyanide when set up for the first measurements failed to give very high pressures. However both membranes have been shown to give higher and higher pressures on each succeeding time of setting up for a measurement.

Since the results obtained with the copper cobalti cyanide membrane during this investigation have proved so promising it is to be expected that it will be found useful in the exact measurement of osmotic pressure. It is to be regretted that it was necessary to suspend temporarily the investigation of the membrane. However the investigation will soon be resumed. It was to be expected in the light of the past experiments that one or two further reinforcements of the membrane would put it in good condition for the accurate measurement of osmotic pressure.

REMOVAL of MEMBRANES:

After membranes have been reinforced many times and have been in use from twelve to eighteen months the membranes become thickened to such an extent that water passes through them very slowly at ordinary temperature and a measurement of osmotic pressure therefore requires a very long time. For the same reason these old cells are peculiarly subject to what is

known as "thermometer and barometer " effects. Such membranes become more active at higher temperatures and can still be used at the higher temperatures with advantage. It is nevertheless highly desirable that these membranes be removed and substituted by new and more active ones. One great disadvantage of the use of cells with thick and too slow membranes is the fact that when used, they monopolize for long periods the rather limited bath space.

Previously, the cells containing membranes in this condition were discarded except for high temperatures, since attempts to remove them and substitute other membranes had not been wholly successful. At first it was attempted to remove these membranes by dissolving with mineral acids. Later ammonia, an ammoniacal solution of tartaric acid, and a solution of Rochelle salts were employed as solvents. Still later the membrane was removed by electrolysis in the presence of tartaric acid. But in all cases the new membrane which was substituted for the older one was found to be defective. The reason for this could not be ascertained. It was suggested however that the openings of the pores into which it is necessary for the membranes to root themselves for support, had in some way become modified by the reagents so that the membranes no longer were so firmly attached to the cell wall as ~~it is~~ in new cells. In view of this explanation it was suggested that perhaps success could be attained by mechanically grinding away a portion of the inner surface of the cell wall,on which the membrane is

located.

To accomplish this a small high speed emery wheel mounted on a mandrel was used. At intervals the grinding was discontinued and the interior of the cell carefully examined by means of a two volt lamp, which was so mounted as to allow it to be introduced to the very bottom of the cell. After it appeared that the membrane had been removed from every part of the interior, the grinding was discontinued and the cells placed to soak in distilled water.

When it had been shown that the zinc ferro cyanide membrane was valueless as a medium for the measurement of osmotic pressure the two cells in which that membrane had been deposited were treated in the manner described above. After the cells had been soaked for a time in distilled water they were subjected to endosmose with a .005 normal lithium sulphate solution to remove the air, as well as any particles which may have gotten into the pores of the cell wall during the grinding. With this treatment the platinum electrode on the interior of the cell became darkened due to a deposition of zinc and the exterior of the cell became colored blue, due probably to complex cyanogen compounds. This showed that there were still roots of the membrane in the cell wall. Consequently the zinc was dissolved from the electrod by nitric acid. The lithium sulphate solution was renewed and the current again turned on, this time passing in the reverse direction so that the zinc ion was carried to the exterior of the cell and at the same time the ferro cyanogen

ion was carried to the interior. The endosmose with the lithium sulphate solution was continued as long as there was any deposition of zinc on the exterior electrode. When this point was reached it was considered that the last traces of the zinc ferro cyanide membrane had been removed.

Since the nickel ferrocyanide membrane had given very satisfactory results it was thought best to deposit this membrane in these cells and thus to test their efficiency. The nickel ferrocyanide membranes were deposited and developed in these cells in the manner already described. When sufficient membrane had been deposited and the resistance of the cells had reached a maximum they were set up for measurements. A complete record of the results obtained with this membrane has been given under the discussion of the zinc ferro cyanide membrane. The results there recorded leave no doubt that the old membranes may be successfully dealt with in the manner described.

BIOGRAPHICAL.

The author was born at Walpole N.H. July 19, 1884. His early education was received in the public schools of his native town. In September 1902 he entered Dartmouth College, from which he graduated in 1906, with the degree of Bachelor of Science. The following year he was instructor of chemistry at the University of Maine. At the close of 1907 he was appointed instructor of chemistry at Massachusetts Agricultural College, where he remained one year. In the fall of 1908 he entered the graduate department of Johns Hopkins University making chemistry his principal subject, and physical chemistry and mineralogy first and second subordinate subjects, respectively.

In the year 1909 - 10 he was assistant to Dr Gilpin and in the year 1910 - 11 assistant to Professor Renouf.