HISTORY AND DEVELOPMENT OF THE DEPOSITION OF COPPER FERROCYANIDE MEMBRANE BY THE ELECTRO-LYTIC METHOD, A DISSERTATION

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DISSERTATION

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History and Development of the Deposition of Copper Ferrocyanide Membrane by the Electrolytic Method.

It is quite unnecessary, in giving an historical account of the work done on semipermeable membranes, to mention more than briefly, the work and investigations of Pfeffer, the theoretical conclusions of van't Hoff founded upon Pfeffer's determinations, the results of Tammann, Hamburger, and De Vries, men working upon van't Hoff's brilliant conclusions. Such were the investigations and conclusions which showed the scientific world the great importance of the subject with which we are now dealing. Notwithstanding the almost insurmountable difficulties of the work, later progress has corresponded to these brilliant beginnings.

No work comparable to that of Pfeffer's has ever been done, following the methods of this investigator, but a new method has come to the front, replaced an old one, given results which are in a class by themselves for accuracy and originality of determination. This practical method of membrane deposition and its application to the work was devised by Morse and Horn, improved upon by Morse and his later co-workers. To them, we owe the first ideas of electrolytic deposition of the semipermeable membrane in the walls of a porous cup.

In the original article of Morse and Horn, they state the object they had in mind in the following words: "It occurred to the authors that if a solution of copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current is passed from an electrode in the former to another electrode in the latter solution, the copper and the ferrocyanogen ions must meet in the interior of the wall and separate as copper ferrocyanide at all the points of meeting, so that in the end there should be built up a continuous membrane well supported on either side by the material of the wall." Such were the first conceived ideas in the progress of the methods of membrane formation.

The first problem which confronted the efforts of this early work was a method of effectively removing the air from the porous cups which, in themselves, furnished but a poor means of supporting the copper ferrocyanide membrane. The purpose of removing the air from the walls of the cell is obviously to overcome the interference in the formation of a sound and homogeneous membrane. The investigators made use of the strong endosmose which appears, when a current is passed through a porous wall, separating two liquid substances. The Morse-Horn method of removing the air from the walls of these porous cups, consisted in the use of a boiled solution of potassium sulphate containing about five-tenths of a gram of salt in a liter of water. This sulphate solution is placed both in the interior of the porous cup and in the jar in which the cup sits. On passing the current between the electrodes in the direction of the electrode within, the liquid in the cup rises with a sufficient rapidity to increase with the dilution of the solution and with the intensity of the current. As the liquid is carried along by the electric current, the air is bodily swept along with the water to the interior of the cell and thence out of the siphon.

The electrodes used for this work are platinum. The inner electrode is fastened to the platinum wire which passes through the rubber stopper. This rubber stopper contains a funnel which admits solution to the interior of the cell and a side tube which serves as an outlet and part of the siphon. As this endosmose takes place, it is found that water and air pass through very rapidly at first. The sulphate is added to the jar occasionally, and the electrolysis is continued until about three hundred cc. of the sulphate has passed out through the siphon. This is found to be sufficient to remove all air that may have been included within the walls of the cell. According to this method, the cells were then placed in a large volume of distilled water to remove the salt that had accumulated in the walls of the cell.

"To form the membrane, the wet cup was placed in a beaker and surrounded with an electrode of sheet copper, which completely encircled it. The other electrode—the one within the cup—was of platinum. After fixing the electrodes and connecting with a dynamo, so that the current should begin to flow the instant the liquids touched the opposite walls of the cup, the copper solution ($N/10$ or $N/5$ sulphate) and that of potassium ferrocyanide ($N/10$ or $N/5$) were introduced as nearly simultaneously as possible. At first, there is considerable endosmose in the direction of the current, *i. e.*, from the copper solution into that of the ferrocyanide, but no copper has ever been found to enter the cup, neither have any of the ferrocyanogen ions made their way into the copper solution. The resistance usually rises quite rapidly, reaching in extreme cases three thousand ohms within an hour, while the endosmose decreases correspondingly. The most rapid rise in resistance is observed in the less porous, hard burned cells. In softer and more porous ones, the resistance may not exceed two hundred to three hundred ohms within an hour; and after a time, in such cases, the resistance begins to fall, owing, apparently, to the action of the accumulated alkali upon the membrane. If the solution of ferrocyanide in the cell is then replaced by a fresh one, the resistance begins to rise again." Such were the observations of Morse and Horn in their original paper.

In the earlier work it was regarded improbable that the osmotic pressure of concentrated solutions could be measured because a *satisfactory* membrane could not be deposited by electrolysis. The difficulty which manifested itself was in the fact that the walls of the cell may contain cavities of such size as to interfere with the best results of membrane formation, in that it is necessary for a "key" to attach the membrane to and then to pack sufficiently a membrane of considerable volume, attached only at a few points. During this stage of the investigation it was found that the walls of the cell must be very compact to start with, then this cell should be burned so that it was very hard. A cell of close texture, however, is found to be an essential feature for a cell of good quality.

Having thus obtained a cell of this character, the next step is to prepare it for the membrane-forming process. The method, formerly employed, consisted in passing a solution of potassium sulphate through the cell and then by endosmose, allowing water to remove any accumulated salt from the walls of the cell. This endosmose is continued until the liquid conducts the current very poorly. The cell is now ready for membrane deposition. To deposit the membrane, the following procedure is employed: A long platinum rod, which serves as the cathode, is lowered into the cell, and a cylinder of copper in copper sulphate solution is used as the anode. Into the cell, there is inserted a siphon, which reaches nearly to the bottom of the cup. The purpose of this siphon is to remove the liquid from time to time in order to prevent the accumulation of alkali, which is believed to be injurious to the membrane. For this deposition, an $N/10$ ferrocyanide solution and an $N/10$ copper sulphate solution are introduced into the cup, the former being placed in the interior of the cup, the latter being placed in the jar in which the cup rests. During the process of actual measurement, potassium ferrocyanide and $CuSO_4$ are used in the solutions for the purpose of mending the momentary ruptures in the membrane, caused by the increasing pressure.

Up to this time, membranes of copper ferrocyanide had received most attention, but at this stage of the work further research in regard to membranes was carried on. It was now found that the electrolytic method is well adapted to the deposition upon or within the walls of a cell of nearly every kind of precipitate which can be formed from electrolytes in solution. The ferrocyanides of tin, zinc, cadmium, manganese and uranyl; phosphates of the iron (trivalent), copper, and uranyl; hydroxides of aluminium and iron (trivalent); cobalti cyanides of cobalt, nickel, iron (bivalent), copper, zinc, cadmium, and manganese were shown to manifest