Journal of the Minnesota Academy of Science

Volume 19 | Number 1 Article 12

4-1951

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Recommended Citation

Wyman, M. E. (1951). Diffusion Through a Membrane. *Journal of the Minnesota Academy of Science, Vol. 19 No.1*, 27-35.
Retrieved from https://digitalcommons.morris.umn.edu/jmas/vol19/iss1/12

Physical Science Section

DIFFUSION THROUGH A MEMBRANE

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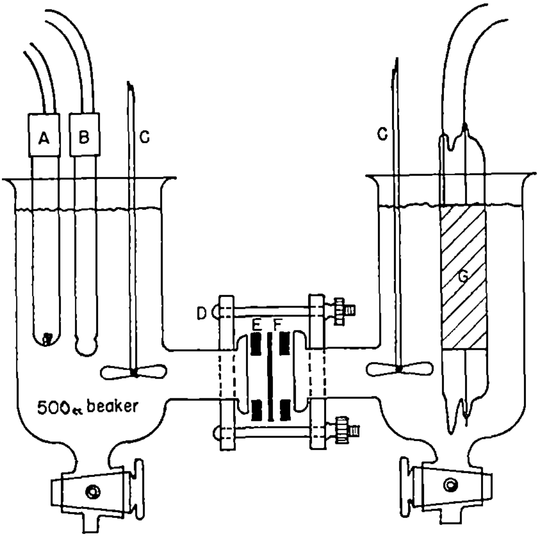
One of the most basic problems in the study of a physiological system is that of the mechanism by which material crosses the membranes involved in the system. One can realize this problem's significance when one understands that our whole human system grew from one cell to its present structure by the passage of materials across cell walls. In the hope that this phenomenon would be more easily describable when one understands more quantitatively the process of a diffusion through a non-living membrane, I have made some measurements on the passage of material through collodion membranes.

The general problem of diffusion is described by Fick's law, generally written as $dn = DA\frac{dc}{dx}dt$. In the case of diffusion through a membrane (measuring it as I have done) one can simplify this relationship somewhat. By stirring the solutions on the two sides of the membrane the concentration gradient remains constant through the membrane. If the one side is essentially zero concentration and the area of the membrane and thickness are constant the amount transported per unit of time becomes proportional to the diffusion coefficient times concentration. By using identical volumes of solution on both sides of the membrane the quantity of material transported can be measured as an increase in concentration, and by taking a ratio, the coefficient is measured as the fraction transported per unit of time.

This coefficient, for the case where one does not have a membrane, remains essentially constant for solutions of small dilution. In these results the transport rate was measured as the per cent transported per minute, which then becomes essentially the diffusion coefficient describing the movement of material across a membrane.

The use of radioactive tracers facilitates this problem greatly, since it permits one to work with extremely dilute solutions with accuracies obtainable by chemical means only in region of high concentration. Figure 1 represents the system used.

The material chosen for the analysis of transport was phosphoric acid, which is convenient because of the availability of the radioactive isotope phosphorus 32 which emits β's. The radioactive material, which is in the form of phosphoric acid, is mixed with the phosphoric acid on the one side of the membrane. The geiger coun-



A. Calomel electrode
B. Glass electrode
C. Stirrers
D. Clamps
E. Soft rubber gasket
F. Membrane
G. Geiger counter

DIFFUSION APPARATUS

Figure 1

ter, which is immersed in the solution on the other side of the membrane, then records the concentration of activity which has arrived on that side. By measuring the activity with the geiger counter as a function of the time, one obtains a linear increase in the activity as the time proceeds. The slope of this curve is directly proportional to the transport rate across the membrane.

If one measures the transport rate in such a fashion for a number of different concentrations of phosphoric acid moving into essentially zero concentration, the graph which is shown in Figure 2 is obtained. With a membrane the coefficient describing the transport is not constant as it would be for a system lacking a membrane. In the low concentration region the ability of the membrane to allow material to move through it is considerably less than at higher concentration. The membrane appears to have an inhibitory property which diminishes as one moves to the higher concentration.

Phosphoric acid is not a completely simple system to use, in that its dissociation constant for the first hydrogen falls in this con-

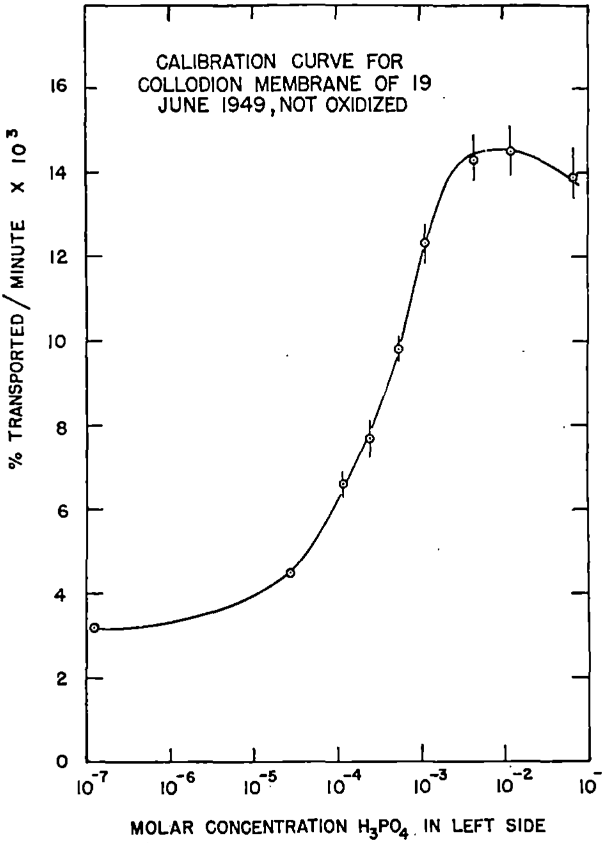


Figure 2

centration region so that in the region where the membrane inhibits the transport most, the phosphoric acid is essentially ionic, while in the region of concentration above 10^{-2}M the phosphoric acid is mostly molecular. One quick and simple explanation of the peculiar curve obtained for the transport rate versus concentration might be that the membrane has a constant diffusion coefficient describing the molecular transport and another (considerably smaller constant) describing the diffusion for the ionic transport. Figure 3 is a graph of the molecular composition of phosphoric acid as a function of concentration. Figure 4 shows the results obtained by calculation, using two different coefficients for molecules and ions. The shape of the curve is very similar to that obtained experimentally, but it is displaced to the higher concentration region by about a factor of 30 in concentration.

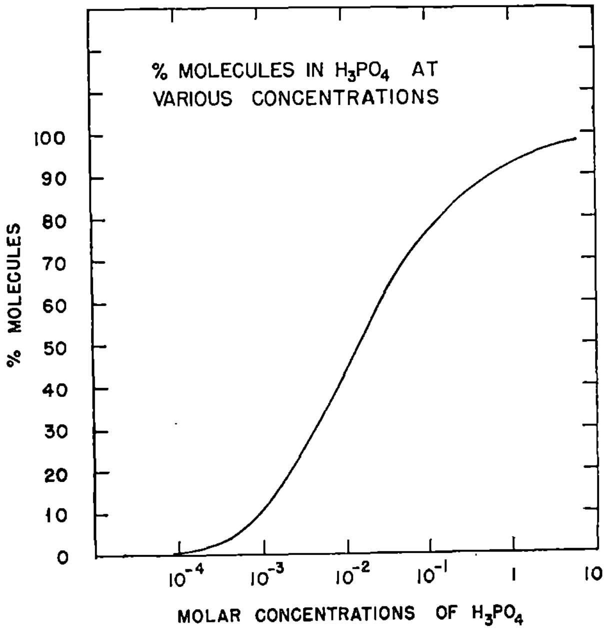


Figure 3

One might assume, quite possibly, that the dissociation constant for phosphoric acid was not correct. This would demand a correction factor in the dissociation constant so large that not even the most relaxed chemists would permit an alteration. By measuring the pH accurately and by running experiments influencing the transport rate with electric fields, I was able to conclude that the dissociation constant was correct and the peculiarities of the S-shaped curve obtained in the transport rate versus concentrations experiments must be due to other factors.

When the concentration of phosphoric acid is increased, the ionic strength of the solution increases even though the per cent of the solution which is ionic decreases. Figure 5 represents some experiments to test the influence of ionic strength on the transport rate. This was done by holding the phosphoric acid concentration constant and increasing the ionic strength by adding completely dissociated neutral salts such as sodium bromide or potassium chloride. It is apparent that the transport rate does increase with ionic strength, but not nearly as rapidly as it does for phosphoric acid. In a second series of experiments the ionic strength of the system was held constant but the acid concentration or pH was increased. Figure 6 represents a few such experiments. These are put

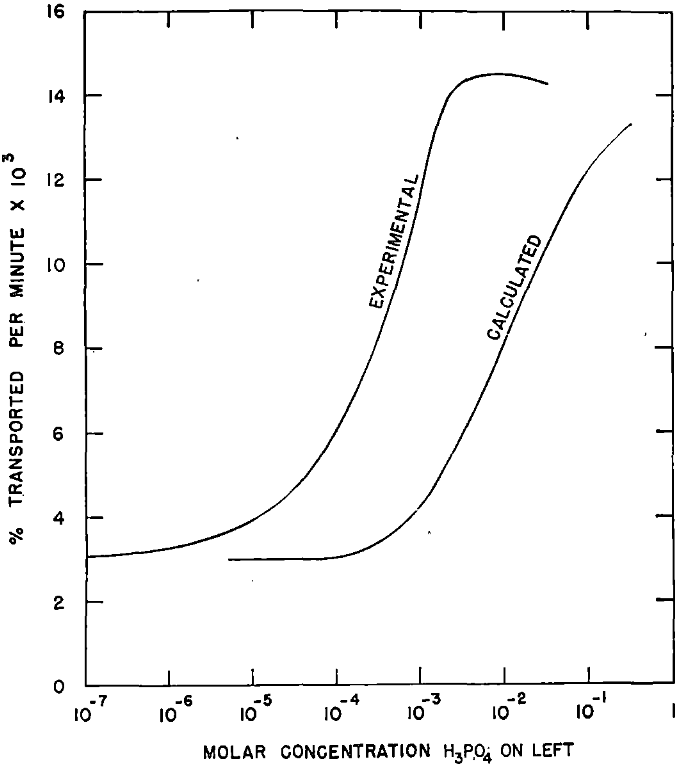


Figure 4

on an arbitrary scale and do not clearly show the complete analysis. A and B are for phosphoric acid alone, C for .02 ionic strength, and F is for an ionic strength of .1. It was true, however, that for any ionic strength used when the pH or acid concentration was great enough the same transport rate was obtained. A third type of experiment was performed in which a small concentration of phosphoric acid was used and the acid concentration was increased by adding hydrochloric acid. By this method the somewhat identical curves shown in Figure 7 were obtained whether the acid concentration was increased by phosphoric acid alone or by hydrochloric acid. From these experiments it may be concluded that there exists in the membrane a mechanism inhibitory to the transport of material and that the inhibitory mechanism is decreased by an increase in ionic strength (probably the cation concentration), but that it is diminished more easily by an increase in the hydrogen ion.

Figure 8 shows schematically a possible type of construction of the membrane. It may be thought of as a meshwork of obstruc-

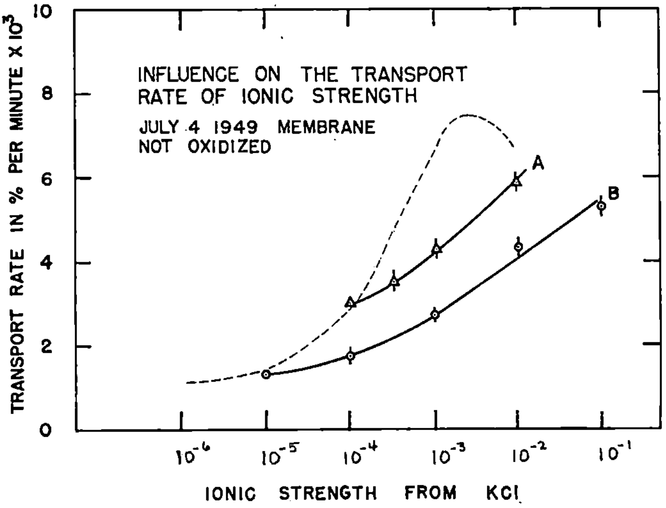


Figure 5

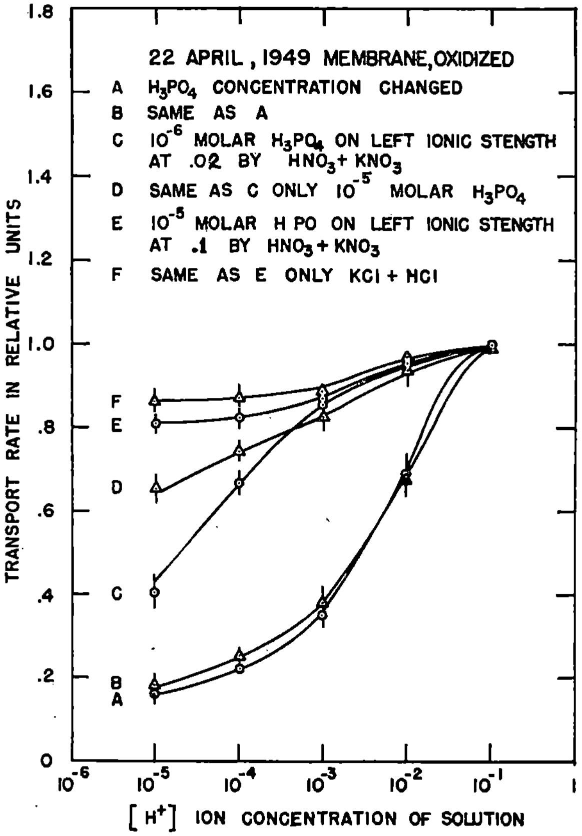


Figure 6

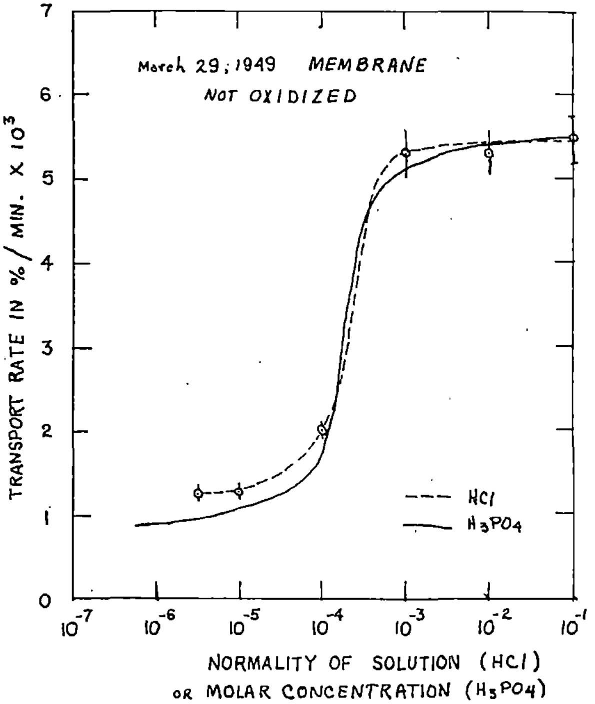


Figure 7

tions, having a large number of pores or passages through which materials can pass. One can conceive of the inhibitory mechanism in the collodion membrane as being due to the fixation of anions on the pore walls. These fixed anions whose cations are in solutions may inhibit or stop the passage of a mobile anion from passing through that channel if the fixed anion is so situated that its repulsive influence extends across the pore spacing. When one conceives of transport with this type of a membrane, one must envision a large number of possible passageways, some of which are completely blocked for anion passage and some of which have no inhibitory property. As the concentrations are increased one might speculate that the increased number of cations are able to linger more easily near these fixed charges and thereby essentially shield the repelling effect of the fixed negative charges for the mobile anions, thereby allowing a greater transport rate. This shielding effect apparently is more easily accomplished by hydrogen cations than by the sodium or potassium cations.

It is possible to give these membranes a greater inhibiting property by affixing more of these negative ions on the pore walls. This

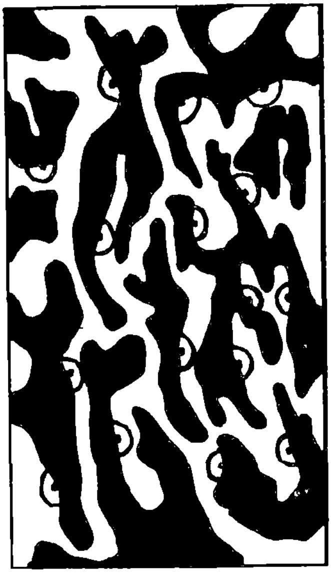


Figure 8

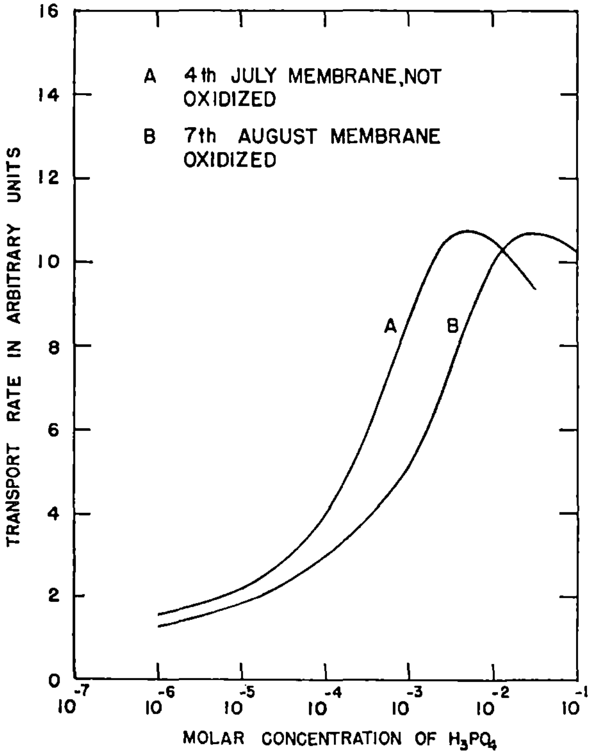


Figure 9

is accomplished by soaking the membranes in sodium hypobromide, the longer the period of time the greater the inhibiting ability of the membrane. If our former hypothesis of shielding of these fixed anions is true one would assume that the diminishing of the inhibiting process would take a higher ionic strength to accomplish the task. Figure 9 shows the results of measuring the transport rate as a function of concentration of phosphoric acid of two membranes, one of which had been oxidized rather strongly. It is observed that the loss of inhibiting property is indeed shifted to the higher concentration region.

The foregoing work was done at the University of Illinois. The studies are being continued at St. Olaf College.

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A PRELIMINARY REPORT ON AN APPARATUS FOR DETERMINING THE THERMO-CONDUCTIVITY OF UNDISTURBED SOIL

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VISUAL FATIGUE AND ILLUMINATION

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Condensation published in Transact. Amer. Acad. Opthalmol. and Otolaryngol., Suppl., Jan.-Feb. 1951.

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X-RAY ABSORPTION METHODS FOR STUDIES ON CELLS

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ABSTRACT

From the pioneering work of Engström at the Karolinska Institute, Stockholm, it is now possible to apply the absorption of monochromatic X-radiation to the quantitative determination of all elements of biological importance, other than hydrogen, in morphological units down to one micron in diameter. A recent modification