The rate of penetration of water into the sea urchin egg was calculated (1) from the data of Lucke and McCutcheon to be about $1 \times 10^{-5}$ cc. per hour per sq. cm. membrane per mm. Hg pressure. This figure is of the same order of magnitude as that found for permeable collodion membranes, but since the egg membrane is probably at most only a thousandth as thick as the collodion it is evident that, for the same thickness of membrane, the egg membrane is very much less permeable to water than the collodion. It seemed possible therefore that if a collodion membrane could be made having per unit thickness approximately the same permeability to water as the egg membrane that it would also have the semipermeability characteristic of the egg membrane. Collodion membranes prepared in the ordinary way by placing in water before drying completely are very much more permeable than the egg membranes, whereas the same membranes when completely dried become practically impermeable. Many attempts have been made in this laboratory to obtain a membrane having an intermediate permeability by changing the length of time of drying etc., but it has always been found that there is a sudden transition from a membrane permeable to most electrolytes to one that was impermeable to water. It occurred to the writer that the desired permeability might be secured by making very thin membranes. This was done by pouring U.S.P. collodion into small test-tubes, inverting the test-tubes at once and allowing them to dry in this position for 48 hours. In most cases the membrane pulls away from the glass at the end of this time and may be easily removed. Such membranes were found to be about 2 to 3μ thick, and were strong enough to work
with. Their permeability was tested by filling with 2 M NaCl and
immersing in 1 M AgNO₃. Membranes showing any precipitate of
silver chloride were discarded. In most cases the precipitate could
be seen to be due to the presence of holes in the membrane, but in the
case of some membranes thin enough to show diffraction fringes the
salt appeared to diffuse through.

The permeability for various solutions was then determined by
placing 1 cc. of the solution in the membrane fastened to the end of a
glass tube and suspending the membrane in 25 cc. of water. The
amount of solute which had diffused through was determined by analy-
sis after varying lengths of time, usually 24 hours. In the case of
water the increase in volume of the solution was noted, or, for the
water vapor determination, the loss in weight of a membrane contain-
ing a small amount of water suspended in a desiccator. The permea-
ability to gases was determined by measuring the rate of flow of the gas
through the dry membrane under a measured pressure. The general
equation for the passage of a substance through such a system may be
written

\[
\frac{dv}{dt} = \frac{CSP}{h},
\]

where \(v\) is the amount of substance diffusing, \(S\) is the surface, \(h\) the
thickness, and \(P\) the pressure or concentration difference on the two
sides of the membrane. The equation would have different forms
depending on the mechanism assumed for the passage through the
membrane, but for comparative purposes may be used in the general
form. If the measurements are made before more than a small per-
cent of the substance has passed through the membrane, \(P\) may be
considered constant and the equation used in the differential form,
i.e.

\[
\frac{C}{h} = \frac{\Delta v}{\Delta tSP_o}.
\]

In the present experiments \(v\) has been expressed in moles, \(t\) in hours,
and \(S\) in sq. cm. \(P\) has been used as the vapor pressure in atmospheres
in the case of gases or as the diffusion pressure in atmospheres in the
case of dissolved substances. (This has been assumed proportional to
the concentration and to be equal to 22.4 atmospheres per mole per
### TABLE I.

**Rate of Diffusion of Substances Through Collodion Membranes.**

<table>
<thead>
<tr>
<th>Substance System measured and concentration etc.</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O vapor</th>
<th>dry air</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles hr.⁻¹ at.⁻¹ sq. cm.⁻¹ × 10³</td>
<td>100 (O.P.)</td>
<td>&lt;1 (D.P.)</td>
<td>10,000 (V.P.)</td>
<td>&gt;40 (D.P.)</td>
<td>10,000 (V.P.)</td>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>3 × 10³(V.P.)</td>
<td>20 × 10³(V.P.)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance System measured and concentration etc.</th>
<th>H₂</th>
<th>H₂S</th>
<th>O₂</th>
<th>N₂</th>
<th>air</th>
<th>HCOOH</th>
<th>CH₂COOH</th>
<th>CH₂CICOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles hr.⁻¹ at.⁻¹ sq. cm.⁻¹ × 10³</td>
<td>300</td>
<td>300</td>
<td>70</td>
<td>&lt;1</td>
<td>50</td>
<td>6</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance System measured and concentration etc.</th>
<th>CH₃CH₂COOH</th>
<th>CH₃COOH</th>
<th>Butyric acid</th>
<th>(CH₃)₂CO</th>
<th>HCHO</th>
<th>C₆H₆OH</th>
<th>Br⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles hr.⁻¹ at.⁻¹ sq. cm.⁻¹ × 10³</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2.5</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance System measured and concentration etc.</th>
<th>H⁺</th>
<th>Urea</th>
<th>(NH₄)₂CO₃</th>
<th>NaHCO₃</th>
<th>HgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles hr.⁻¹ at.⁻¹ sq. cm.⁻¹ × 10³</td>
<td>2</td>
<td>about 1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The following substances were tested in m/10 solution, where possible, and found to pass at less than 10⁻⁸ moles per hour per atmosphere diffusion pressure per sq. cm.: Lactic acid, glycine, oxalic, succinic, sugar, glycerine, HCl, H₂SO₄, H₂O₂, HBr, NaCl, KCl, KI, NH₄Cl, AlCl₃, FeCl₃, CuCl₂, SnCl₄, CaCl₂, Na₂S, NaOH, LiOH, KOH, Ba(OH)₂, Ca(OH)₂, and the following ammonium salts: -CrO₄, -citrate, -SO₄, -salsicylate, -Br, -Cl, -oxalate, -nitrate, -tartrate, -molybdate.

O.P. = per atmosphere osmotic pressure.
V.P. = " vapor "
D.P. = " diffusion "

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Permeability of Colloid Membranes

In the case of water the rate may be expressed either per atmosphere vapor pressure or per atmosphere osmotic pressure. The results therefore are in terms of moles per hour per atmosphere per sq. cm. membrane surface. All experiments were carried on at about 25°C. The figures are the average of 6 to 8 determinations. The variation in the membranes is considerable and the figures are significant only as to the order of magnitude.

The results of the experiments are summarized in Table I in which the substances have been arranged approximately in the order of their permeability. The membrane is permeable to water, ammonia, HCl gas, much less so to CO₂, O₂, and H₂ and to weak acids, whereas it is practically impermeable to salts, strong acids and bases, and sugar and glycerine. The permeability in a general way resembles that found for living cells by Osterhout (2), Lillie (3), and others. The results are qualitatively the same as those of Collander (4) and Fujita (5). The value for water, 1 × 10⁻⁶ moles hr⁻¹, sq. cm⁻¹, at.⁻¹ may be compared to 3 × 10⁻⁴, which is the approximate figure for the permeability of the sea urchin egg in the same units. Since these membranes are still probably several hundred times thicker than the egg membrane the permeability per unit thickness is probably of about the same order of magnitude. The permeability to NH₄OH, acetone, etc., is not due to an effect on the membrane, since no chloride ion passes when NaCl is present in the solution during the experiment. Alkali stronger than about .01 m destroys the semipermeability, as do concentrated solutions of alcohol, acetone, acetic acid, etc. The results with gases show that they do not pass through holes in the membrane, since the rate of effusion would then be inversely proportional to the square root of the density and hydrogen would pass most rapidly; whereas the experiments show that a number of gases pass much more rapidly than hydrogen. The membrane therefore in the case of gases cannot be considered as a sieve. It is evidently more nearly analogous to a rubber membrane than to a porous plate. The same conclusion is brought out by the fact that immersing the membrane in water has no effect on the rate of passage of the gas. When the membrane is immersed any pores would be filled with water and the rate of passage of the gas would therefore be changed if it flowed through pores in the dry membrane. Taken as a whole, the results
indicate that the substance dissolves in and then diffuses through the membrane. The rate of passage will therefore be determined by the diffusion coefficient of the substance in collodion and by its solubility in collodion, since the latter property fixes the concentration gradient in the membrane. In general, diffusion coefficients differ much less for various substances than solubilities so that the solubility is probably the more important factor.

SUMMARY.

Dry thin collodion membranes have been prepared which are permeable to water, ammonia, weak acids of low molecular weight, HCl gas, O₂, CO₂, and H₂S, but are impermeable to strong electrolytes and substances of high molecular weight. The permeability to gases does not depend on the density, so that the gases do not pass through pores in the membrane.

BIBLIOGRAPHY.