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Absorption of Water by Films of Cellophane and Polyvinyl Alcohol

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The absorption of water and dehydration of these films is found to obey a diffusion equation by means of which a diffusivity may be defined. This is not a constant but depends on the water concentration in the foils. A rapid change in water content immediately after changing the ambient conditions suggests the presence of adsorbed surface layers. The total absorption is found to increase faster than the relative humidity.

INTRODUCTION

FOR experiments on scattering of high energy protons by hydrogen carried out by the authors at Princeton University in 1941 it was decided to use pure Cellophane as a scattering foil. In order to obtain the absolute value of the scattering cross section it was necessary to know accurately the percentage of hydrogen by weight in the foils. Very pure Cellophane was prepared for us by Dr. Nelson Allen of the Cellophane Analytical Research Division of DuPont. This eliminated the uncertainty due to small amounts of glycerine usually added to this material. However the Cellophane was found to absorb amounts of water depending upon the relative

humidity of the atmosphere and it was necessary to understand this phenomenon quantitatively in order to know the true hydrogen content of the material.

METHOD AND RESULTS

Disks of the foil $\frac{1}{2}$ " in diameter (1.27 cm^2 in area) were punched with a special tool from a sheet placed between clean paper. These were handled with tweezers and weighed in a quartz fiber microbalance built along the lines of that described by Strong¹ and put in a chamber which could be evacuated.

The rate of dehydration of the foil in vacuum was investigated as well as the rate at which it picked up water again when air of a known relative humidity was re-admitted to the balance

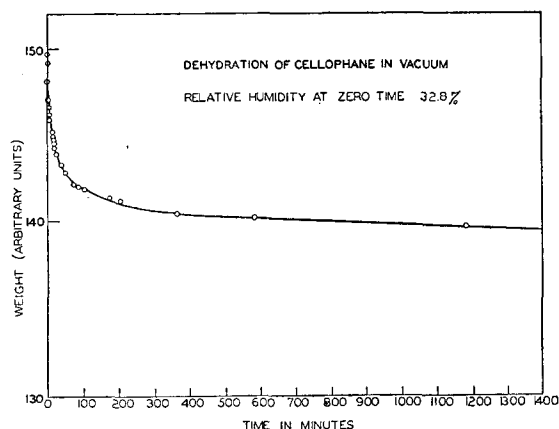


FIG. 1. Weight of $\frac{1}{2}$ " diameter Cellophane foil .0005" thick as a function of time it was left in vacuum after having been initially in equilibrium with air of relative humidity 32.8 percent.

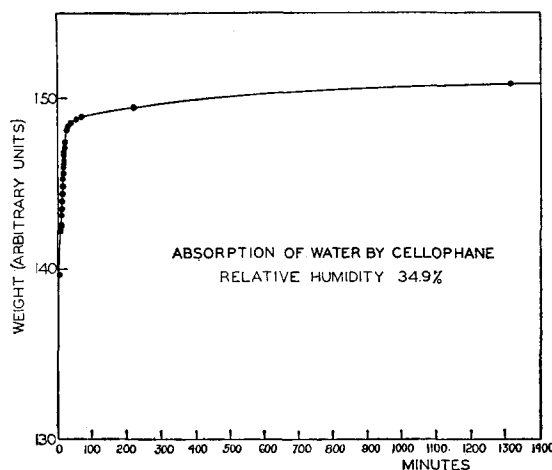


FIG. 2. Weight of Cellophane foil as a function of time after having been immersed in air of relative humidity 34.9 percent. Foil was initially in vacuum.

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*** This work was done in 1940 but not published because of war work.

¹Strong, *Procedures in Experimental Physics* (Prentice-Hall, Inc., New York, 1942), p. 215.

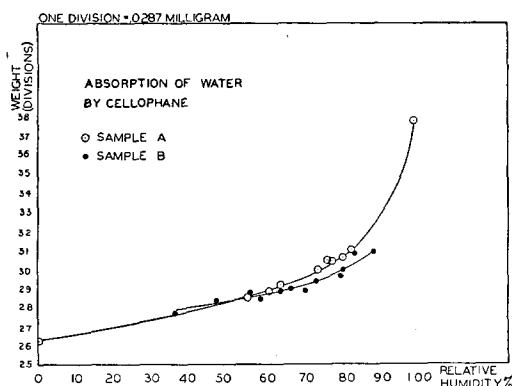


FIG. 3. Weight of .0001" Cellophane foils in equilibrium with air of various relative humidities.

chamber. Relative humidities were measured with a sling hygrometer.

Figure 1 shows the weight of a Cellophane foil about .0005 inch thick as a function of the time it was left in the evacuated chamber after having been initially in equilibrium with air at 32.8 percent relative humidity at approximately 30°C. The total loss in weight after 20 hours when the weight had become constant was 0.264 mg or 0.208 mg per square centimeter.

Figure 2 shows the weight of the Cellophane as a function of time after air of relative humidity 34.9 percent had been admitted to the chamber. In this case the total gain in weight was larger than the initial loss as expected since the air was now of higher relative humidity.

Figure 3 shows the weight of two different samples of Cellophane about 0.0001 inch thick as a function of relative humidity of the air with which they are in equilibrium. For these thinner foils equilibrium was reached in about two hours. Only one reading was taken in a day allowing sufficient time for the foil to reach a steady state at the particular value of the humidity which existed. The point at 100 percent was taken by placing a dish of water inside the balance chamber and sealing it up. In this case the weight gain was 0.336 mg.

Figure 4 shows the weight loss in vacuum of polyvinyl alcohol film type B after standing in air of relative humidity 57.5 percent and the regain of weight when the air was re-admitted. Weight change was 0.217 mg.

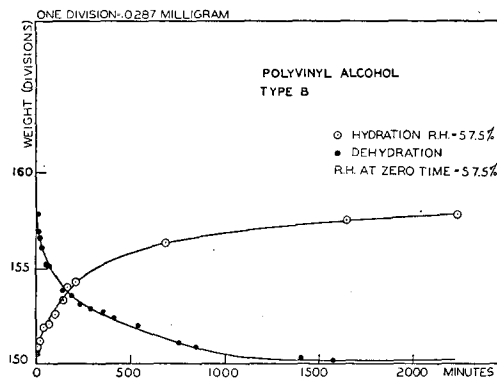


FIG. 4. Weight of $\frac{1}{2}$ " diameter foil of polyvinyl alcohol type B during dehydration, and hydration, in air of relative humidity 57.5 percent.

DISCUSSION²

The diffusion of moisture into and out of the foil might be expected to follow the equation

$$h^2(d^2M/dx^2) = dM/dt, \quad (1)$$

where M is the concentration of water in the foil in grams per cm^3 , x is measured along the thickness of the foil, t is the time, and h^2 is the diffusivity. Since the diameter of the foil is large compared to the thickness, it may be treated as an infinite slab. The boundary conditions for the case of dehydration when the foil whose surfaces are in the planes $x=0$ and $x=L$, is placed in vacuum, are as follows:

$$\begin{aligned} M &= M_0, & 0 < x < L & \text{ for } t=0, \\ M &= 0, & x=0 & \text{ or } L, & \text{ for all } t, \end{aligned} \quad (2)$$

the general solution of Eq. (1),³

$$M = A \exp(-h^2\gamma^2 t) \begin{pmatrix} \sin \gamma x \\ \cos \gamma x \end{pmatrix} \quad (3)$$

then becomes:

$$M = M_0 - \sum_{n=0}^{\infty} \frac{1}{2n+1} \exp \left[- \left\{ \frac{h^2\pi^2(2n+1)^2}{L^2} \right\} t \right] \times \sin \pi x \left[\frac{(2n+1)}{L} \right], \quad (4)$$

to fit the boundary conditions for dehydration.

² For an excellent general discussion of this problem see R. M. Barrer, *Diffusion in and through Solids* (Cambridge University Press, New York, 1941).

³ Ingersoll and Zobel, *Mathematical Theory of Heat Conduction* (Ginn and Company, 1913), p. 105.

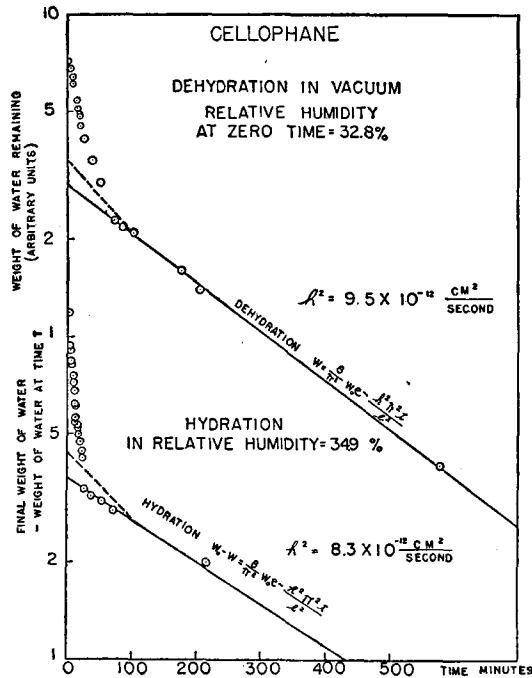


FIG. 5. Semi-logarithmic plots of weight of Cellophane foil during dehydration in vacuum and rehydration in air. The diffusivities, h^2 , are computed from the straight parts of the curves at times greater than 50 minutes. The ordinate of the lower curve is the final weight of water (after many hours) minus the weight of water at the time indicated by the abscissa. This number is larger than the corresponding ordinate for the upper curve because the final weight corresponds to 34.9 percent relative humidity rather than 32.8 percent which was the initial value in the case of dehydration.

For the case when moist air is again let into the chamber around the dry foil, the boundary conditions are

$$\begin{aligned} M &= M_0, \quad x=0 \text{ or } L, \quad \text{for all } t, \\ M &= 0, \quad 0 < x < L, \quad \text{for } t=0. \end{aligned} \quad (5)$$

The solution then is

$$\begin{aligned} M &= M_0 \left\{ 1 - \sum_{n=0}^{\infty} \frac{1}{2n+1} \right. \\ &\quad \times \exp \left[-\frac{h^2 \pi^2 t (2n+1)^2}{L^2} \right] \sin \frac{\pi x (2n+1)}{L} \left. \right\}. \end{aligned} \quad (6)$$

For comparison with the experiment we wish to know the total amount of moisture in the foil at any time or

$$W = \text{area} \cdot \int_0^L M dx. \quad (7)$$

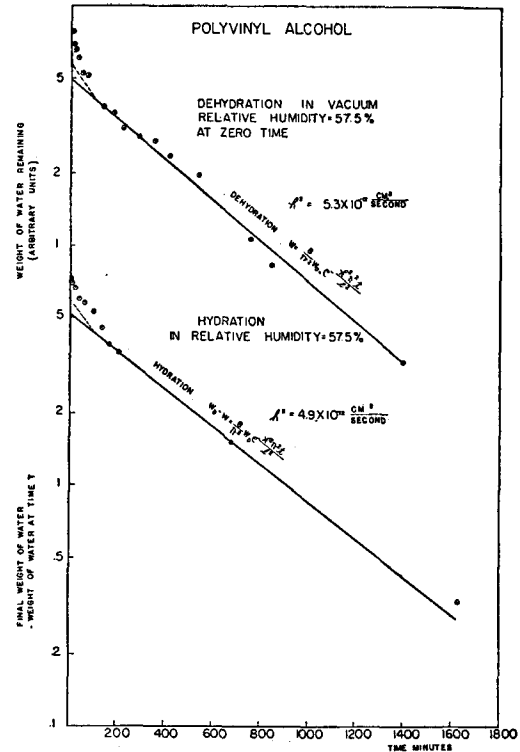


FIG. 6. Semi-logarithmic plots of weight of polyvinyl alcohol films during dehydration and hydration. The diffusivities, h^2 , are computed from the straight parts of the curves at times greater than 100 minutes. The lower curve shows the final weight of water (after many hours), minus the weight at the time indicated by the abscissa.

For the case of dehydration this is, integrating Eq. (4) term by term,

$$\begin{aligned} W &= W_0 \sum_{n=0}^{\infty} \frac{8}{\pi^2} \\ &\quad \times \left\{ \exp \left[-\frac{h^2 \pi^2 t (2n+1)^2}{L^2} \right] \frac{1}{(2n+1)^2} \right\} \end{aligned} \quad (8)$$

where W_0 is the initial total weight of moisture.

For dehydration, integrating Eq. (6) gives

$$\begin{aligned} W &= W_0 \left(1 - \sum_{n=0}^{\infty} \frac{8}{\pi^2} \right. \\ &\quad \times \exp \left[-\frac{h^2 \pi^2 t (2n+1)^2}{L^2} \right] \frac{1}{(2n+1)^2} \left. \right). \end{aligned} \quad (9)$$

For large values of time t , terms with $n > 0$ may be neglected and the diffusivity h^2 may be found from the slope of the experimental plot of

$\log W$ against time. The terms with $n > 0$ are important only for $t < \sim 100$ minutes. Thus the ratio of the second term to the first term for the case of Cellophane for various times is as follows:

T (min.)	Second term
	First term
0	1/9
50	0.023
100	0.005

The first term is 81 percent of the total sum even at $t=0$. An approximation to the theoretical curve may thus be made using only the first term of the series for $t > 100$ minutes and increasing this by 19 percent $\times (1-t/100)$ for $t > \sim 100$. This gives too large a value to the sum for $t < \sim 100$ except at $t=0$. This correction is shown by the dotted lines in Figs. 5 and 6.

It is seen from the semi-logarithmic plots that (1) a single exponential term gives a good fit to the data for $t > \sim 50$ minutes for Cellophane and for $t > \sim 100$ minutes for polyvinyl alcohol; (2) increasing the single term by 19 percent $\times (1-t/100)$ to correct for all the remaining terms at values of $t > 100$ (theoretically too large a correction except for $t=0$) does not give values on the dehydration curve as large as the experimental ones at small t .

The second fact noted above has led us to conclude (a) the diffusivity h^2 of water in these substances is not a constant but increases as the water content increases and (b) there is water absorbed on the surface of the foil in layers 100 or more molecules thick. This can account for part of the large deviation of the experimental data from straight exponential plots in the case of dehydration. Another effect noticed was that the weight gain when the foil is in equilibrium with air of various relative humidities is not linear but increases faster than the relative humidity. This is in agreement with the hypothesis of Peirce⁴ of alpha- and beta-water in

cotton where alpha-water is chemically combined and beta-water is condensed at high relative humidity in spaces between the hexose units where it is held by capillary forces.

That the increase of diffusivity with water content cannot be the only effect is shown by the hydration curves Figs. 5 and 6 where $\log (W_0 - W)$ has been plotted. At small t these curves also are seen to deviate upward from the theoretical lines even though in this case the water content is increasing with time so the diffusivity should initially be small if the above conclusion is true. This deviation we believe to be caused by surface absorption. To account for the observed differences between the extrapolated dotted lines and the observed weight at $t=0$, about 100 molecular layers would be required in the case of polyvinyl alcohol and about 2000 in the case of Cellophane, assuming the true surface area to be just the geometric value for a smooth disk. Actually the effective surface may be much larger due to irregularities of the order of molecular dimensions. Schiff⁵ has shown that adsorbed surface layers of the order of 100 molecules thick can be accounted for by Van der Waals' forces in the special case of helium II.

The opposite effect, namely initial rapid evaporation of absorbed surface water in the case of dehydration would tend to make those curves too steep initially, so the effect of the change of h^2 is less pronounced than at first apparent from the initial part of dehydration curves. The real change of h^2 should tend to make the average slope of the hydration curves steeper than that of the dehydration curves at times from 100 to 500 minutes, since the foil is dryer in the case of dehydration and the average diffusivity will be smaller. This effect is apparently smaller than the accuracy of the data resulting from the subtraction required to obtain the hydration curves (Figs. 5 and 6).

⁴ Peirce, J. Text. Inst. (T) 20, 133 (1929).

⁵ L. I. Schiff, Phys. Rev. 59, 839 (1941).