

## Effect of Water on Permeation, Diffusion, and Solution of Gases in Cellophane

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### Synopsis

The laminate method for studying the permeability and diffusivity of moistened cellophane to gases is described and the humidity dependence of the transport parameters for H<sub>2</sub>, He, and Ne is presented. In the relative humidity region of about 0% to 60%, a small increase in the permeability was observed, which is caused by a comparatively small increase in the diffusivity owing to the plasticizing effect of sorbed water and a decrease in the solubility. On the other hand, an extremely large increase in the permeability observed in the relative humidity region above 60% is mainly based on the diffusion coefficient of gas enhanced by the swelling effect of sorbed water. The presence of a minimum in the solubility–relative humidity curves has been confirmed and is discussed.

### INTRODUCTION

It is well known that the permeation rate for gases through cellophane is accelerated by the presence of water vapor. It has been reported by many workers<sup>1-4</sup> that the permeabilities to oxygen, nitrogen, and carbon dioxide increase several hundred times or more as the relative humidity increases from zero to saturation.

In order to investigate the water effect on the permeability of cellophane to gases, it has been recommended by Notley<sup>4</sup> and Stannett<sup>5</sup> to use a laminate composed of cellophane and hydrophobic polymer film such as polyethylene. In their studies, however, measurements were limited only to the steady state of gas permeation or a condition under which a concentration gradient of sorbed water existed in cellophane. Therefore, permeability, diffusivity, and solubility of cellophane in equilibrium with the given relative humidity had not yet been obtained.

In this paper, we will describe an improved laminate method to determine the permeability and diffusion coefficients of gases in cellophane which is approximately in equilibrium with the given relative humidity, and discuss the mechanism of the water effect on the basis of the experimental results for H<sub>2</sub>, He, and Ne as penetrant gases.

### PRINCIPLE OF THE EXPERIMENT

Consider a laminate 12 composed of lamina 1 and lamina 2, and a flow of water vapor from the side of lamina 1 having higher permeability into the side of lamina 2 having lower permeability to water vapor.

After a steady state of water vapor flow was reached in which the concentration of sorbed water remained constant at all points of laminate 12, the distribution of the concentration can be expressed by eq. (1):

$$p_0 - p_2 = \frac{\bar{P}_2}{l_2} \left( \frac{l_1}{\bar{P}_1} + \frac{l_2}{\bar{P}_2} \right) (p_1 - p_2) \quad (1)$$

where  $\bar{P}_1$ ,  $\bar{P}_2$ , and  $l_1$ ,  $l_2$  are the permeabilities to water vapor and the thicknesses of lamina 1 and lamina 2, respectively;  $p_0$  and  $p_2$  are the pressures of water vapor on both sides of laminate 12; and  $p_1$  is the pressure of water vapor in the gap between two laminae. It is obvious from eq. (1) that, under the condition of  $l_1/\bar{P}_1 \ll l_2/\bar{P}_2$ , lamina 1 is practically in equilibrium with the given pressure  $p_0$ , as shown schematically in Figure 1.

If the time-lag measurement for a penetrant gas is carried out under the conditions stated above and the permeability and diffusivity of lamina 2 are not influenced by the presence of water vapor, the permeability and diffusivity of lamina 1 in equilibrium with  $p_0$  can be evaluated by following methods.

The permeability coefficient  $P_{12}$  of gas in lamina 12 is obtained from the slope of the linear portion of the time-lag curve measured.  $P_{12}$  is related to the permeability coefficient  $P_1$  in lamina 1 and the permeability coefficient  $P_2$  in lamina 2 by the following well-known equation:

$$\frac{l_1 + l_2}{P_{12}} = \frac{l_1}{P_1} + \frac{l_2}{P_2} \quad (2)$$

If the gap between two laminae is small enough to be neglected, laminate 12 may be regarded as a simple two-layer laminate. According to the theoretical treatments of the time lag for gas diffusion in multiple laminates,<sup>6,7</sup> the time lag  $\theta_{12}$  for such a two-layer laminate is given by

$$\theta_{12} = \frac{\frac{l_1^2}{D_1} \left( \frac{l_1}{6P_1} + \frac{l_2}{2P_2} \right) + \frac{l_2^2}{D_2} \left( \frac{l_1}{2P_1} + \frac{l_2}{6P_2} \right)}{\frac{l_1}{P_1} + \frac{l_2}{P_2}} \quad (3)$$

In this treatment, it has been postulated that the gas diffusivity of each lamina is independent of its gas concentration, and Henry's law governs the distribution

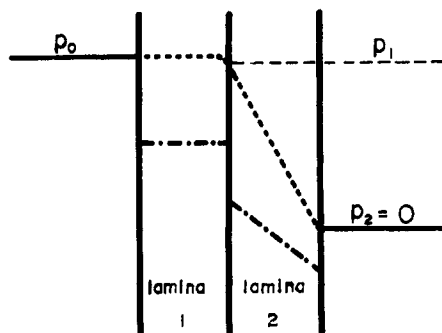


Fig. 1. Schematic diagram of concentration distribution of sorbed water in a laminate: (—) water vapor pressure given; (---) pressure gradient of water vapor in a laminate assumed to be equilibrated with sorbed water; (- · - ·) concentration gradient of sorbed water in a laminate.

of gas between laminae. Hence,  $P_1$  and  $D_1$  at various values of  $p_0$  can be calculated by introducing the measured values  $P_{12}$  and  $\theta_{12}$  into eqs. (2) and (3), if  $P_2$ ,  $D_2$ ,  $l_1$ , and  $l_2$  are previously known. And the solubility coefficient  $S_1$  of gas in moistened lamina 1 is determined by

$$P_1 = D_1 \cdot S_1 \quad (4)$$

## EXPERIMENTAL

### Materials

The cellophane examined as lamina 1 was cut from a sheet of uncoated cellophane manufactured by Tokyo Cellophane Co. Ltd., which contained about 10% plasticizer by weight. The plasticizer consists mainly of glycerin and a small amount of urea. The thickness of the sheet was  $2 \times 10^{-3}$  cm.

A low-density polyethylene film was used as lamina 2 whose thickness was  $4 \times 10^{-3}$  cm.

Hydrogen, helium, and neon were used as penetrant gases. Gas purity exceeded 99.999% for hydrogen and 99.99% for the others.

### Apparatus and Procedure

The experimental apparatus is shown in Figure 2. A permeation cell was placed in a constant-temperature bath ( $25.0^\circ \pm 0.1^\circ\text{C}$ ). The cell, with a mercury seal to protect the films from contact with the bath water, consisted of two compartments separated by a cellophane sheet placed on top of a polyethylene film, as shown in Figure 3. One compartment facing the cellophane was connected to the high-pressure (gas-feed) system of the apparatus, and the other compartment facing the polyethylene film was connected to the low-pressure (gas-measuring) system of the apparatus. These films, hereafter simply called a laminate, were pressed with two porous metal disks attached to each compartment to eliminate a gap between the two films.

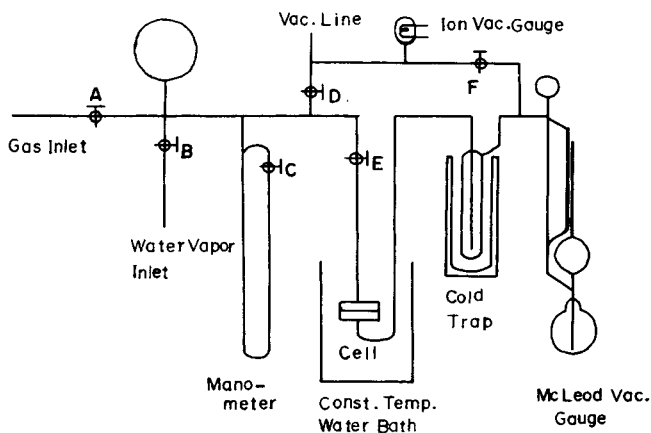


Fig. 2. Schematic diagram of permeation apparatus.

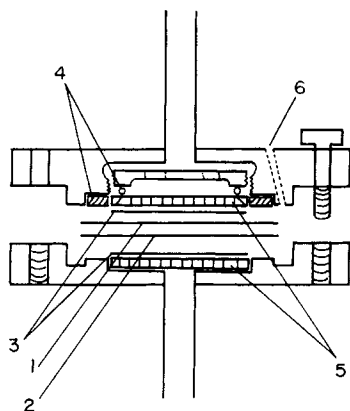


Fig. 3. Permeation cell: (1) cellophane; (2) polyethylene film; (3) filter paper; (4) rubber gasket; (5) porous metal disk; (6) mercury inlet.

Before a series of time-lag measurements at various relative humidities, the whole apparatus with the test laminate in place was evacuated at  $65^{\circ}\text{C}$  to less than  $10^{-5}$  mmHg for a few days in order to remove sorbed water from the laminate.

After the temperature of the bath was lowered and maintained at  $25.0^{\circ}\text{C}$  for a few hours, valve D was closed and water vapor was vaporized slowly from the water vapor inlet into the high-pressure system of the apparatus until a desired pressure was attained.

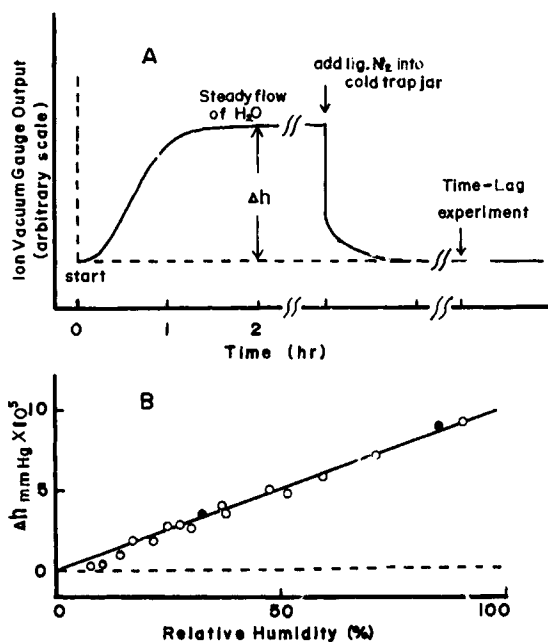


Fig. 4. (A) Typical ion vacuum gauge trace for water vapor flow through the laminate at 65% R.H. (B) Plot of water vapor pressure ( $\Delta h$ ) inside the vacuum line at steady flow of water vapor vs. relative humidity (R.H.): (O) laminate; (●) polyethylene film.

The permeation rate of water vapor through the laminate was monitored by an ion vacuum gauge (ULVAC, Model GI-TL) attached to the vacuum line. After steady-state water vapor permeation was reached, liquid nitrogen was added to the cold-trap jar to eliminate an increase in pressure caused by the permeated water vapor (Fig. 4).

Then, valve F was closed, valve A was opened in order to introduce the penetrant gas into the high-pressure system of the apparatus, and its pressure and the time were recorded. The pressure of the permeated gas in the low-pressure system of the apparatus was measured by a McLeod vacuum gauge.

Before each run was repeated at various relative humidities, the whole apparatus was always evacuated at the experimental temperature for not less than 2 hr.

The sorption isotherm of the cellophane was obtained by the gravity method using a sensitive quartz spring balance at  $25.0^\circ \pm 0.5^\circ\text{C}$ .

## RESULTS AND DISCUSSION

Typical time-lag curves for hydrogen permeation through the laminate are shown in Figure 5. The slopes of linear portions and the time lags of these curves are apparently dependent on the given relative humidity. In the determinations of the time lags  $\theta_{\text{exp}}$  and the slopes of linear portions, all time-lag curves were corrected by subtracting a small increase in pressure caused by the inevitable

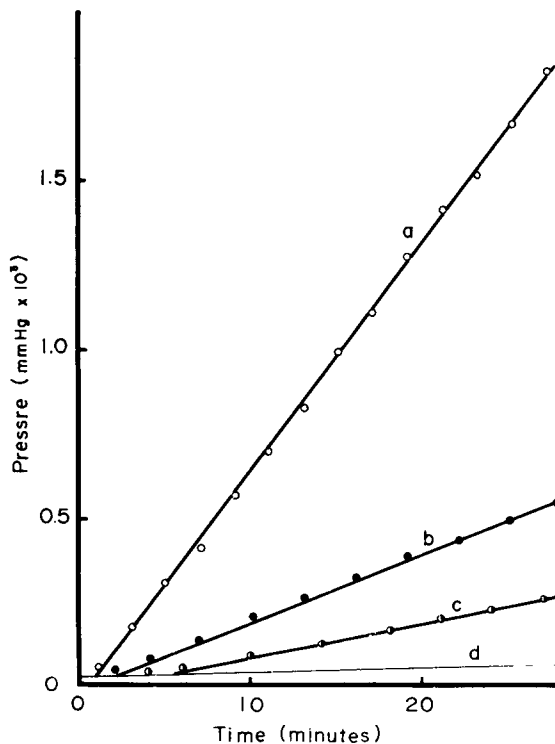


Fig. 5. Typical time-lag curves for  $\text{H}_2$ : (a) at 61% R.H.,  $P^{\text{H}_2} = 31.6$  cm Hg; (b) at 38% R.H.,  $P^{\text{H}_2} = 39.4$  cm Hg; (c) at 20% R.H.,  $P^{\text{H}_2} = 45.3$  cm Hg; (d) gas leakage of low-pressure system of the apparatus.

TABLE I  
Transport Parameters of the Dry Films at 25.0°C

Film	Cellophane			Polyethylene		
Thickness	$2 \times 10^{-3}$ cm			$4 \times 10^{-3}$ cm		
Penetrant gas	H <sub>2</sub>	He	Ne	H <sub>2</sub>	He	Ne
Permeability coefficient, cm <sup>3</sup> (S.T.P.)·cm/cm <sup>2</sup> ·sec·cm Hg	$1.6 \times 10^{-13}$ 2.8 <sup>a</sup>	8.6 12.1 <sup>a</sup>	0.17 0.27 <sup>a</sup>	$8.1 \times 10^{-10}$	5.3	1.9
Diffusion coefficient, cm <sup>2</sup> /sec	$1.1 \times 10^{-9}$	6.7	0.33	$1.2 \times 10^{-6}$	6.5 <sup>b</sup>	0.33
Solubility coefficient, cm <sup>3</sup> (S.T.P.)/cm <sup>3</sup> ·cm Hg	$1.5 \times 10^{-4}$ 2.5 <sup>a</sup>	1.3 1.8 <sup>a</sup>	0.50 0.82 <sup>a</sup>	$6.8 \times 10^{-4}$	0.8 <sup>b</sup>	5.8

<sup>a</sup> Values measured after a series of the time-lag measurements at varying relative humidity.

<sup>b</sup> Average of literature values (Ref. 8).

gas leakage of the low-pressure system of the apparatus, as shown in Figure 5. Then, the permeability coefficients  $P_1$  and the diffusion coefficients  $D_1$  of gases in the cellophane at various relative humidities were calculated by introducing  $P_{12}$  and  $\theta_{\text{exp}}$  into eqs. (2) and (3). In this calculation, it is assumed that the permeability and diffusion coefficients in polyethylene film are not influenced

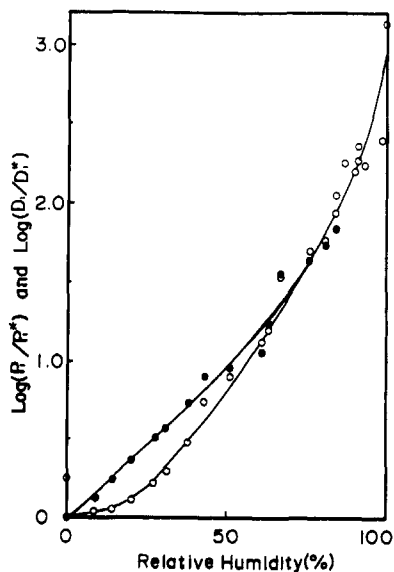


Fig. 6. Relative permeability and diffusivity of cellophane to H<sub>2</sub> as a function of relative humidity: (O) relative permeability; (●) relative diffusivity.

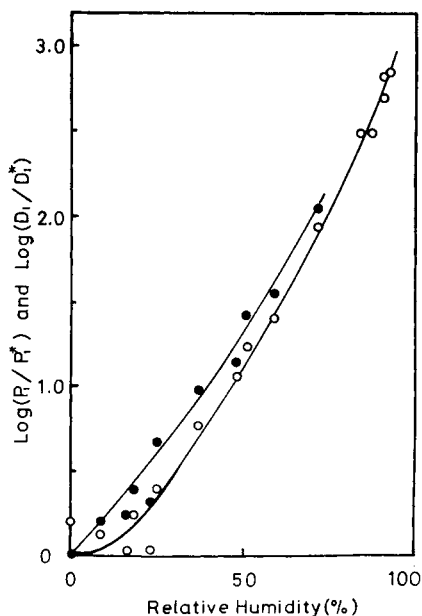


Fig. 7. Relative permeability and diffusivity of cellophane to Ne as a function of relative humidity: (○) relative permeability; (●) relative diffusivity.

by the presence of water vapor. The thickness  $l_1$  of the cellophane certainly varies with relative humidity, but the variation may be ignored for the purposes of this paper. Therefore, each value at 0% R.H. shown in Table I was used as  $P_2$ ,  $D_2$ ,  $l_1$ , and  $l_2$  at all relative humidities.

The results for  $H_2$ , He, and Ne are shown in Figures 6, 7, and 8. The ordinates represent, on a logarithmic scale, the relative permeability  $P_1/P_1^*$  and the relative

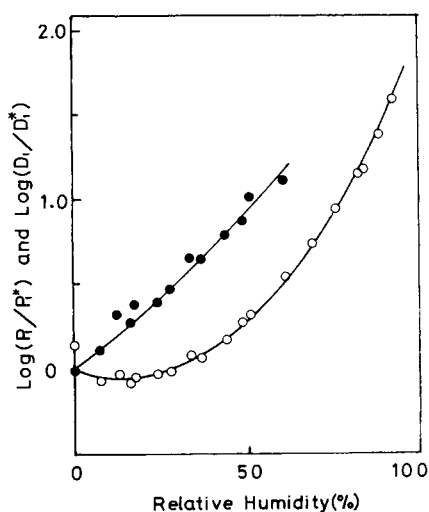


Fig. 8. Relative permeability and diffusivity of cellophane to He as a function of relative humidity: (○) relative permeability; (●) relative diffusivity.

diffusivity  $D_1/D_1^*$ , where  $P_1$  and  $D_1$  are the permeability and diffusion coefficients in the cellophane at a given relative humidity, and  $P_1^*$  and  $D_1^*$  are the coefficients at 0% R.H. The measured values of  $P_1^*$  and  $D_1^*$  for each gas are summarized in Table I. As shown in this table, the values of the permeability coefficients in the cellophane at 0% R.H. measured before were smaller than the values of the coefficients measured after the time-lag measurements at varying relative humidities above 70%. However, there was no change in the permeability at 0% R.H. after a series of the time-lag measurements at relative humidities below 70%. On the other hand, the diffusion coefficients at 0% R.H. remained constant in all cases. The variation in the permeability coefficient, therefore, is apparently based on that in the solubility. This will probably be caused by the microstructural changes of cellulose on water desorption of the highly moistened cellophane being mounted in the permeation cell. In this paper, the permeability and solubility coefficients in the cellophane at 0% R.H. measured before a series of the time-lag measurements at relative humidities above 70% were used as the standard values, i.e.,  $P_1^*$  and  $S_1^*$ , for convenience in all relative humidity region examined.

The effects of water vapor on the relative permeabilities, as shown in Figures 6, 7, and 8, are very similar to the effects obtained for  $O_2$  and  $CO_2$  by Pilar.<sup>1</sup> Although its effects on the relative diffusivities are analogous to its effects on the relative permeabilities, it is interesting to note that the increase in the relative diffusivities is larger than the increase in the relative permeabilities at low relative humidity, and that the slopes of these curves at high relative humidity have a tendency to come close to each other. The latter fact suggests that the increase in the permeability of the cellophane containing a large amount of sorbed water depends mainly on the increase in the diffusion coefficient.

The solubilities of gases in the cellophane containing various amount of sorbed water are calculated by eq. (4). In Figure 9, the relative solubilities  $S_1/S_1^*$  are plotted as a function of water content, which is based on the weight of the cellophane after evacuating to a constant weight at 65°C. Curves a, b, and c in Figure 9 correspond to three values of  $S_1$  which were calculated by use of three values of  $D_1$  obtained by the different ways of correction for evaluating it from  $\theta_{exp}$ . Values of  $D_1$  calculated directly by the relation  $D_1 = l_1^2/6\theta_{exp}$  are used for curve a, and values of  $D_1$  by eq. (3) for curve b. In the case of curve c, assuming the presence of a plane gap ( $l_3 = 10^{-4}$  cm and  $S_3 = 1/76$  cm<sup>3</sup>(S.T.P.)/cm<sup>3</sup>·cm Hg) between the cellophane and the polyethylene film, the correction for evaluation of  $D_1$  is done by eq. (5), which was derived from introducing the conditions  $l_3/P_3 \ll l_1/P_1, l_2/P_2$ , and  $D_3 \gg D_1, D_2$  into the theoretical expression for the time lag of a three-layer laminate obtained by Barrie et al.<sup>6</sup> and Ash et al.<sup>7</sup>:

$$\theta_{132} \simeq \theta_{12} + \frac{l_3 \cdot S_3}{(P_1/l_1) + (P_2/l_2)} \quad (5)$$

where the subscript 3 is used to denote lamina 3, i.e., the gap postulated above.

Coincidence of three solubility curves in the region of water content about 0 to 0.1 (about 0% to 50% R.H.) proves that the presence of the polyethylene film or the gap makes an extremely small contribution to  $\theta_{exp}$ , and that the solubility minimum on the curves is clearly attributable to the characteristics of the cellophane containing sorbed water.



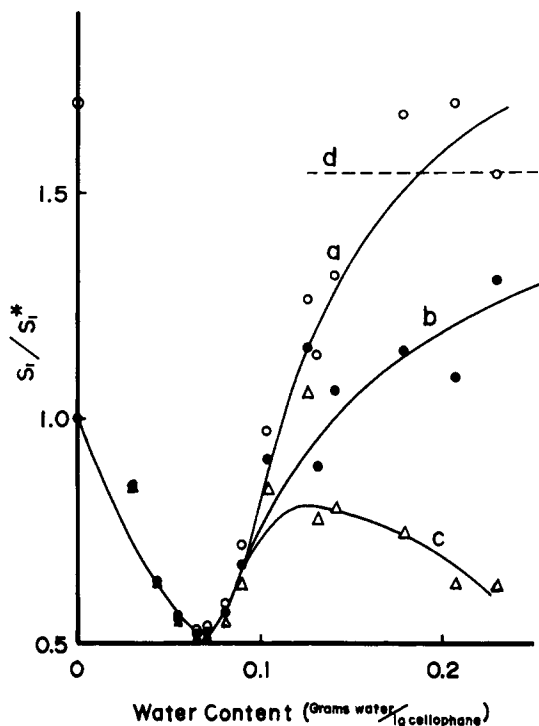


Fig. 9. Relative solubility of cellophane to  $H_2$  as a function of water content: (a) no laminate correction for  $D_1$ ; (b) laminate correction using eq. (3); (c) laminate and gap correction using eq. (4); (d) ratio of the hydrogen solubility of water to  $S_1^*$ .

On the other hand, it is undoubtedly owing to the presence of the polyethylene film or the gap that these solubility curves diverge in the region of water content above 0.1. The true solubility curve may be set between curve b and curve c, because the descent of curve c at high water content is considered to be caused by the assumption of the gap being too thick ( $l_3 = 10^{-4}$  cm), and  $S_1$  in curve b is slightly overestimated by neglecting an increase in thickness  $l_1$  with the swelling.

Results similar to Figure 9 were obtained for Ne. The diffusion coefficients of He at high relative humidity, however, were not determined because the time lags were too short to measure them accurately, and therefore the solubility minimum was not observed, but only suggested by the abrupt drop in the solubility at low relative humidity.

On the basis of the above experimental results, a mechanism of the water effect on the gas transport in cellophane may be proposed as follows.

The relatively small increase in the diffusivity at a small amount of sorbed water results from the weak stimulation of the segmental motion of cellulose which is commonly called the plasticizing effect of sorbed water. The reduction in the solubility is caused by the penetration of water into the microvoids or the matrixes of amorphous cellulose which supposedly make a relatively large contribution to the gas solubility. Such penetration of water into the empty spaces among the molecules has been suggested by previous studies of the density of moistened cellophane<sup>9</sup> and the sorption of vapors into cellulose.<sup>10</sup>

On the other hand, the water effect at a large amount of sorbed water is related to the swelling of amorphous cellulose. Namely, the swelling which greatly increases the segmental mobility serves to extremely increase the gas diffusivity, and the increase in the solubility may be due to the expansion of the matrixes of amorphous cellulose caused by the swelling.

Finally, it is necessary to discuss whether a concentration gradient of sorbed water exists in the cellophane or not. Under the condition that the evacuation rate of the oil diffusion pump has been much faster than the permeation rate of the water vapor, the water vapor pressure ( $\Delta h$ ) inside the vacuum line is considered to be approximately proportional to the permeation rate of water vapor through the laminate. Then, from Figure 4B it is obvious that the permeation rate of water vapor through the laminate increases linearly with the given relative humidity and is almost equal to the rate through the polyethylene film only in the relative humidity region above 20%. In this region, therefore, it can be concluded that the rate-determining step of water vapor permeation through the laminate is the permeation process through the polyethylene film of the laminate and that the cellophane is virtually in equilibrium with the given relative humidity. On the other hand, because of the deviation from the straight line in the relative humidity region below 20%, it can be presumed that the concentration gradient in the cellophane is not small enough to be neglected, that is, the cellophane is not in equilibrium with the given relative humidity. The latter fact, however, is in no essential contradiction to the mechanism of the water effect discussed above.

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