(calcd. S, 30.84). The low value is an indication of the instability of the salt.

S-Carbomethoxymethylthiosalicylic Acid.—Thiosalicylic acid (3.85 g., 25 millimoles) was treated with dilute alkali until a *p*H corresponding to the monosodium salt was obtained. Upon addition of 2.20 ml. (25 millimoles) of methyl chloroacetate, homogeneity was obtained almost instantly. Within twenty minutes (room temperature) a considerable amount of precipitate had formed which was filtered after forty minutes, dried and found to melt at 113–122°. Recrystallization from ethanol raised the melting point to 126–127°, in agreement with the established value.[11] The compound could be hydrolyzed with alkali to S-carboxymethylthiosalicylic acid, which, after one recrystallization from glacial acetic acid, melted at 208–213°.[12]

An analogous trial utilizing methyl fluoroacetate and thiosalicylic acid produced no precipitate after several hours standing at room temperature. The solution was boiled for one and one-half hours, cooled and filtered to yield a small amount of yellow solid, which, after three recrystallizations, melted at 281–284° and was thought to be the disulfide (dithiodisalicylic acid, m. p. 289°).[19]

Acidification of the original filtrate allowed nearly quantitative recovery of thiosalicylic acid.

***p*-Bromophenacyl Fluoroacetate.**—A water solution of sodium fluoroacetate and *p*-bromophenacyl bromide was refluxed according to the usual procedure[15a] resulting in the isolation of *p*-bromophenacyl fluoroacetate. Recrystallization from aqueous ethanol afforded white crystals, m. p. 96.5–97.0°.

Anal. Calcd. for $C_{10}H_8O_3BrF$: C, 43.67; H, 2.92. Found: C, 43.94; H, 3.05.

Reaction Products of Fluoroacetic Acid and *p*-Toluidine.—To 2 g. (20 millimoles) of sodium fluoroacetate was added 4.28 g. (40 millimoles) of recrystallized *p*-toluidine. Approximately 2 ml. (24 millimoles) of concentrated hydrochloric acid was added and the mixture was refluxed in a 20-cm. test-tube supported in an oil-bath at 140°. After two hours one ml. of benzene was added and heating continued for a few minutes until refluxing stopped and the reaction appeared complete.

The mixture was boiled briefly with 15 ml. of ethanol and then poured into 150 ml. of hot water. A brown oil separated immediately and turned granular upon agitation. The mixture (still hot) was filtered and the precipitate dried to yield 1.66 g. (6.5 millimoles) of impure *p*-toluinoacetyl-*p*-toluide. The filtrate was cooled in ice to yield white crystals which, after filtration and drying, yielded 1.15 g. (6.9 millimoles) of fluoroacetyl-*p*-toluide.

Both compounds had suitable solubility coefficients in aqueous ethanol or ligroin, but the latter seemed to purify them more effectively. Recrystallized repeatedly from ligroin (b. p. 87–95°), the mono- and disubstituted compounds melted at 129–130° and 136–137°, respectively. The mixed melting point was depressed some 20°.

Anal. Calcd. for $C_9H_{10}ONF$: C, 64.68; H, 6.03. Found: C, 64.81; H, 6.10. Calcd. for $C_{16}H_{18}ON_2$: C, 75.56; H, 7.13. Found: C, 75.81; H, 7.12.

Reaction of Fluoroethanol with Thiosulfate.—A rate measurement was attempted using methods described above for the analogous reaction with fluoroacetate. At 85°, an aqueous solution of fluoroethanol (1 ml., 17.3 millimoles) and thiosulfate (4.29 g., 17.3 millimoles) showed only 1% reaction after four and one-half hours, and 3.4% after twenty-one hours. The concentration of reactants was 346 mM and the total volume was 50 ml.

Reaction of Fluoroethanol with Hypoiodite.—Use of the standard techniques[15d] employed for the haloform test gave indication of a negative reaction. Addition of 1 ml. (17.3 millimoles) of fluoroethanol to 50 ml. of 0.876 *N* iodoform reagent (42.8 milli-equivalents) and 2 ml. of 10% sodium hydroxide caused a decrease in iodine titer of only 7% after five hours at 50–70°.

Summary

Methyl fluoroacetate is soluble to the extent of about 15% in cold water. It hydrolyses very slowly, only about 2.5% in sixty hours in distilled water. The hydrolysis is catalyzed by alkali to a much more marked degree than by acid.

The fluorine in fluoroacetates is remarkably inert, but was slowly displaced by thiosulfate to the extent of 50% in several hours at 88°.

The *p*-bromophenacyl ester and the *p*-toluide of fluoroacetic acid have been characterized.

Neither fluoroacetate nor fluoroethanol is attacked by dilute aqueous hypochlorite.

NOTRE DAME, INDIANA RECEIVED SEPTEMBER 12, 1946

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[19] Gattermann, *Ber.*, **32**, 1150 (1899).

[CONTRIBUTION NO. 215 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY, INC.]

Diffusion of Vapors in Films

BY PRINCE E. ROUSE, JR.

The permeation of vapors through films of organic polymers has considerable theoretical interest and is of great practical importance if the film is to be used as a protective wrapping. The interactions of vapors with organic materials have been investigated by measurements of permeation and of sorption, but there have been few studies of the diffusion coefficient of a vapor in a film. Since knowledge of the behavior of the diffusion coefficient should provide useful information concerning the nature of the association of the vapor with the film a method of investigating the dependence of the diffusion coefficient upon the concentration of the vapor in the film has been developed. This paper will describe this method and will present some typical results obtained with it.

A method introduced by Daynes[1] and developed by Barrer[2] obtains the diffusion coefficient of gases through films from the time-lag in the establishment of the steady state of transfer. In this method the rate of transfer is measured at intervals until the rate becomes constant; the intercept, *L*, of the straight line representing the steady state upon the time axis is related to the diffusion coefficient by the equation

$$D = t^2/6L$$

where *t* is the thickness of the film. The deriva-

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[1] H. Daynes, *Proc. Roy. Soc.* (London), **97A**, 286 (1920).

[2] R. M. Barrer, *Trans. Faraday Soc.*, **35**, 628, 644 (1939); *ibid.*, **36**, 1235 (1940); *Phil. Mag.*, **28**, 148 (1939).

tion of this equation involves the following assumptions: (1) that the diffusion coefficient is independent of the concentration of gas in the film, (2) that the surfaces of the film are always at equilibrium with the gas with which they are in contact, and (3) that the diffusion coefficient is independent of the position within the film, *i. e.*, the film is uniform.

The method of Barrer was applied by Doty, Aiken and Mark[3] to the diffusion of water vapor through films of organic polymers. However, it has been shown in the present work and in several other studies[3-7] that for many materials the rate of transmission of water vapor is not directly proportional to the vapor pressure difference. For such systems it is obvious that the diffusion coefficient is not a constant, and a method is presented here which avoids that assumption. The assumptions that the film is uniform and that the surfaces are at equilibrium with the vapor are retained. Results confirming the validity of these assumptions will be discussed later. This method makes possible the construction of curves representing the steady-state distribution of the effective vapor pressure and of the concentration of vapor within the film. The same method of calculating the diffusion coefficient has been developed independently by G. King[7] and similar methods have recently been discussed by Barrer.[8]

Theory

Diffusion of a vapor through a film is a flow under a potential gradient and can be treated in the same way as any other transfer caused by a potential difference. The essential difference between the treatment given here and those most commonly used is that the rate of transfer is assumed to depend upon the potential as well as upon the potential gradient. For mathematical simplicity, this work has been concerned only with the steady state.

For a membrane which has a constant concentration at each surface and through which the diffusing material is passing at a constant rate G, Fick's law can be written

$$G = -D(C)\frac{\mathrm{d}C}{\mathrm{d}x} \qquad (1)$$

where $D(C)$ is the diffusion coefficient at the concentration C of the diffusing material, and x is the distance from the surface of higher concentration.

Assuming that the diffusion coefficient is a function only of concentration at constant temperature, equation 1 can be integrated from the surface $x = 0$ where $C = C_1$ to the surface $x = t$ where $C = C_2$.

$$G\int_0^t \mathrm{d}x = -\int_{C_1}^{C_2} D(C)\mathrm{d}C$$

$$Gt = -\int_{C_1}^{C_2} D(C)\mathrm{d}C \qquad (2)$$

For any particular pair of vapor pressures the value of the right-hand side of equation 2 will be a constant at constant temperature if each surface of the film is at equilibrium with the vapor. Thus, if this assumption and the assumption that the diffusion coefficient is a function only of concentration are valid the product of the rate of transmission and the film thickness will be a constant. Conversely, when it is found experimentally that the product Gt is a constant it is probable that the two assumptions are obeyed by the system used.

If the vapor pressure on the second surface is zero, C_2 is assumed to be zero also and equation 2 can be written

$$G_pt = \int_0^{C_p} D(C)\mathrm{d}C \qquad (3)$$

where G_p is the rate of transmission with the vapor pressure p on one surface and zero pressure of vapor on the other surface, and C_p is the equilibrium concentration of vapor in the film at the pressure p. Taking the derivative of equation 3 with respect to C_p gives the equation

$$t\frac{\mathrm{d}G_p}{\mathrm{d}C_p} = D(C_p) \qquad (4)$$

If several values of G_p and the corresponding values of C_p are known, G_p can be expressed as a function of C_p, either graphically or analytically. The value assumed by the derivative of this function at a particular C_p multiplied by the thickness of the film gives the value of the diffusion coefficient at that value of C_p. Thus an expression for the diffusion coefficient as a function of the concentration of the vapor in the film is obtained.

In order to construct the gradient of vapor pressure within the film when the film is at a steady state with the vapor pressure of the liquid $p = a$ on one face and with zero pressure on the other face, the following method can be used. Equation 1 is integrated from the plane x, at which the vapor pressure is p, to the dry surface.

$$G_a\int_x^t \mathrm{d}x = -\int_{C_p}^{0} D(C)\mathrm{d}C$$

$$G_a(t-x) = \int_0^{C_p} D(C)\mathrm{d}C$$

$$= G_pt$$

$$x = t(1 - G_p/G_a) \qquad (5)$$

Equation 5 provides a means for calculating the value of x corresponding to the pressure p at the particular steady state being considered. If several values of G_p are known, x can be found for several values of p and the gradient of the vapor pressure can be constructed.

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(3) P. Doty, W. H. Aiken and H. Mark, *Ind. Eng. Chem., Anal. Ed.*, **16**, 686 (1944).

(4) P. M. Hauser and A. D. McLaren, paper in preparation.

(5) R. L. Taylor, D. B. Hermann and A. R. Kemp, *Ind. Eng. Chem.*, **28**, 1255 (1936).

(6) S. Wosnessenski and L. M. Dubnikow, *Kolloid-Z.*, **74**, 183 (1936).

(7) G. King, *Trans. Faraday Soc.*, **41**, 479 (1945).

(8) R. M. Barrer, *Proc. Phys. Soc.*, **58**, 321 (1946).

When this curve has been obtained, the values of C_p can also be plotted as a function of x. This produces a curve representing the concentration gradient of the vapor within the film.

The curve representing the pressure gradient within the film at the steady state can be used to calculate the rate of transmission at the steady state with any particular pair of vapor pressures on the surfaces by the following method. The values of x corresponding to the vapor pressures in question can be obtained directly from the curve. The difference between these two values, $x_2 - x_1$, gives the thickness of film which transmits water at the rate G_a with these pressures on its surfaces. When it has been shown that the product of the rate of transmission and the film thickness is a constant, the permeation through a film of thickness t can be calculated by the relation

$$G = G_a(x_2 - x_1)/t$$

Calculations based upon this method have been made by Hauser and McLaren.[4] The results are in good agreement with the measured rates of permeation.

Experimental

Permeation.—In order to maintain known, constant pressures of water vapor at the surfaces of the membrane, the measurements of permeation rates were made in a vacuum system represented diagrammatically in Fig. 1. The membrane F was mounted in a cell, C, consisting of two short sections of glass tubing ($2^1/_4''$ heavy-walled Pyrex). The ends between which the film was held were flanged and ground flat. Gaskets G of butyl rubber $^3/_{32}$ in. thick were used on each side of the membrane. The gaskets restricted the exposed area of the film to 25.7 sq. cm. The membrane was supported by a wire screen, S. The seal was surrounded with mercury and the cell was immersed in a water thermostat which held the temperature at 25.0 ± 0.1°. Tube A contained liquid water and was surrounded by a Dewar flask which served as a thermostat. This supplied a source of water vapor at a known, constant pressure. The thicknesses of the film samples used were measured with a Waltham dial gage, which could be read directly to 0.0001 inch.

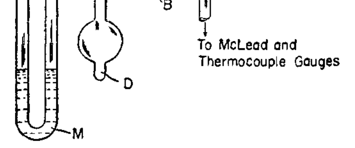

Fig. 1.—Permeation apparatus.

Attempts to measure the water vapor passing through the film with a McLeod gage and with a thermocouple-type Pirani gage gave irreproducible results, probably because of sorption of water vapor by the glass walls of the system. To overcome this difficulty, a gage similar to that described by Müller[9] was used. This gage consisted of a mercury manometer M and a known volume V of about 40 cc. The vapor was collected in the gage by immersing the tip, D, in liquid nitrogen, and the amount collected was measured by closing the stopcock 4, warming the volume V to room temperature, and reading the manometer with a micrometer slide. While stopcock 4 was closed the tip B was immersed in liquid nitrogen to prevent the pressure of water vapor in the system from becoming appreciable. The vapor frozen out at B was transferred to D immediately upon the reopening of the stopcock.

In the use of this gage, it was found that the first few readings were uncertain but that later readings were quite satisfactory. This probably was caused in some way by variations in the amount of water adsorbed on the glass. The difficulty was avoided by introducing a pressure of about 2 mm. of water vapor into the gage before starting a determination.

In order to measure a permeation rate, the system was evacuated overnight with the film in place. Water vapor at a pressure of 2 mm. was introduced into the gage by opening stopcock 2 for a very short time and pumping rapidly until the pressure of vapor in the system was reduced to about 0.15 mm. The residual vapor was frozen out at D and the system was then re-evacuated for a short time. The system was disconnected from the vacuum pump by closing stopcocks 1 and 3. A blank determination was made before each run, with readings being taken at intervals of fifteen minutes until the rate of accumulation of water vapor was fairly constant or was shown to be too small to measure. Stopcock 2 was then opened to admit the desired pressure of water vapor to the film and the run was continued with readings at fifteen-minute intervals until it was certain that a steady state had been reached. By this method permeation rates were obtained that could be reproduced within ±5% with different samples of a film.

Sorption.—Measurements of water sorption were made using a spring balance in an evacuated tube. The extension of the spring was followed with a cathetometer which could be read directly to 0.01 mm. The spring used was made of 7 mil nichrome wire and was intended only for use in exploratory measurements until a quartz spiral could be obtained. However, this spring showed such excellent properties that it was used throughout this work. It consisted of 40 turns 1.6 cm. in diameter and had a free length of about 8 cm. The sensitivity under a load of 0.50–0.75 g. was 4.8 mg./mm. Since the extension of the spring could be determined to 0.01 mm. the sorption could be measured to 0.01% of the sample weight. However, since the measurements were made in a constant temperature room in which the temperature was held at 25 ± 2°, the accuracy was probably not better than about ±0.02% of the sample weight. For use in the calculations the measured sorptions were converted to concentrations by multiplying by densities of 0.92 for polythene and 1.14 for nylon.

Results

In order to illustrate the use of the methods developed above and the character of the results which can be obtained, data will be presented for the diffusion of water vapor at 25° through polythene and nylon. These materials show quite different modes of interaction with water vapor and the results are probably typical of those which would be found with many other materials.

The validity of the assumptions that the surfaces of the film are at equilibrium with the vapor and that the diffusion coefficient is independent of the position within the film has been investigated

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(9) F. H. Müller, *Physik. Z.*, **42**, 48 (1941); *Kolloid-Z.*, **100**, 355 (1942).

by measurements of permeation rates through films of different thicknesses. For polythene films of thicknesses from 2.5×10^{-3} to 15×10^{-3} cm. it has been found in many measurements that the product of the film thickness and the transmission under a particular pair of vapor pressures is a constant. For nylon the product was 8% higher at a thickness of 6.7×10^{-3} cm. than it was at a thickness of 3.8×10^{-3} cm. with vapor pressures of 1 cm. and zero. This is a constant within the experimental error.

Polythene.—The material used in this work was an electrical grade of ethylene polymer obtained from the Ammonia Department of E. I. du Pont de Nemours and Company. Water vapor passed through films of this material at a rate which was proportional to the vapor pressure difference (Fig. 2a), indicating that the gradient of vapor pressure within the film was approximately linear. The film sorbed water vapor only very slightly at a vapor pressure of 1.0 cm. but at higher pressures, the sorption became relatively large. The magnitude of the sorption and the shape of the isotherm at pressures of the order of 1 cm. and below is a matter of conjecture. In Fig. 2b the isotherm has been drawn as a smooth curve. The rapid increase in sorption with increasing pressure causes the curve for the transmission G_p as a function of the concentration in the wet surface C_p to follow the course shown in Fig. 2c. This curve is much steeper at low concentrations than at high ones indicating that the diffusion coefficient is large at low concentrations and decreases rapidly with increasing concentration as shown in Fig. 2d.

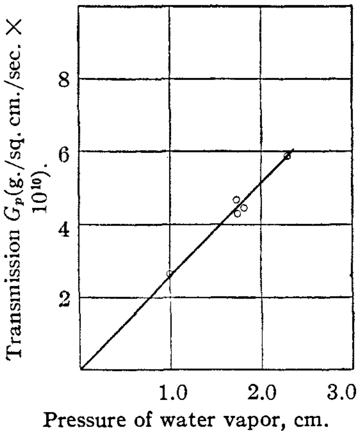

Fig. 2a.—Transmission of water vapor through polythene at 25°; film thickness, 0.0139 cm.

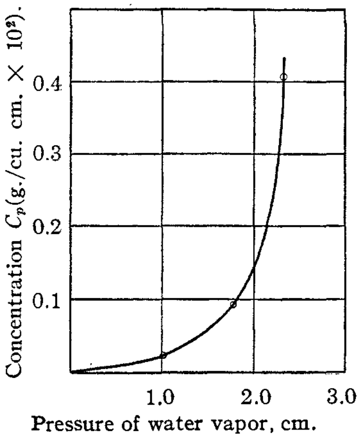

Fig. 2b.—Sorption of water vapor by polythene at 25°.

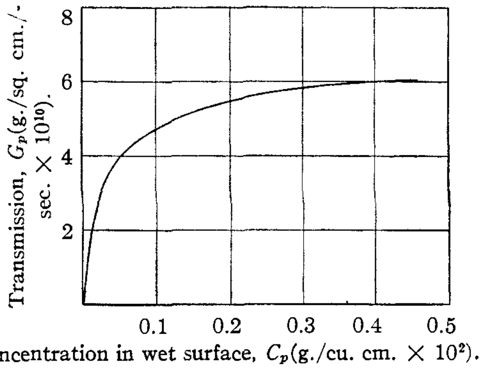

Fig. 2c.—Transmission of water vapor through polythen at 25°; film thickness, 0.0139 cm.

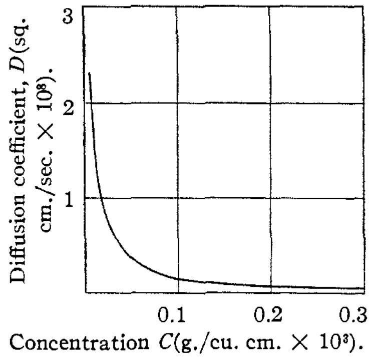

Fig. 2d.—Diffusion coefficient of water in polythene at 25°.

A value of the diffusion coefficient calculated in this way is an average for all the water present in the film at a particular vapor pressure. The shape of the sorption isotherm and the chemical nature of polythene suggest that the concentration of water becomes large only when the water molecules associate with one another to form clusters. This association would simultaneously decrease the average mobility of the molecules and increase the sorption. Apparently in polythene these effects approximately counterbalance one another.

The linear decrease in the vapor pressure across the film is shown in Fig. 2e, which also shows the concentration gradient of the water in the film. The latter curve must, of course, be steep in regions of high concentration because the diffusion coefficient is low in those regions. This concen-

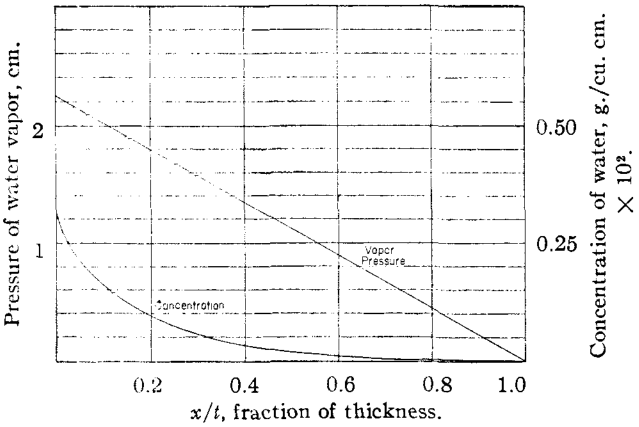

Fig. 2e.—Gradients of concentration and vapor pressure of water in polythene at the steady state at 25°.

tration gradient is similar in shape to that found in soft vulcanized rubber by direct measurement by Taylor, Hermann and Kemp.[5] They found that the transmission through this material increased linearly with increasing pressure difference up to a pressure of about 2 cm.; above that pressure the transmission increased somewhat more rapidly. Apparently, there is some similarity between the permeation processes in rubber and in polythene.

Nylon.—The material used in these experiments was a polymer prepared from a mixture of 40 parts (by weight) of hexamethylenediammonium adipate, 30 parts of hexamethylenediammonium sebacate, and 30 parts of ϵ-caprolactam. The results obtained were very different from those obtained with polythene. The transmission of water vapor (Fig. 3a) through the nylon film increased very rapidly with increasing vapor pressure on the wet surface. Since the sorption isotherm (Fig. 3b) is not very sharply curved, the plot of transmission against the concentration in the wet face of the film also shows a continuous increase (Fig. 3c). This results in a diffusion coefficient which increases with increasing concentration as shown in Fig. 3d. This behavior is similar to that found for water vapor in keratin by King[7] but the diffusion coefficient increases more uniformly in nylon and does not show the very rapid increase at pressures approaching saturation.

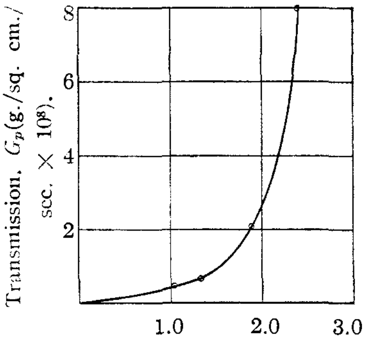

Fig. 3a.—Transmission of water vapor through nylon at 25°; film thickness, 0.0053 cm.

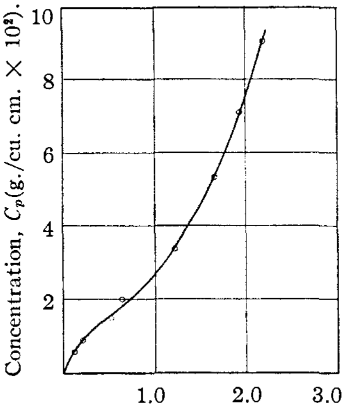

Fig. 3b.—Sorption of water vapor by nylon at 25°.

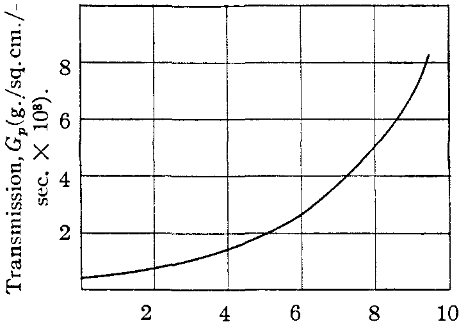

Fig. 3c.—Transmission of water vapor through nylon at 25°; film thickness, 0.0053 cm.

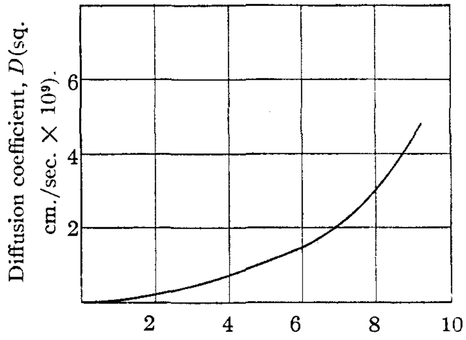

Fig. 3d.—Diffusion coefficient of water in nylon at 25°.

This behavior could be explained as a result of the swelling and plasticization of the nylon by the increasing water concentration. If the polymer molecules became more free to move, the motion of the water molecules between them should be made less difficult. An alternative explanation would be one similar to that given by King. The first molecules entering will mostly be held at points of low energy, and at higher concentrations more and more water molecules will be held relatively loosely. This will result in an increase in the average mobility as the concentration increases.

Both the concentration and vapor pressure gradients, shown in Fig. 3e, drop very steeply near the dry surface of the film. Throughout the rest of the film, the concentration is high and the water molecules have high mobility.

Acknowledgment.—The author wishes to express his thanks to Dr. A. F. Smith of the Chemical Department for his continued guidance and interest in this work and to the Rayon Technical Division, E. I. du Pont de Nemours and Company, for generous support of this research.

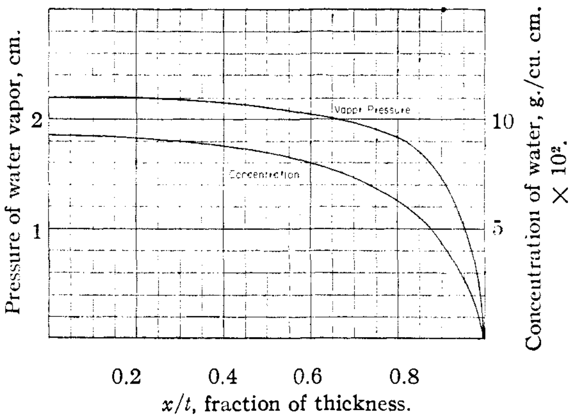

Fig. 3e.—Gradients of concentration and vapor pressure of water in nylon at the steady state at 25°.

Summary

1. A method is given for calculating the diffusion coefficient of a vapor within a film as a function of concentration. Data required are the permeation rates under several vapor pressure differences and the sorption isotherm. The method also furnishes a means for constructing the gradients of the effective vapor pressure and of the concentration of the vapor within the film through which vapor is passing at a steady state.

2. Data are presented for water permeation and water sorption of polythene and nylon, and the diffusion coefficients of water vapor in these films at 25° are obtained as functions of concentration. Curves representing the vapor pressure and concentration gradients are also presented.

WILMINGTON, DELAWARE RECEIVED NOVEMBER 8, 1946

[CONTRIBUTION FROM THE APPLIED SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI]

Studies of Fluorophosphoric Acids and Their Derivatives. XIII. Preparation of Anhydrous Monofluorophosphoric Acid[1]

BY WILLY LANGE[2] AND RALPH LIVINGSTON[3]

It has recently been shown that the esters of monofluorophosphoric acid, H_2PO_3F, which were previously known to be highly toxic,[4,5] have a probable usefulness in the treatment of glaucoma and myasthenia gravis, the di-*i*-propyl ester being especially suited for this purpose.[6] Unpublished observations by the present senior author have also shown that the esters possess insecticidal properties and may act as fumigants.

McCombie and Saunders have devised two convenient methods for the synthesis of these esters, but their prospective uses make a cheap, direct synthesis from monofluorophosphoric acid seem desirable. Although the salts of this acid have been studied in considerable detail,[7] the free acid has not been isolated previously and so the present study was undertaken to see whether the acid could be prepared in pure form.

In previous investigations 100% orthophosphoric acid had been allowed to react with hydrofluoric acid containing up to 41% hydrogen fluoride.[8] In new studies started in 1941, the reaction with liquid anhydrous hydrogen fluoride was investigated. As expected, in reaction of the anhydrous components in 1:1 molar ratio, a substantial portion of the orthophosphoric acid, namely, 67%, was transformed into a fluorinated derivative. However, it was found that the monofluorophosphoric acid, formed in the reaction, entered into a new equilibrium reaction with unreacted hydrogen fluoride, resulting in the formation of difluorophosphoric acid, while some orthophosphoric acid was still present. These equilibrium reactions take place according to the following equations

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(1) A portion of a thesis by R. Livingston, submitted to the Faculty of the Graduate Department of Applied Science, College of Engineering and Commerce, University of Cininnati, in partial fulfilment of the requirements for the Degree of Doctor of Science, May, 1943.

(2) Present address: The Procter & Gamble Company, Ivorydale 17, Ohio.

(3) Present address: Monsanto Chemical Company, Clinton Laboratories, Oak Ridge, Tenn.

(4) W. Lange and G. v. Krueger, *Ber.*, **65**, 1598 (1932).

(5) H. McCombie and B. C. Saunders, *Nature*, **157**, 287 (1946).

(6) Honorable R. P. Patterson, *Chem. Eng. News*, **24**, 1029 (1946).

(7) (a) W. Lange, *Ber.*, **62**, 793 (1929); (b) W. Lange, *Nature*, **126**, 916 (1930).

(8) (a) W. Lange, *Ber.*, **62**, 1084 (1929); (b) W. Lange and G. Stein, *ibid.*, **64**, 2772 (1931).