

Permeability of Various Polymers to 90% Hydrogen Peroxide

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I. INTRODUCTION

With the exception of an incidental reference to the measurement of hydrogen peroxide diffusion in a collodion membrane¹ and a report of the shelf life of 30% hydrogen peroxide in a polyethylene bottle,² no information concerning the diffusion of hydrogen peroxide through polymers was found in the literature. In the present work, a method suitable for measuring the steady state diffusion rate of 90% hydrogen peroxide was developed. The permeabilities of various polymers were determined both at room and elevated temperatures. Since some compounds react with hydrogen peroxide, compatibility tests with polymers in this reagent were made prior to the permeability measurements as a safety measure and for screening purposes.

II. THEORY

The experimental arrangement corresponds very closely to the situation illustrated in Figure 1. With the assumptions that Fick's law holds and that the diffusion coefficient D remains constant, it is readily shown³ for the given boundary conditions ($C_1 = \text{constant}$, $C_2 = \text{constant} = 0$) that the amount of hydrogen peroxide Q which flows across area A of the lower surface in time t is:

$$Q = \frac{A(C_1 - C_2)D}{l} \left[\alpha t - 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} (\exp \{-n^2 \alpha t\} - 1) \right] \quad (1)$$

where $\alpha = \pi^2 D/l^2$. A plot of Q as a function of αt in Figure 2 shows the type of curve to be expected under these conditions. The permeability of the polymer is simply related to the slope of the linear portion of this curve.

Daynes⁴ has shown that the diffusion coefficient can be calculated by the "lag time" method if the

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exact zero time for initiation of diffusion is known. In the present work, the 90% hydrogen peroxide was placed in contact with the polymer film in the permeameter at room temperature. The entire

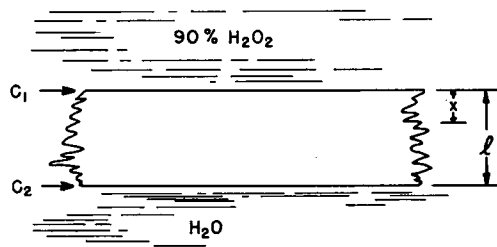


Fig. 1. Experimental conditions in permeameter.

assembly was allowed to reach the desired temperature in an oven and then measurements were initiated. Thus the exact zero time at the elevated temperature was not known, and only the steady state diffusion was measured. The diffusion

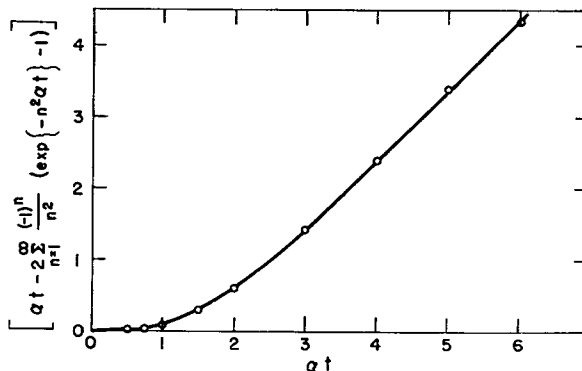


Fig. 2. Theoretical diffusion curve.

coefficient can be measured by heating the peroxide and the permeameter separately and subsequently pouring the 90% hydrogen peroxide into the permeameter to establish the zero time. This procedure is somewhat hazardous, especially at the high temperatures.

III. EXPERIMENTAL PROCEDURE

Polymer samples were molded between sheets of Teflon-coated aluminum foil. Since trace metals catalyze the peroxide decomposition, cleanness of the sample and glassware is very important. Before immersion in 90% hydrogen peroxide the films were washed with a detergent-water solution and subsequently rinsed with distilled water. The glassware cleaning process included washing in water-detergent solution and chromic acid-sulfuric acid solution, followed by rinses of distilled water, 30% hydrogen peroxide, and 90% hydrogen peroxide. This process was repeated until no bubbles were observed on the Vycor surface in contact with 90% hydrogen peroxide.

Films of polymers were immersed under 90% hydrogen peroxide in a vented Vycor vessel and heated at 74°C. for 96 hours in order to determine the effect of the polymer on the decomposition rate of the peroxide. Periodically the peroxide concentration was determined by removing small samples and analyzing by the standard potassium iodide-ammonium molybdate-sodium thiosulfate titration method.

A sketch of the permeameter used for the diffusion measurements is shown in Figure 3. The apparatus consisted of two flanged hollow cylinders of Teflon, separated by the sample, which was compression sealed by means of bolts through the flanges. Initially ca. 5 g. 90% hydrogen peroxide was placed in the upper cylinder and a measured quantity of distilled water was poured through a side tube into the lower chamber. The permeameter was subsequently rocked on a slowly oscillating platform in an air oven. As soon as the desired temperature was reached, 3 ml. of liquid were removed from the lower chamber and replaced by 3 ml. of distilled water at the same temperature. This was repeated after measured time intervals.

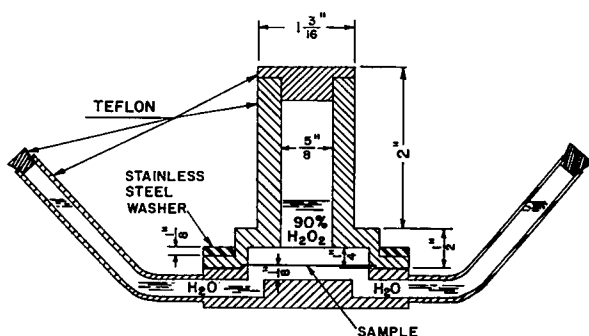


Fig. 3. Hydrogen peroxide permeameter.

Ten drops of titanil sulfate solution were added to the portion removed. The TiOSO_4 solution was prepared by mixing 2.5 g. of TiOSO_4 with 80 ml. of concentrated sulfuric acid and 40 ml. of distilled water, followed by heating, settling for 24 hours, and subsequent decantation. This solution reacts with H_2O_2 to form a yellow color due to pertitanic acid. The optical densities of the solutions were measured at 4050 Å. with a DK or DU Beckman spectrophotometer. The H_2O_2 concentration was determined from a concentration-optical density curve constructed from measurements with standard samples of known H_2O_2 concentrations to which had been added a corresponding amount of reagent. In the range of concentrations used, the optical density was found to be directly proportional to the concentration of H_2O_2 in agreement with Beer's law as reported⁶ in the literature. With the use of a 1 cm. path in the spectrophotometer, the minimum concentration that could be detected by this method was ca. 3×10^{-7} g. H_2O_2 per ml. of solution. Thus the analytical method is quite sensitive. However, inaccuracies in the sampling technique widened the margin of error to 10 or 20%.

IV. RESULTS AND DISCUSSION

The results of compatibility tests are shown in Table I. It will be noted that some polymers cause rather rapid decomposition of the H_2O_2 , while others show practically no effect.

In many cases, prolonged contact with hydrogen peroxide changes the appearance of the polymer. Mylar becomes pebbly in appearance and loses transparency. Polyvinyl chloride (Geon 118) be-

TABLE I
Decomposition of 90% H_2O_2 by Polymers at 74°C.

Material immersed	Loss in concentration of 90% H_2O_2 after 96 hr., %	Appearance of film after immersion
Kel-F 3700 (uncured)	67	unchanged
Kel-F 800	17	unchanged
Silastic S9711	15	unchanged
Kel-F 5500 (uncured)	11	degraded
Geon 118 (44% plasticizer)	7.2	yellow
Polyethylene (high density)	6.7	white, brittle
Kel-F 820	3.7	unchanged
Blank	2.7	—
Geon 118 (35% plasticizer)	1.1	milky
Teflon 100-X	1.1	unchanged

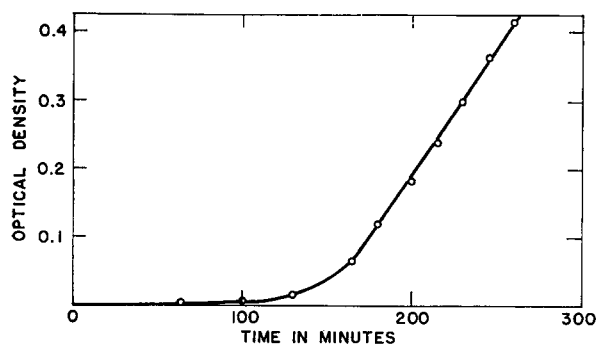


Fig. 4. Diffusion of 90% H_2O_2 through a 0.0301-in. plasticized polyvinyl chloride film at 46°C.

comes bleached and transparent on prolonged contact. Polyethylene is bleached slightly at low temperatures, and this effect becomes more pronounced at high temperatures. The effect on polyvinylidene chloride (Saran) is noticeable only on prolonged contact, the film becoming cloudy white in appearance. The value recorded for the "blank," which is greater than that for the last two polymers, indicates the magnitude of inherent experimental errors.

A typical experimental diffusion curve obtained at 46°C. with Geon 118 containing 35% plasticizer is shown in Figure 4. Instead of plotting the quantity of permeated hydrogen peroxide as a function of time, it was more convenient to plot the measured optical density (corrected for the sampling dilution) of the test solution as a function of time. Since Q and the optical density differ in a given case by a constant factor, the shape of the curve is unaffected by this procedure. A comparison of this curve with the one in Figure 2 suggests that, for the most part, we are dealing with a simple diffusion process in which the diffusion coefficient is constant. In a few cases a slight decrease in the steady rate was noted at very long times at the elevated temperature, and it is possible that in these instances the diffusion coefficient was varying with time. The fact that the appearance of some polymers changed with time would tend to support this hypothesis.

The permeabilities of a few polymers to 90% H_2O_2 measured at room temperature are presented in Table II. No changes in the films were observed during the relatively short time necessary for the permeability measurements, hence, no correction for polymer-induced peroxide decomposition was deemed necessary. The results reported were reproducible as evidenced by at least two measurements with films of different thicknesses.

The polyvinyl chloride and polyvinylidene chlo-

ride hydrogen peroxide permeabilities reported in Table II were measured with Geon 118 containing 35% plasticizer and Saran 517, respectively.

The hydrogen peroxide permeability of Saran at 74°C. was found to be inversely proportional to the thickness of the film as predicted in eq. (1). Since not all the films studied by us were 0.001 in. thick, the permeabilities reported in Table II for H_2O_2 were calculated by assuming the permeation rate to be inversely proportional to the thickness. Shown also for comparison are representative water vapor permeabilities selected from the literature.^{6,7} Because of similarities between molecules of H_2O_2 and H_2O , one might expect the permeabilities to follow the same order. On the basis of the limited data presented in Table II, it appears that this correlation does exist.

TABLE II
Permeability of Polymer Films at 25°C.

Polymer	Hydrogen peroxide, g. $\text{H}_2\text{O}_2/0.001$ in./100 in. ² /24 hr.	Water vapor, 10 ⁻⁸ cm. ³ $\text{H}_2\text{O}/\text{mm.}/\text{cm.}^2/\text{sec.}/\text{cm. Hg}^a$	Water vapor, 10 ⁻⁸ cm. ³ $\text{H}_2\text{O}/\text{mm.}/\text{cm.}^2/\text{sec.}/\text{cm. Hg.}^b$
Polyvinyl chloride	2.5-8.0	11.6, 12.3	15.6
Polyester (Mylar Type A)	3.3	—	13
Polyethylene (low density)	0.10	6.1	8
Polyvinylidene chloride	0.03	0.20	0.14

^a Reference 6.

^b Reference 7.

In Table III are listed the hydrogen peroxide permeabilities measured at 74°C. It is interesting to note that the permeabilities vary over a very

TABLE III
90% Hydrogen Peroxide Permeabilities at 74°C.

Material	g. $\text{H}_2\text{O}_2/0.001$ in./100 in. ² /24 hr.
Geon 118 (44% plasticizer)	147
Geon 118 (35% plasticizer)	74
Silastic S9711	55
Polyethylene (low density)	9
Saran 517	2.8
Kel-F 820	0.44
Kel-F 800	0.28
Teflon	0.09
Polyethylene (high density)	0.04
Teflon 100-X	<0.01

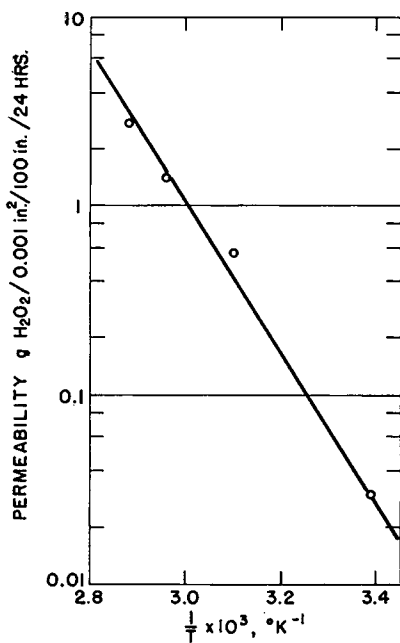


Fig. 5. Influence of temperature on the permeability of 90% H_2O_2 through Saran.

wide range. As expected, the H_2O_2 permeability is higher in the low density polyethylene (with an approximate crystallinity of 60%) than in the high density type which is ca. 90% crystalline.

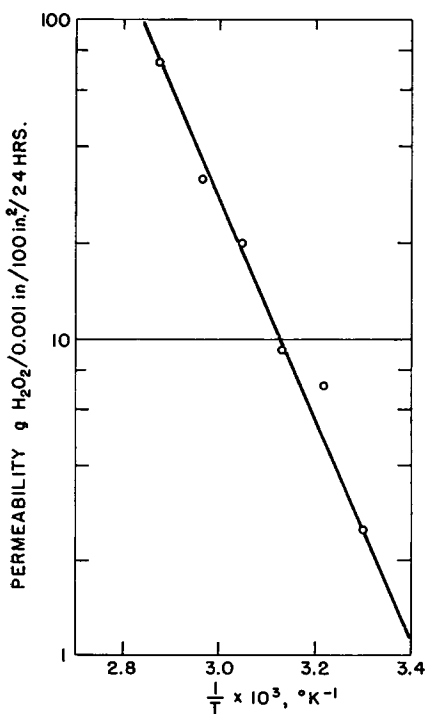


Fig. 6. Influence of temperature on the permeability of 90% H_2O_2 through polyvinyl chloride.

With two polymers the permeability was measured at a number of different temperatures. Plots of the logarithm of permeability versus reciprocal absolute temperature in Figures 5 and 6 are reasonably linear. This suggests that the equation:

$$P = P_0 \exp \{-E/RT\} \quad (2)$$

is also valid here, where P is the permeability, P_0 is a constant, E is the activation energy for the permeation process, R is the gas constant, and T the absolute temperature. This also suggests that hydrogen peroxide diffusion is truly an activation process. On the basis of these assumptions, the activation energy for hydrogen peroxide permeation is ca. 18 kcal./mole through Saran and ca. 16 kcal./mole through polyvinyl chloride containing 35% plasticizer.

The above value for the energy of activation for permeation of hydrogen peroxide through Saran is only slightly higher than the corresponding value (17.5 kcal./mole) reported by Doty⁸ for water vapor permeation. He found that the effect of adding 25% plasticizer to polyvinyl chloride-acetate copolymers increased E as much as 5 kcal./mole for water vapor permeation. Thus the unexpected high E value for hydrogen peroxide permeation through plasticized polyvinyl chloride seems reasonable.

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Synopsis

The theory and experimental work are described for the determination of the hydrogen peroxide permeability for various polymers at room and elevated temperatures. Compatibility tests indicate that many polymers decompose 90% hydrogen peroxide appreciably, while the effects of others are negligible. The appearance of some polymers remains unchanged after immersion in this reagent. The steady-state diffusion rate through several polymers was

measured in a permeameter constructed of Teflon. The hydrogen peroxide which permeated any film was determined quantitatively by means of a spectrophotometric method. Experimental curves of the amount permeated as a function of time agree with those predicted theoretically. A correlation was found between water vapor and hydrogen peroxide permeabilities for several polymers at room temperature. The hydrogen peroxide permeabilities of many polymers measured at 74°C. vary over four orders of magnitude. The temperature dependence of hydrogen peroxide permeabilities was found to conform to the Arrhenius type relationship. Activation energies for hydrogen peroxide permeation through plasticized polyvinyl chloride and polyvinylidene chloride were found to be 16 and 18 kcal./mole, respectively.

Résumé

On décrit la théorie et les expériences pour la détermination de la perméabilité du peroxyde d'hydrogène pour différents polymères à température de chambre et à des températures plus élevées. Des tests de compatibilité indiquent que beaucoup de polymères décomposent le peroxyde d'hydrogène à 90%, tandis que les effets d'autres sont négligeables. L'aspect de certains de ces polymères reste inchangé après immersion dans ce réactif. La vitesse de diffusion à l'état stationnaire à travers plusieurs polymères a été mesurée dans un perméamètre construit en Teflon. L'eau oxygénée qui diffusait à travers un film était quantitativement déterminée par une méthode spectrophotométrique. Les courbes expérimentales de la quantité qui a passé la membrane en fonction du temps est en plein accord avec la théorie. On a trouvé une relation entre les perméabilités de la vapeur d'eau et de l'eau oxygénée pour plusieurs polymères à température de chambre. Les perméabilités au peroxyde d'hydrogène de beaucoup de polymères mesurées à 74°C

varient sur quatre ordres de grandeur. La dépendance de la température des perméabilités de l'eau oxygénée répond à une relation du type d'Arrhenius. Des énergies d'activation pour la perméation du peroxyde d'hydrogène à travers le chlorure de polyvinyle et de chlorure de polyvinylidene s'élèvent respectivement à 16 et 18 Kcal/moles.

Zusammenfassung

Eine Theorie, sowie experimentelle Untersuchungen der Bestimmung der Permeabilität verschiedener Polymerer für Wasserstoffperoxyd bei Raumtemperatur und bei höherer Temperatur werden beschrieben. Eine Prüfung der Verträglichkeit zeigt, dass viele Polymere 90% iges Wasserstoffperoxyd in beträchtlichem Ausmass zersetzen, während die Wirkung anderer Polymerer vernachlässigbar ist. Die Diffusionsgeschwindigkeit durch mehrere Polymere für den stationären Zustand wurde in einem aus Teflon gebauten Permeameter gemessen. Das Wasserstoffperoxyd, das durch den Film hindurchtrat wurde auf spektrophotometrischem Weg quantitativ bestimmt. Die experimentellen Kurven für die durchgetretene Menge als Funktion der Zeit stehen mit den theoretisch vorausgesagten in Übereinstimmung. Eine Beziehung zwischen der Durchlässigkeit für Wasserdampf und Wasserstoffperoxyd wurde bei mehreren Polymeren bei Raumtemperatur gefunden. Die Permeabilität vieler Polymerer, für Wasserstoffperoxyd, die bei 74°C gemessen wurde, variiert über den Bereich von vier Größenordnungen. Es wurde gefunden, dass die Temperaturabhängigkeit der Wasserstoffperoxydpermeabilität einer Arrheniusbeziehung entspricht. Die Aktivierungsenergien für die Permeation von Wasserstoffperoxyd durch weichgemachtes Polyvinylchlorid und Polyvinylidenchlorid lagen, wie gefunden wurde, bei 16 bzw. 18 kcal/Mol.

Received May 21, 1959