this type of reaction is not available, the formation of a suitable complex of the desired material as the nutrient, with its subsequent decomposition in a gel can be used as the growth method.

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Transport of Toluene Through Fully Swollen Polyethylene

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Experiments have been carried out to measure the permeation of tritium-labeled toluene through polyethylene films fully swollen with chlorobenzene, mesitylene, cumene, toluene, ethylbenzene, cyclohexane, tetrahydronaphthalene, and decahydronaphthalene. The results show characteristic Arrhenius temperature dependence over the range 25 to 40°C. The permeation of toluene through the films appears to be enhanced by increased solubility of the swelling agent (estimated from the work of others) in the film and there also appears to be a rough correlation between permeability of toluene and the boiling points and vapor pressures of the swelling agents. The range of permeabilities measured at 25°C. is 2.09 $\times$ 10^{-7} to 0.51 $\times$ 10^{-7} sq.cm./sec., the extremes of measured permeation activation energy, E_p, are 11.41 to 16.68 kcal./mole, and the pre-exponential factor, P_o, falls within the interval 36.59 to 1.29 $\times$ 10^5 sq.cm./sec. A very definite linear relationship or compensation effect is evident between P_o and E_p. Except as mentioned above, none of these quantities appears to correlate uniformly with the following properties of swelling solvent: molecular weight, dipole moment, specific gravity, vapor pressure, boiling point, heat of vaporization, critical temperature, viscosity, surface tension, molar volume, molecular area or other molecular dimensions.

In the many reported studies of transport of gases and vapors through polymers, experimental measurements almost always involve a significant partial pressure or concentration gradient within the material. In such experiments the solute or diffusing species interacts with the polymer, frequently causing swelling, and thereby brings about nonuniform transport properties in the medium along the direction of the concentration gradient. Because of this phenomenon the ordinary form of the diffusion equation,

$$D\nabla^2 C = \frac{\partial C}{\partial t} \tag{1}$$

is inapplicable to such systems. However the more fundamental form of the diffusion equation,

$$\text{div}(D\text{grad}C) = \frac{\partial C}{\partial t} \tag{2}$$

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does apply to diffusion in polymers. Neither is there reason in such circumstances to doubt the local validity of Fick's law,

$$J = -D \operatorname{grad} C \qquad (3)$$

which, of course, is the basis for Equation (2).

Nonuniformity of properties along the path of transport leads to difficulties in experimental measurement of permeation or diffusion in polymers. Recognizing that diffusivity is a function of concentration of the diffusing species, this functional dependence is frequently assumed to be exponential (*1 to 3*)

$$D = D'e^{ac} \qquad (4)$$

Equation (4) may then be used with Equation (2) and numerical techniques employed to fit values of the parameters D' and a to experimental data if solubility information is also available. Since diffusivity is a rather strong function of concentration, as described by Equation (4), the concentration gradient will be largest in that portion of the polymer where concentration is the smallest. Thus the resistance offered to transport will vary along the concentration gradient and the usual kind of experiment will be inherently more accurate for regions of polymer where concentration is low. In many cases, where solubility of diffusing species in the polymer is large and swelling occurs, the local value of permeability or diffusivity can vary over a tenfold range or more along the transport path. Under such circumstances the swollen portion of the polymer offers negligible resistance to transport as compared to those regions of polymer where concentration is small. Experiments under these conditions cannot be expected to yield accurate results within the highly swollen domain.

The experiments reported below were undertaken to measure permeation in fully swollen polymer films. As has been explained, transport under these conditions is not easily measured using the usual experimental techniques. The experimental results reported below also demonstrate rather well the applicability of Equation (3), Fick's law, to transport in swollen polymers. The experimental technique rests upon the use of radioactively labeled diffusing molecules. First, the polymeric membrane is equilibrated with an organic swelling solvent; then a labeled molecular species is introduced on one side of the membrane and its increase in concentration is followed on the other side of the membrane as a function of time. Under these experimental conditions Equation (1) is applicable because the film is uniformly swollen and the transport properties are essentially uniform along the diffusion path. It is not necessary that the permeating species be identical to the swelling solvent since the experimental technique allows accurate results to be obtained using extremely small concentrations of labeled diffusing species. It should be mentioned that radioactive tracers have been employed before (*4 to 7*) to measure permeation in polymers, but it seems that this technique has not been used too often to focus on the polymer in the fully swollen condition. Long (*2*) reports one such measurement for toluene in polypropylene.

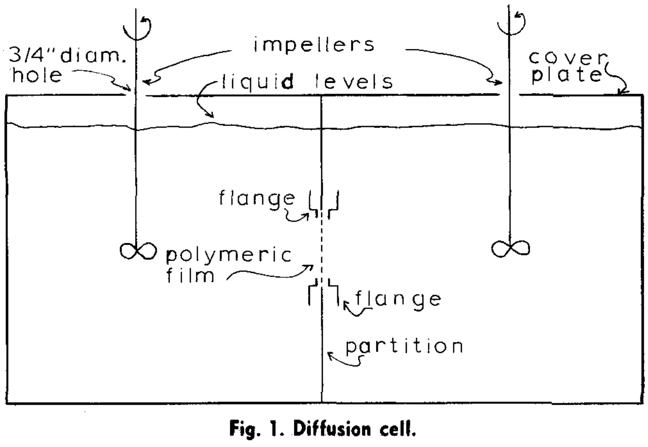

Fig. 1. Diffusion cell.

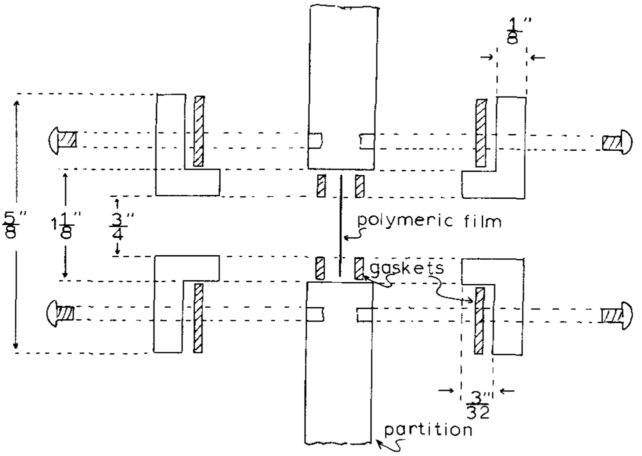

Fig. 2. Flange assembly.

EXPERIMENTAL APPARATUS AND PROCEDURE

Experiments were carried out in an extremely simple apparatus which consisted of two compartments separated by a partition containing a circular, central, 1.125 in. diameter, hole in which a polymeric film was mounted. The film was sealed in position by means of a system of flanges and gaskets. This is shown schematically in Figure 1. The entire apparatus, including flanges and cover, was fabricated from brass stock. The brass plates were joined together by silver soldering and the flanges were secured by brass machine screws. Gaskets were made from thiokol rubber.

The apparatus and its contents were maintained at constant temperature in a controlled water bath (to ± 0.02°C.), by immersion almost to the level of the cover plate. Liquid placed in each compartment of the apparatus was agitated by ordinary laboratory stirrers fitted with glass impellers. The interior of each compartment was approximately a cube with a 2 in. edge, by no means a critical dimension.

The flanges mentioned above and described by Figure 2 were dimensioned in such a way that the raised portions of the flanges could make contact when they were secured to the central partition by four brass machine screws. Four gaskets were used; two were used between the flanges and the partition separating the chambers and two smaller gaskets were fashioned to fit between the raised portions of the flanges. It was between these latter gaskets that the polymeric film was placed.

The polymeric film used in the experiments was polyethylene, of number average molecular weight ranging from 40,000 to 50,000. The density was 0.92 to 0.93 g./cc. and the measured thickness was 1.5 mils. There was no detectable (using a micrometer with a sensitivity of ± 0.01 mil) change in this thickness after swelling in any of the organic liquids used in these experiments. The liquids used as swelling agents were ethylbenzene, tetrahydronaphthalene, mesitylene, cyclohexane, toluene, chlorobenzene, decahydronaphthalene, and cumene. All of these were Baker analyzed reagent grade except cyclohexane which was of high purity and tetrahydronaphthalene which was Baker practical grade.

In each of the experiments reported here the diffusing species was toluene. This was labeled using tritiated toluene-4. Radioactivity concentrations were measured by the technique of liquid scintillation spectrometry. For this, the scintillation solution was prepared by adding 0.3 g. of 1,4-bis-[2-4 (methyl-5-phenyloxazolyl)] benzene and 5.0 g of 2,5 diphenyloxazole to toluene and making up to a final volume of 1 liter.

To prepare for an experiment a disk of polyethylene film was mounted between the flanges using gaskets preswollen with the particular swelling solvent to be used. Next, 120 ml. of swelling solvent was added to the right-hand chamber of the apparatus and, after checking for leaks, 119 ml. of the same solvent was added to the other side. The apparatus was maintained in the constant-temperature bath for about 40 hr. to permit equilibrium swelling of the polyethylene membrane. During this period each chamber was stirred at a constant rate and the average evaporation rate noted. After equilibration, the liquid level in each cell was brought back to its original position by the addition of liquid at the same temperature.

To carry out an experiment, 1 ml. of toluene with a radioactive tritium concentration of 0.141 millicuries/ml. was added to the left chamber, thereby bringing both chambers to the same volume. Both chambers were stirred during the experiment, as before, thereby insuring that all resistance to transport resided in the polymer film. After addition of tracer, ½ ml. samples were withdrawn at 30 min. intervals from each chamber using a pipette. These samples were mixed with appropriate amounts of the scintillation solution in standard vials and were subsequently counted using a Packard Tri-Carb Liquid Scintillation Spectrometer. Standard counting procedures were followed and care was taken to insure constant detection efficiencies for all samples counted.

RESULTS

The experimental procedure outlined above gave results closely approximating a situation of constant radioactivity concentration gradient across the film. Due to the dimensions of polymer film and diffusion-cell chambers, magnitude of the permeability, and duration of an experiment, the concentration gradient, and therefore the transport rate through the film, remained effectively constant throughout an experiment. For example, for toluene diffusing through a toluene-swollen film, the measured concentration in the left-hand compartment changed from 9.84×10^5 to 9.82×10^5 counts per min./ml. during a 4 hr. experiment; during the same time and right-hand compartment concentration changed from 3.42×10^3 to 2.92×10^4 counts per min./ml. Thus the concentration gradient changed by no more than about 3% during this experiment although the concentration in the right-hand compartment changed by about a factor of ten, thereby permitting an accurate assessment of average transport rate.

The volumes in the cell compartments were not constant due to the removal of samples and evaporation. During a 4 hr. experiment this volume change did not amount to more than about 5 ml. and, therefore, was less than about 5%. The mean volume, computed from the values at the beginning and end of an experiment, was used to compute the constant transport rate from the slope of the straight-line plot of measured right-hand compartment concentration vs. time. Typical experimental results are shown plotted in Figure 3 where the good conformity of the data to straight-line behavior is apparent.

The results computed from the data are permeabilities rather than diffusivities. Integrating Equation (3) written in one dimension for the case of constant diffusional flux $|\bar{J}|$ gives:

$$D = |\bar{J}| \frac{\Delta x}{C'_L - C'_R} \tag{5}$$

Since the concentrations at the left-hand and right-hand surfaces of the film, C'_L and C'_R, were not measured it is necessary to multiply each side of Equation (4) by the Henry's law solubility constant or distribution coefficient, σ, to give the permeability,

$$P = D\sigma = |\bar{J}| \frac{\Delta x}{C_L - C_R} \tag{6}$$

where $C_L = C'_L/\sigma$ and $C_R = C'_R/\sigma$ are the concentrations in the liquid on the left and right-hand sides of the film respectively. In order to compute permeabilities using Equation (6), values of $|\bar{J}|$ were taken as the product of average right-hand chamber volume and the slope of the plot of right-hand chamber concentration vs. time, divided by the cross-sectional area of the polymer film. $C_L - C_R$ was taken to be the mean of the concentration differences between left-hand and right-hand compartments at the beginning and end of each experiment; Δx was the measured polymer film thickness. The transport rate, $|\bar{J}|$, could be expressed in millicuries/sq. cm., sec. and C_L and C_R in millicuries/cc. or, since radioactivity detection efficiency was maintained constant throughout an experiment, it was also possible to use units of counts per min./sq. cm., sec. and counts per min./cc. respectively.

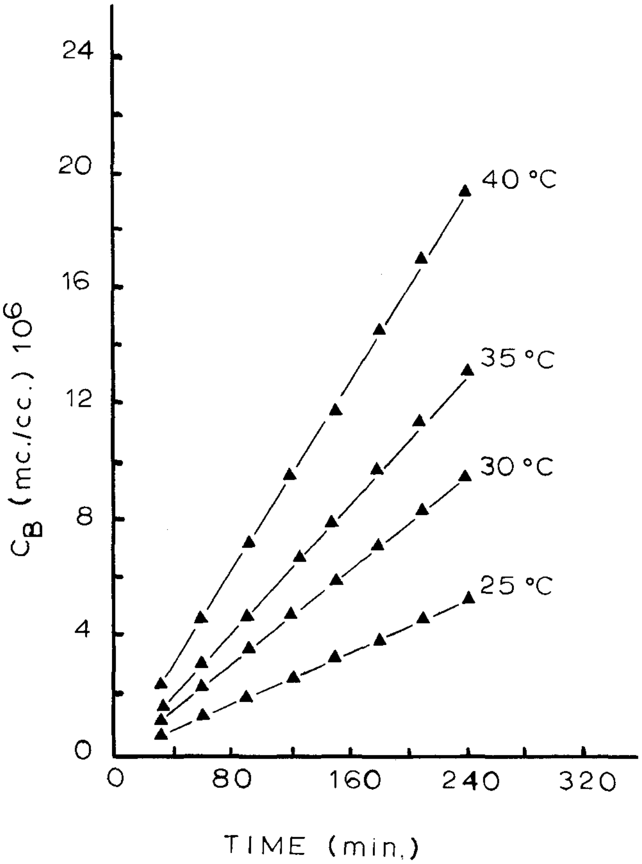

Fig. 3. C_B vs. time for the toluene-polyethylene system.

The values of permeability obtained from a least squares fit of straight lines to data like those shown in Figure 3 are presented in Table 1. Here each value of permeability was obtained by fitting a straight line to eight data points. From the regression analysis and the experimental errors in sampling and volume measurement, these values of permeability are estimated to have an accuracy of about ±2% at the 90% confidence level. These permeability data are also shown on a semilogarithmic plot vs. reciprocal temperature in Figure 4. Here the conformity to straight-line behavior indicates activated permeation in accord with the expression,

$$P = P_o \exp\left(-\Delta E_p/RT\right) \tag{7}$$

The values of P_o and ΔE_p obtained from a least-squares fit of these data are also given in Table 1. Here a regression analysis indicated a standard deviation (at the 95% confidence level) of about 5% in ΔE and about 10% in P_o. It was not possible to employ the time-lag technique (*8*, *9*) in these experiments to directly compute a value of diffusivity using the expression:

$$D = \frac{(\Delta x)^2}{6\theta} \tag{8}$$

where Δx is the film thickness and θ the time lag or time

TABLE 1. PERMEABILITY OF TOLUENE IN FULLY SWOLLEN POLYETHYLENE

Swelling Solvent	Temp., °C.	P, (sq. cm./sec.) × 10^7	P_o, sq. cm./sec.	$10^{-3}\lambda[\sigma_o \exp(\Delta S/R)]^{1/2}, A$	ΔE_p, kcal./mole
toluene	25.0	1.34			
	30.0	2.38			
	35.0	3.22	4.89×10^4	5.38	15.77
	40.0	4.80			
chlorobenzene	25.3	1.21			
	30.0	2.09			
	35.0	2.85	9.13×10^4	7.40	16.22
	39.3	4.13			
mesitylene	25.4	1.25			
	30.0	1.76			
	35.0	2.67	3.40×10^3	1.43	14.25
	40.0	3.83			
cumene	25.4	0.80			
	30.0	1.21			
	35.4	1.98	1.29×10^5	8.75	16.68
	39.8	2.92			
ethylbenzene	25.0	1.57			
	30.0	2.22			
	35.4	3.00	36.59	0.148	11.41
	40.0	3.95			
cyclohexane	25.0	2.09			
	29.6	3.01			
	35.0	4.65	1.33×10^4	2.81	14.75
	39.8	6.60			
tetrahydronaphthalene	25.2	0.51			
	30.0	0.89			
	34.8	1.91	67.28	0.200	12.17
	39.8	1.82			
decahydronaphthalene	25.2	0.78			
	30.0	1.24			
	35.0	1.89	1.01×10^5	7.75	16.54
	39.7	2.84			

intercept on a plot of quantity permeated vs. time. This technique was inapplicable to the experimental data reported here because the very thin films employed resulted in small time lags which could not be accurately estimated by extrapolating the experimental data. This explains why the lines through the data points in Figure 3 appears to pass through the origin.

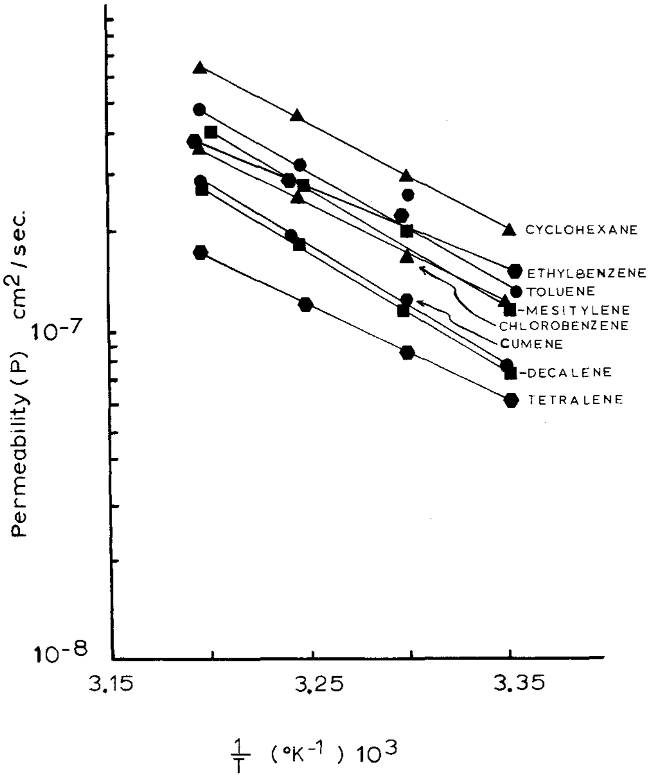

Fig. 4. $\text{Log}_{10}(P)$ vs. $1/t$.

DISCUSSION

The data in Table 1 display a wide range of values of P, P_o, and E_p for the permeation of toluene through the same film swollen with each of the eight different solvents employed. It is interesting that at 25°C. the permeation rate of toluene is larger through the films swollen with ethylbenzene and cyclohexane than it is through a film swollen with toluene itself. At about 40°C. a film swollen with cyclohexane continues to display a larger permeability for toluene than a toluene-swollen film but the toluene-permeability of a film swollen with ethylbenzene is significantly lower than in either of the other two cases at this temperature. This change in relative behaviors as the temperature is increased may reside in the plasticizing effect of the side chain of the ethylbenzene. This effect may be prominent at lower temperatures but may become obscured at higher temperatures as compared to a possible larger plasticizing effect due to thermal motion of the smaller toluene and cyclohexane molecules in films swollen with those solvents. This behavior is also evident from Figure 4 where the data points for toluene permeation in an ethylbenzene-swollen membrane determine a line that intersects the line for toluene permeation in a toluene-swollen membrane. All of the other lines on this graph are roughly parallel except the line for the mesitylene-swollen membrane, although in this case the behavior is less pronounced than that in the ethylbenzene-swollen film. It is clear from Figure 4 that toluene permeation is fastest through the cyclohexane-swollen membrane over the temperature range investigated (~25 to ~40°C.). It is conceivable that the permeability may be most strongly influenced by the solubility of the swelling solvent in the film. For example, Hildebrand (*11*) lists the solubility of toluene in polyethylene as about equal to the solubility of chlorobenzene but he gives a much larger value for the corresponding solubility of cyclohexane. Also the data of Barrer (*9*) for transport of permanent gases through rubbers display a strong correlation between permeability and solubility.

The data of Table 1 do not show uniform correlation with individual properties of the swelling solvent, regardless of whether one considers P, P_o, or E_p. For this, the following properties of the swelling solvents were considered: molecular weight, dipole moment, specific gravity, vapor pressure, boiling point, heat of vaporization, critical temperature, viscosity, surface tension, molar volume, area, and molecular dimensions. The nearest approach to uniform correlations with single properties of swelling solvent was found between the boiling point of the swelling solvent and toluene permeability at 40°C.:

	tetralene	decalene	cumene	mesitylene	toluene	ethylbenzene	chlorobenzene	cyclohexane
Boiling pt., °C.	207	197	152	165	111	136	132	81
$P \times 10^7$ sq. cm./sec., 40°C.	1.82	2.84	2.92	3.38	4.8	3.95	4.13	6.60

Here the correlation would be fulfilled if the positions of cumene and mesitylene in the listing were exchanged. This approximate correlation becomes less satisfactory when measured permeabilities at 25°C. are considered. The data suggest some indication of correlation (although less satisfactory than that considered above) between permeability and molecular weight, vapor pressure, or critical temperature of swelling solvent. The swelling solvent does not influence the membrane in accord with its own transport parameters, for if it did we would expect more evidence of correlation between permeability and viscosity of swelling solvent. This means that a correlation based on toluene diffusivity in the swelling solvents would also be unsuccessful. It is interesting to note that there is more indication of some correlation between permeability and the properties of swelling solvent than there is between P_o or E_p and these properties.

There is evidence of rough agreement between the present data and those measured by other workers. For example, using an experimental technique quite similar, Long (*2*) measured the diffusivity and solubility of toluene in fully swollen polypropylene and found respectively 3×10^{-6} sq. cm./sec. and 15 g./100 g. of dry polymer (in the temperature range 20 to 40°C.). From this one computes $P \approx 4.5 \times 10^{-7}$ sq. cm./sec. vs. 4.8×10^{-7} sq. cm./sec. measured in the experiments reported here. Similarly, values of solubility on the order of about 0.1 g./g. polymer were reported by McCall (*10*) for benzene and *n*-hexane in polyethylene; however the measured values of diffusivity were lower in the latter work.

The Henry's law solubility constant or distribution coefficient can be written:

$$\sigma = \sigma_0 e^{-\Delta H/RT} \qquad (9)$$

where $-\Delta H$ is the partial molal enthalpy associated with the passage of a mole of toluene from solution in swelling solvent to solution in swollen polymer. Since for activated diffusion

$$D = D_0 e^{-E_D/RT} \qquad (10)$$

it is also possible to write:

$$P_o = \sigma_o D_o \qquad (11)$$

and

$$E_p = E_D + \Delta H \qquad (12)$$

Usually E_D is larger than E_p since for most cases ΔH refers to an exothermic process. The measured values of E_p corresponding to the eight different swelling solvents cover a range of 11.41 to 16.68 kcal./mole and it is believed that this variation may be attributed largely to differences in E_D since it is expected that $|\Delta H|$ would be small for the passage of a mole of toluene from a dilute solution in swelling solvent to a dilute solution in polyethylene saturated with the same swelling solvent. Moreover, it is also expected that the differences between the various values of ΔH would also be small since the heats of mixing of toluene with the various swelling solvents are rather small. This is suggested by the fact that the heat of mixing is proportional to $(\delta_1 - \delta_2)^2$ where the δ's are solubility parameters (*11*). The swelling solvents used in this study possess values of δ covering a rather restricted range.

Using the prediction of absolute reaction rate theory (*16*) for D_o we can write:

$$P_o = 2.72\, \sigma_o \frac{kT}{h} \lambda^2 \exp\left(\Delta S^{\ddagger}/R\right) \qquad (13)$$

which permits computation of the quantity, $\lambda[\sigma_o \exp(S^{\ddagger}/R)]^{1/2}$, also shown in Table 1. These values are more than three orders of magnitude larger than $\lambda[\exp(\Delta S^{\ddagger}/R)^{1/2}$ for diffusion in solutions of organic liquids (*12*) and more than one order of magnitude larger than $\lambda[\exp(\Delta S^{\ddagger}/R)]^{1/2}$ for diffusion of permanent gases through polymers (*12, 13*). It is difficult to comprehend these differences in terms of larger values of σ_o alone and there is no correlation between $\lambda[\sigma_o \exp(\Delta S^{\ddagger}/R)]^{1/2}$ and the Hildebrand solubility parameter of the swelling solvents. It appears reasonable to expect larger values of λ in the present work since the unit jump distance, λ, for the act of diffusion could be considerably larger in polymers fully swollen with organic solvents than in either liquids or polymers partially swollen by permanent gases. Since the diffusing toluene molecules in the work reported here are considerably larger than the diffusing species in the other two cases previously mentioned, larger values of $\Delta S^{\ddagger}$ would also be expected as reflecting the greater extent of steric accommodation necessary for a diffusing molecule to pass over a repulsive energy barrier between two holes. Aside from these considerations, it does not appear possible to reconcile the various values of $\lambda[\sigma_o \exp(\Delta S^{\ddagger}/R)]^{1/2}$ with the general properties of the swelling solvents. One might speculate that λ, σ_o, and $\Delta S^{\ddagger}$ be larger in cases of greater solubility of swelling solvent. The potential energy barrier for diffusion arises when a diffusing molecule squeezes through a network of polymer chains in the membrane. This energy may be supplied in part by the membrane molecules and in part by the diffusing molecules; this means that the energy for diffusion is distributed among the many degrees of freedom of the membrane molecules themselves as well as the degrees of freedom of the diffusing molecule. This sharing among many degrees of freedom may be interpreted either in terms of the notion of large entropy of activation $\Delta S^{\ddagger}$ or, considering the distribution of molecular segments in space, in terms of large unit jump distances λ.

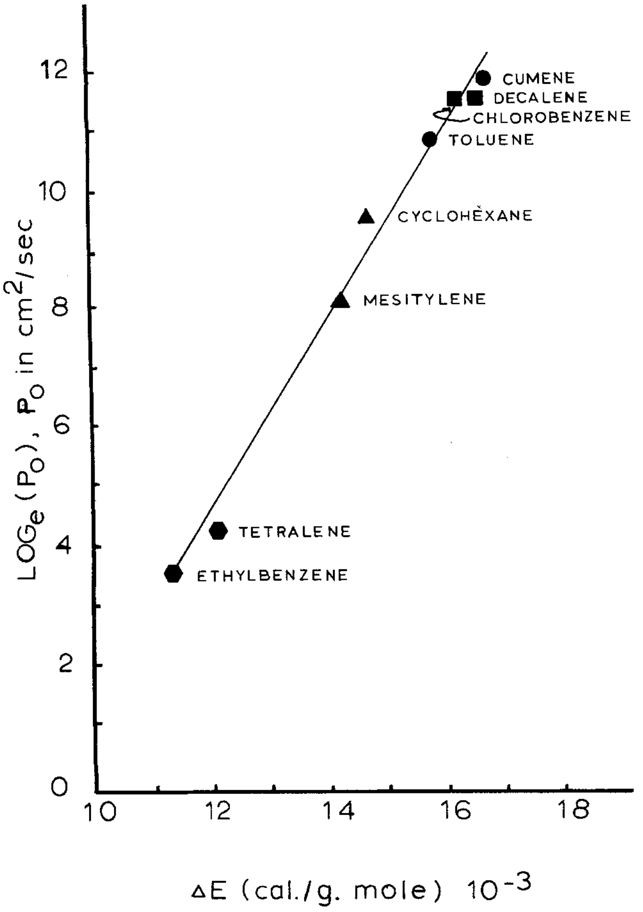

Fig. 5. $Log_e(P_o)$ vs. ΔE.

When P_o is plotted vs. E_p a rather well-defined straight line is obtained as shown in Figure 5. Although similar relationships for diffusion in polymers have been observed and discussed by others (*9*, *14*, *15*) the data found in this work appear to exhibit greater than usual conformity to such a relationship. This kind of relationship is generally thought to imply an equivalent mechanism or equivalent transition state for a series of reactions so related. For example, this kind of behavior is often observed for the kinetics of a series of related reactions over the same catalyst or for the same reaction over a series of different catalysts. In the latter context, the relationship is usually termed a compensation effect since the simultaneous increase in activation energy and in pre-exponential factor compensate each other in a way that tends to preserve the value of the rate constant relatively unchanged.

Two interpretations have been advanced (*9*) for this kind of relationship as observed for diffusion in polymers. The first interpretation rests upon the expected relationship between the magnitude of activation energy and the number of degrees of freedom which is related to $\Delta S^{\neq}$. This consideration leads directly to a similar relationship between log P_o [via Equation (12)] and E_p. The other viewpoint focuses on the fact that the values of log P usually span a considerably smaller range than the values of E_p or log P_o. Then the expression

$$\log P_o = \log P + E_p/4.6T \qquad (13)$$

becomes

$$\log P_o \approx \text{constant} + 0.217\, E_p/T$$

For the data and conditions of this investigation, the constant in the above equation has limits lying between —7.99 and —6.18 whereas log P_o ranges from 5.11 to 1.56 and E_p from 11.41 to 16.54. Thus, for the present situation, it would not be at all accurate to consider log P constant relative to the range of variation of E_p and log P_o. Nevertheless the range in values predicted by Equation (13) for the slope of the straight line in Figure 5 is 0.728 $kcal.^{-1}$ to 0.694 $kcal.^{-1}$ which compares well with the actual estimated slope of about 0.707 $kcal.^{-1}$.

One other interpretation of the relationship between P_o and E_p depicted in Figure 5 is analogous to an argument that has been used to rationalize the compensation effect in catalysis. In the latter context Sosnovsky (*18*) argued that when the compensation effect is observed for a reaction over a suite of differently prepared catalysts, the observed increase in activation energy with increase in pre-exponential factor could correspond to an increased number of active sites (here viewed as emergent dislocations) which interact with one another; as the density of active sites is increased, thereby causing an increase in pre-exponential factor, the interaction between sites changes their energy in such a way that an increased activation energy is required for the catalytic reaction. Studies of diffusion and dissolution of permanent gases in polyethylene by Michaels and Bixler (*19*) indicate that the crystallites in polyethylene are impenetrable and are randomly distributed. Existing crystallites would be destroyed by absorption of organic swelling solvents. If the extent of this destruction depends on the nature of the solvent absorbed, the observed relationship between P_o and E_p can be explained. The more perfectly ordered crystallites would be the most resistant to attack by swelling solvent and, even after some plasticization, might be expected to present larger energy barriers to diffusing molecules. Thus, the production by absorption of organic solvent of additional amorphous regions where diffusion can take place with relatively more ease than in crystallites, would be accompanied by larger barrier energies for the act of diffusion.

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NOTATION

a = constant in Equation (4)
C = molar concentration
D = diffusivity
D' = constant in Equation (4)
D_o = pre-exponential factor in Equation (10)
E_D = energy of activation for diffusion
E_p = energy of activation for permeation
e = base of natural logarithms
ΔH = partial-molar enthalpy change associated with the transfer of 1 mole of toluene from liquid solution to solution in swollen polymer membrane
h = Planck's constant
$|J|$ = molar transport flux
k = Boltzmann's constant
P = permeability
P_o = pre-exponential factor in Equation (7)
R = ideal gas constant
$\Delta S^{\neq}$ = entropy of activation
T = absolute temperature
t = time

Greek Letters

Δx = film thickness
λ = unit jump distance traversed by a diffusing molecule in passing over activation barrier

σ = distribution coefficient or Henry's Law constant relating concentration of toluene in liquid to equilibrium concentration of toluene in membrane
σ_0 = pre-exponential factor in Equation (9)
θ = lag time in Equation (8)
div = divergence
grad = gradient

Subscripts

L = left side of membrane
R = right side of membrane

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Vaporization at the Base of Bubbles of Different Shape During Nucleate Boiling of Water

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Differently shaped bubbles were observed growing during nucleate boiling of water at atmospheric pressure. The surface temperature beneath the bubbles was measured simultaneously with a fast response surface thermocouple. The evaporation from the base necessary to account for the observed cooling was calculated. A comparison of the ratio of vapor volume formed at the base to the total volume of the bubble shows a dependency on bubble shape. The ratio is smallest for spherical bubbles, largest for hemispherical and intermediate for oblate bubbles.

Although nucleate boiling is widely used in modern technology it is still not a well understood phenomenon. A fundamental understanding demands a better knowledge of the bubbles which so clearly characterize nucleate boiling.

In the last few years it has been shown clearly that significant evaporation occurs beneath the bubbles. This evaporation has been named microlayer vaporization. This work was undertaken to determine how much of bubble volume is due to evaporation at the base and whether the amount of microlayer vaporization is a function of bubble shape. Water boiling at atmospheric pressure was studied.

Moore and Mesler (*13*) measured surface temperature fluctuations in nucleate pool boiling of water at atmospheric pressure using a fast response surface thermocouple (*9*). They found that the surface temperature occasionally dropped 20 to 30°F. in about 2 msec. This indicated a rapid extraction of heat during a short time. They postulated that the surface was cooled during initial bubble growth by evaporation of a microlayer into the bubble. Rogers and Mesler (*15*) experimentally showed that the surface temperature drops only when a bubble grows over the fast response surface thermocouple (*9*). Almost at the same time Hendricks and Sharp (*4*) and Bonnet, et al. (*1*) carried out similar work and obtained additional support for this hypothesis. Bonnet, et al. made some preliminary calculations on two bubbles formed on a stainless steel surface. They showed that about 98% of the total vapor generated in these bubbles came from the vaporization at the base of the bubbles. Cooper and Lloyd (*2*) have reported on the evaporation of a microlayer beneath toluene bubbles on a glass surface.

METHOD OF STUDY

The preliminary data for this study was a high-speed motion picture of bubbles growing on a surface instrumented with a fast response surface thermocouple. The thermocouple signal was photographically recorded superimposed on the bubble pictures. From such data both the bubble growth rate and the rate of heat transfer beneath the bubble can be evaluated.

If the measured surface temperature was considered to be the surface temperature of a semi-infinite solid the heat

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