The Effect of Pressure on the Permeation of Gases and Vapors through Polyethylene. Usefulness of the Corresponding States Principle

S. A. STERN, J. T. MULLHAUPT, and P. J. GAREIS

Union Carbide Corporation, Tonawanda, New York

The permeation of carbon dioxide through polyethylene membranes has been studied at pressures up to 54.4 atm. and at temperatures above and below the critical temperature of the gas (31.0°C.). The permeability coefficient is independent of pressure at the highest experimental temperature (61.0°C.), but becomes increasingly pressure-dependent as the temperature is lowered. The principle of corresponding states can be used to correlate the solubility of both gases and vapors in polyethylene over a wide range of temperatures. This principle can also be invoked to obtain an upper limit for the penetrant pressure above which the permeability coefficient becomes pressure-dependent. The effect of pressure on the permeability, solubility, and diffusivity of gases and vapors in polyethylene is discussed in some detail.

Although the mechanism of gas permeation through plastic membranes has been studied by many investigators, surprisingly little information is available on the effect of gas pressure on the rate of permeation. In general, the literature suggests that the permeation of gases with low critical temperatures, such as helium, hydrogen, oxygen, and nitrogen, can be described under steady state conditions by a simple form of Fick's law, and that the permeability coefficients for these gases are independent of pressure (*1*). Carbon dioxide and hydrogen sulfide have been reported to exhibit a similar behavior (*1* to *3*). On the other hand, the permeability coefficients for many organic vapors, which are characterized by high critical temperatures, were found to be strongly pressure dependent (*1*, *4*, *5*).

However, most permeability measurements have been made at relatively low pressures, usually not higher than atmospheric, and near ambient temperatures. The few measurements performed under more extreme conditions indicate that the effect of pressure on the permeation of gases through membranes is perhaps more complex than visualized at present. For example, Sir James Dewar, who was the first to investigate this effect, measured the rate of carbon dioxide and hydrogen permeation through pure rubber at pressures up to 21.4 atm. (*6*). He found that, at 0°C., the permeability coefficient for carbon dioxide increased markedly with increasing pressure. Interestingly, even the permeability coefficient for hydrogen exhibited a slight pressure dependence under these conditions. It appears, therefore, that present concepts on the mechanism of gas and vapor permeation must be re-examined in the light of this behavior.

The purpose of this paper is to report the results from an investigation of two aspects of the above problem. First, new data are presented for the permeation of carbon dioxide through polyethylene at pressures up to 54.4 atm. and at temperatures above and below the critical temperature of the gas (31.0°C.). Second, it is shown that the principle of corresponding states can be invoked to obtain an upper limit for the gas pressure above which the permeability coefficient becomes pressure-dependent. It is further shown from the principle of corresponding states, that it is possible to correlate the solubility of both gases and vapors in polyethylene with their reduced temperatures. This correlation is independent of temperature and, therefore, appears to be more general than that proposed by Michaels and Bixler (*7*), which expresses the solubility as a function of the Lennard-Jones force constant of the solute. Similar concepts and correlations may conceivably apply also to membranes other than polyethylene, and thus contribute to a more detailed and general description of the mechanism of gas and vapor permeation through plastic materials.

EXPERIMENTAL PROCEDURE

Two permeability cells were used in this research for measurements below and above 8 atm., respectively. Both cells were of the variable-volume type and have been described elsewhere (*8*), together with the experimental procedure.

The possible sources of error in the permeability measurements have also been discussed (*8*). It was concluded that the accuracy of the experimental permeability coefficients determined by the described method is of the order of ±5%, the thickness of the membrane being the least accurate of the measured variables. The values of the permeability coefficients are averages over the pressure differential across the membrane.

One of the potential problems examined in some detail was the question of whether the permeability measurements were affected by a resistance to gas flow in the porous stainless steel support for the membrane. It was determined that the apparent permeability of the support was at least four orders of magnitude larger than that of the membrane and, consequently, could not have affected the measurements. This was ascertained by measuring the flow of gases through the support, and by studies with membranes which were considerably more permeable than polyethylene. Moreover, if the flow through the porous substrate had been controlling, the dependence of the flow rate on temperature and pressure would have been different from that observed, which was characteristic of Fickian diffusion through plastic membranes.

Carbon dioxide used in this research was stated to be at least 99% pure. The membrane was 0.001 in. thick Alathon 15 polyethylene.

S. A. Stern is at Syracuse University, Syracuse, New York.

RESULTS

The permeability coefficient, P, for the system carbon dioxide-Alathon 15 polyethylene is shown graphically in Figure 1 as a function of the pressure differential across the membrane, Δp, at the temperatures of 0.4, 9.0, and 40.5°C. The measurements were made with the low-pressure permeability cell for values of Δp of up to 6.1 atm. The permeability coefficient was calculated from the expression

$$P = \frac{q \cdot t}{A \cdot \Delta p} \qquad (1)$$

where q is the rate of gas permeation [cc.(STP)/sec.] through a membrane sample of area A (sq.cm.) and thickness t (cm.), under a pressure differential Δp (cm. Hg.). The units of P are therefore $\frac{\text{cc.(STP)} \cdot \text{cm.}}{\text{sec.} \cdot \text{sq.cm.} \cdot \text{cm. Hg.}}$, as used also by other investigators.

Referring to Figure 1, it is seen that at the highest experimental temperature, 40.5°C., the permeability coefficient is independent of the pressure differential across the membrane. The experiments were performed by varying the pressure on the high pressure side of the membrane, while maintaining the pressure on the opposite side constant and close to atmospheric. Consequently, the permeability coefficient at 40.5°C. is also independent of the applied gas pressure. At 9.0°C., the permeability coefficient increases very slightly with increasing pressure differential (or applied pressure). At the lowest temperature, 0.4°C., the increase in P with increasing Δp is more marked than at 9.0°C.

The permeability coefficient measured under pressure differentials higher than 6.1 atm. is shown in Figure 2 for seven different temperatures. Below the critical temperature of carbon dioxide, 31.0°C., the pressure applied on the membrane is limited by the vapor pressure of the gas. The general trend noted in Figure 1 is more clearly apparent at higher pressure differentials across the membrane. At the highest temperature, 61.0°C., P is independent of Δp over the entire pressure range investigated, that is, up to Δp values of close to 54.4 atm.; at lower temperatures P is seen to increase with increasing Δp. The increase in P is more marked the lower the temperature.

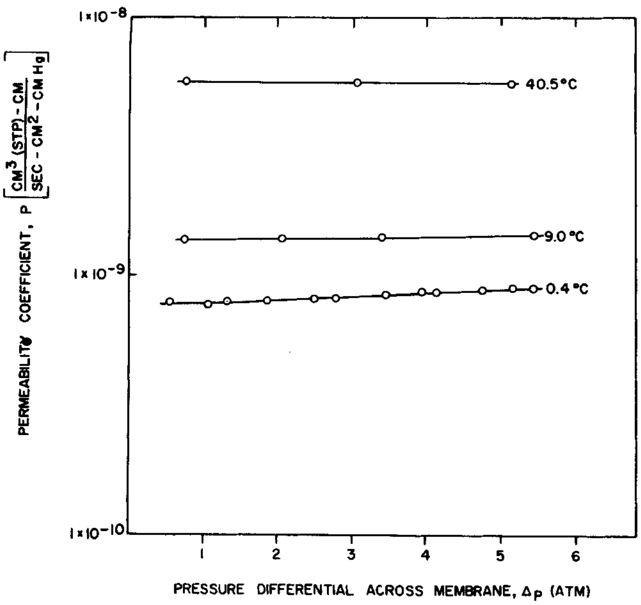

Fig. 1. Permeability coefficient for the system carbon dioxide-Alathon 15 polyethylene as a function of pressure differential up to 6.0 atm.

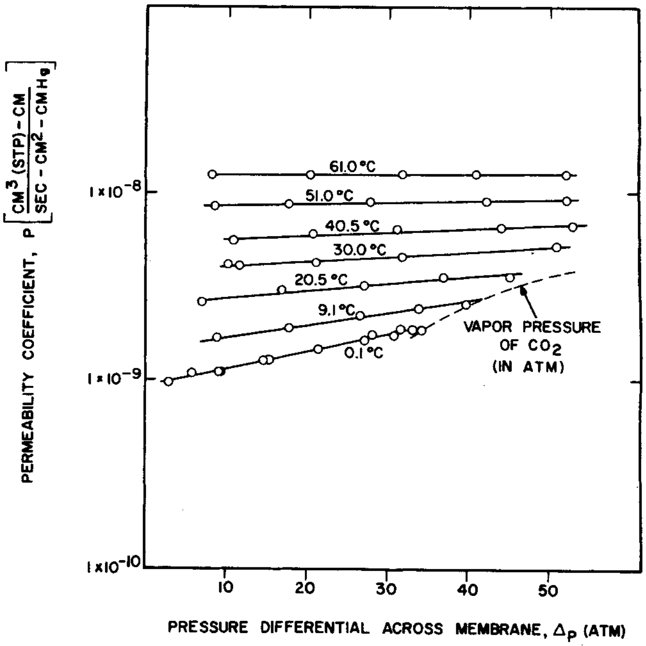

Fig. 2. Permeability coefficient for the system carbon dioxide-Alathon 15 polyethylene as a function of pressure differential up to 54.4 atm.

The effect of temperature on the permeability of Alathon 15 polyethylene to carbon dioxide is shown in Figure 3 in the form of an Arrhenius plot, with the pressure differential across the membrane as a parameter. Figure 3 was obtained by crossplotting the data presented in Figure 1 and 2; the values of the permeability coefficient at $\Delta p = 0$ atm. and $\Delta p = 6.8$ atm. were obtained by extrapolation. The energy of activation of the permeation process decreases with increasing Δp from 7,550 cal./mole at $\Delta p = 0$ atm. to 5,200 cal./mole at $\Delta p = 47.6$ atm., indicating that the membrane is plasticized by the permeating gas.

The present work is in general agreement with similar data reported in the literature. For example, at ambient temperature, the permeability coefficient is essentially independent of pressure differential at Δp's of the order of 1 atm. or less, which correspond to the experimental conditions used by many other investigators. More recently, Li and Henley (*3*) have reported that the permeability coefficient for carbon dioxide and polyethylene at 33°C. is independent of pressure up to about 10.9 atm., while the present data indicate a slight dependence of P on applied pressure and Δp at this temperature. The two sets of data are not strictly comparable, however, because Li and Henley varied their total pressure, but maintained the pressure differential across the membrane constant at only 0.56 atm.

DISCUSSION OF RESULTS

The permeation of gases through plastic membranes is generally visualized as a complex process which is controlled by the activated diffusion of the gas in the membrane (*1*). Under steady state conditions, the diffusion usually obeys Fick's law. If the diffusion coefficient is independent of gas concentration, and the solubility of the gas in the membrane obeys Henry's law, then Fick's law can be integrated to yield Equation (1). The permeability coefficient can be expressed under these circumstances by the relation

$$P = D \cdot S_o \qquad (2)$$

where D is the diffusion coefficient and S_o is the solubility coefficient in Henry's law. P, as defined, should be independent of pressure differential or applied pressure. As

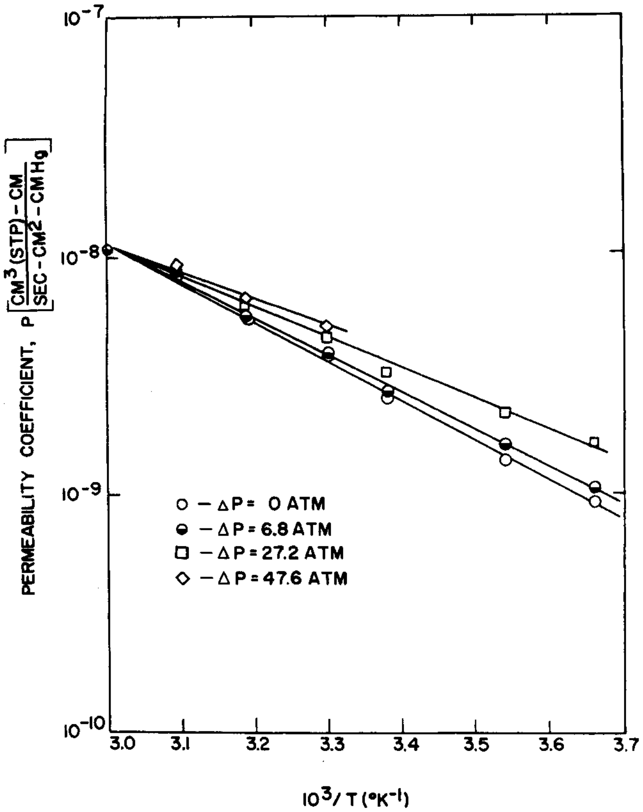

Fig. 3. Effect of temperature on permeability of alathon 15 polyethylene to carbon dioxide as a function of pressure differential.

seen from Figures 1 and 2, this is the case only at the highest experimental temperature or, possibly, for low values of the pressure differential across the membrane.

In analyzing the above data, it is necessary to inquire first whether the dependence of P on Δp could be attributed to the nonideality of the gas phase. In order to test this hypothesis, Henry's law was expressed in terms of fugacity, rather than pressure, and the following relation was obtained for the permeability coefficient

$$P = \frac{q \cdot t}{A \cdot \Delta f} \tag{3}$$

where Δf is the fugacity differential across the membrane corresponding to the pressure differential Δp. The fugacity was evaluated from the generalized charts of Lydersen, Greenkorn, and Hougen (*9*). It was found that the use of Equation (3) accentuated, rather than decreased, the dependence of P on Δp. Consequently, this effect connot be attributed to the nonideality of the gas phase.

The data in Figures 1 and 2 can be represented by the relations

$$P = P' \, e^{m \cdot \Delta p} \tag{4}$$

where P' and m are constants, or by

$$P = P'' \, e^{m \cdot p_H} \tag{5}$$

where $P'' = P' \, e^{-m \cdot p_L}$, p denotes the gas pressure, the subscripts H and L refer to the high- and low-pressure sides of the membrane, respectively, and $(p_H - p_L) = \Delta p$. The constant m decreases with increasing temperature.

This behavior may be due either to the fact that the diffusion coefficient is not independent of the gas concentration in the membrane, or to deviations from Henry's law, or both. Rogers, Stannett, and Swarc (*4*) studied the solution, diffusion, and permeation of several organic vapors in polyethylene and found that the solubility isotherms could be represented by the expression

$$S = \frac{c}{p} = S_o \, e^{\sigma c} \tag{6}$$

where c is the concentration of the organic vapor dissolved in polyethylene at the pressure p, S is the solubility coefficient, S_o is the limiting value of S at $c = o$, and σ is a constant characterizing the concentration dependence of S. They also found that the mean diffusion coefficient, $\overline{D}$, was a similar function of the vapor activity, a_1,

$$\overline{D} = D_o \, e^{\alpha a_1} = D_o \, e^{\alpha\left(\frac{p}{p^o}\right)} \tag{7}$$

where $\overline{D}$ is defined as usual, D_o is the diffusion coefficient at zero activity, pressure, and concentration, and α is a constant characteristic of the penetrant-membrane system at a specified temperature. The vapor activity is given approximately by the relation $a_1 = p/p^o$, where p^o is the vapor pressure of the pure penetrant.

The permeability coefficient can be defined in terms of the mean diffusion coefficient by an expression similar to Equation (2):

$$P = \overline{D} \cdot S \tag{8}$$

By substituting Equations (6) and (7) into (8), one obtains

$$P = (S_o D_o) \, e^{(\sigma c + \alpha a_1)} = P_o \, e^{\left[\sigma c + \alpha\left(\frac{p}{p^o}\right)\right]} \tag{9}$$

where $P_o = D_o S_o$. If the solubility obeys Henry's law, that is, $\sigma = 0$, then Equation (9) reduces to

$$P = P_o \, e^{\beta p} \tag{10}$$

where $\beta = \alpha/p^o$. Equation (10) is formally similar to the empirical relation (5), which has been used to represent the experimental data.

The similarity between Equations (10) and (5) would suggest that the dependence of the permeability coefficient for the carbon dioxide-polyethylene system on applied pressure, or pressure differential across the membrane, could be attributed mainly to the fact that the diffusion coefficient is a function of the gas concentration in the membrane, rather than to deviations from Henry's law. Whether or not this behavior is real cannot be determined at the present time, since neither the solubility nor the diffusivity of carbon dioxide in polyethylene has been measured at higher pressures. However, the general effect of pressure on the solubility, diffusivity, and permeability of gases and vapors in polyethylene is discussed in some detail in the following sections.

GENERAL RELATIONS

SOLUBILITY

Henry's Law Behavior

It was mentioned earlier that the permeability becomes pressure-dependent if the solubility of the penetrant does not obey Henry's law, if the diffusivity is concentration-dependent, or for both these reasons. In this section, general relations describing Henry's law behavior and deviations from it will be explored.

Solubilities have been measured for a variety of solutes in polyethylene. At temperatures near ambient and at pressures at or below atmospheric, Michaels and Bixler (*7*) found that the solution of thirteen gases and vapors was described by Henry's law. Eastburn (*10*) found this to be true for carbon dioxide also at 55°C. up to several atmospheres pressure. In addition, Myers, *et al.* (*11*), established that water vapor obeys Henry's law up to its vapor pressure at 25°C. Durrill and Griskey (*12*) found no deviation from Henry's law in thermally softened polyethylene at 188.4°C. up to 20 atm. for five gases, four of which were studied by Michaels and Bixler.

On the other hand, Rogers, Stannett, and Szwarc (*4*) found large deviations from Henry's law for fourteen organic vapors at temperatures near ambient. Similar results were reported by Eastburn for methane at 33°C. and for ethane at 55°C. at pressures below atmospheric. Henley and Souza Neto (*13*) found a less pronounced deviation from Henry's law for propane at 34°C. at several atmospheres pressure. At temperatures in the range 125° to 228°C., Lundberg, *et al.* (*14*), reported large departures from Henry's law for nitrogen and methane, but at pressures of the order of hundreds of atmospheres.

An examination of these data reveals two main trends. First, the solubility in the Henry's law limit increases as the critical temperature of the solute increases. Secondly, the pressure at which deviation from Henry's law becomes appreciable decreases as the critical temperature of the solute increases. These observations suggest that the principle of corresponding states may provide a unifying correlation of solubility for both gases and vapors. Data from the references cited above were compared on a common basis, in units of moles of solute per unit weight of amorphous polymer per unit pressure. Where necessary, solubilities for partially crystalline polyethylene were converted to values for the amorphous polymer; thermally softened polyethylene was considered to be completely amorphous.

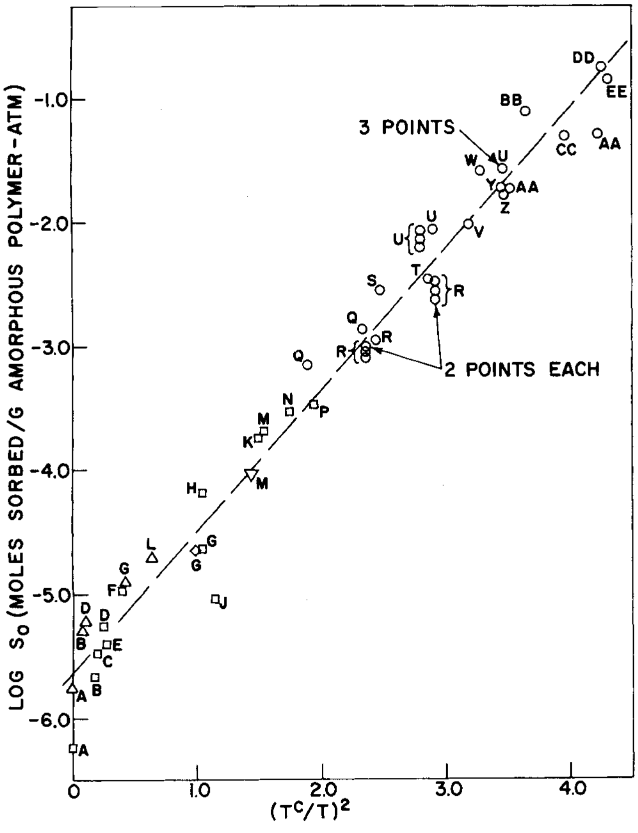

Fig. 4. Correlation of Henry's law solubility coefficient (S_o) in polyethylene with reduced temperature (T/T^c). ○ = data of (*4*), □ = data of (*7*), △ = data of (*12*), ▽ = data of (*13*), and ◇ = data of (*10*). A = helium, B = nitrogen, C = carbon monoxide, D = argon, E = oxygen, F = methane, G = carbon dioxide, H = ethane, J = sulfur hexafluoride, K = propylene, L = difluorochloromethane, M = propane, N = Allene, P = methyl chloride, Q = isobutylene, R = methyl bromide, S = normal pentane, T = ethyl bromide, U = normal heptane, Y = cyclohexane, Z = carbon tetrachloride, AA = benzene, BB = normal octane, CC = toluene, DD = para-xylene, EE = ethyl benzene.

From the principle of corresponding states, one expects the Henry's law solubility coefficient (S_o) to be a unique function of the reduced temperature (T/T^c), where T^c is the appropriate critical temperature. That this is the case can be demonstrated by plotting, in the usual manner, $\log S_o$ against (T^c/T). The solubility data for twenty-eight different substances, having values of S_o spanning five orders of magnitude and having critical temperatures in the range 5.20 to 619.6°K., delineate a single curve. Water vapor, with $S_o = 2.1 \times 10^{-4}$ moles/g.-atm. at 25°C. and $T^c = 647.30$°K., does not fit the correlation.

A more detailed examination of the data shows that $\log S_o$ is a linear function of $(T^c/T)^2$, as is depicted in Figure 4. Solubility data for the twenty-eight gases and vapors (water excluded) are plotted. The data can be represented quite well by a linear regression of $\log S_o$ on $(T^c/T)^2$ which leads to the equation

$$\log S_o = -5.64 + 1.14\,(T^c/T)^2$$

Most of the data fall within a relatively narrow band, Michaels and Bixler's S_o values for helium and sulfur hexafluoride being the most prominent exceptions. The multiplicity of circles at certain values of (T^c/T) is explained by the fact that S_o values were obtained for methyl bromide and normal hexane in polymers of different densities.

The data of Lundberg, *et al.* (*14*), were not used in the correlation because experimental data were not obtained below about 60 atm. pressure, so that reliable values of the Henry's law solubility cannot be determined accurately. Also, since concentrations were reported, rather than solubilities, the pressure dependence of S would have to be obtained from the published plots of c vs. p.

The results reported by Eastburn (*10*) for methane and ethane were also excluded from the correlation. The solubility coefficients for these gases were found to be strongly dependent on pressure, even below 1 atm., in contrast to general experience and in sharp disagreement with the results of Michaels and Bixler. In addition, the solubility coefficient in the limit of zero absolute pressure approaches zero for ethane and becomes negative for methane, according to the data given by Eastburn. Neither result is consistent with Henry's law behavior in the limit of zero concentration. For these reasons, the data must be considered questionable. Eastburn's solubility data for carbon dioxide are subject to some doubt even though they are independent of pressure, because the same experimental technique was used.

Several characteristics of the correlation are of interest. First, solubility coefficients of both gases and vapors are represented by a single equation, so that no artificial distinction need be made. The failure of the correlation to reproduce the solubility of water vapor in polyethylene probably is due to the fact that the corresponding states correlation for nonhydrogen-bonded substances is not suitable for strongly polar, hydrogen-bonded ones. One would expect the correlation to predict with reasonable accuracy the solubilities in the Henry's law region for such substances as hydrogen, deuterium, neon, carbon tetrafluoride, ethylene, nitrous oxide, dichlorodifluoromethane, and ethylene oxide, but not for substances like ammonia, hydrogen chloride, or methanol.

The second feature of the correlation is the linear dependence of $\log S_o$ on $(T^c/T)^2$, instead of (T^c/T), which would be expected from the work of Michaels and Bixler (*7*). They proposed that $\log S_o$ (at 25°C.) was a linear function of (ϵ/k), the molecular force constant evaluated from the Lennard-Jones intermolecular potential function. Values of (ϵ/k) are proportional to the critical temperature T^c, so that at constant experimental temperature T, log S_o would vary linearly with (T^c/T).

The correlation proposed in the present paper is preferred for the following reasons. First of all, the correlation based on $(T^c/T)^2$ encompasses data of several other investigators, in addition to those of Michaels and Bixler, over wider ranges of S_o and (T^c/T). The data of Michaels and Bixler or of Rogers, Stannett, and Szwarc, taken separately, might be approximated by straight-line plots of log S_o vs. (T^c/T). When taken together, the curvature becomes evident. Secondly, the use of T^c in place of (ϵ/k) avoids the disadvantages of Michaels and Bixler's correlation: values of (ϵ/k) are available for relatively few materials, and (ϵ/k) varies with the intermolecular potential function assumed in the calculation of ϵ.

The third feature of the correlation is that the temperature dependence of S is included. Thus, different solutes need not be compared at the same experimental temperature, nor the S_o values of a single solute considered separately. For nine of the twenty-eight substances, data at different temperatures are available so that a check can be made of the temperature dependence predicted by the correlation. In Figure 4, S_o values at various temperatures for a given solute are indicated by symbols with a common letter designation. The shape of the symbols identifies the different investigators who obtained the data. The observed temperature dependence for each of the nine solutes is given by the slope of a line (not shown in Figure 4) through the data at different temperatures. The predicted dependence is, of course, the slope of the heavy, broken line through the data. The agreement with the correlation is as good as can be expected from the scatter in six cases: carbon dioxide, propane, isobutylene, methyl bromide, normal hexane, and benzene.

However, in the case of the other three solutes, helium, nitrogen, and argon, the observed temperature dependence indicates a decrease in S_o with increasing (T^c/T) in contrast to the increase predicted and observed in the other six cases. Part of the reason for this discrepancy may be associated with the heats of solution. Michaels and Bixler found that the apparent heat of solution in polyethylene decreases as the value of (ϵ/k) for the solute increases; similar behavior is observed if T^c is used instead of (ϵ/k). The point of special interest here is the fact that, as the value of T^c increases, the heat of solution decreases from positive values for helium and nitrogen, to a value near zero for argon, to negative values for carbon dioxide and substances with higher critical temperatures. This sequence reflects the similar sequence (but with opposite sign) exhibited by the temperature dependences in Figure 4. Thus, the dependences increase from large negative values for helium and nitrogen, to nearly zero for argon, to positive values for carbon dioxide and the other solutes. As the value of S_o increases, the plasticizing effect of the solute may also have to be considered. In spite of the discrepancy in the temperature dependences of S_o for helium, nitrogen, and argon, the correlation can represent reasonably well the values of S_o over a wide range of experimental temperatures for the following reason. The values of (T^c/T) corresponding to the experimental temperatures are closely spaced, so that the changes in magnitude of S_o are comparable to the scatter in the correlation.

Deviations From Henry's Law Behavior

The success of corresponding states in correlating Henry's law solubilities led to the application of this principle in a more unorthodox fashion. It is of interest to know the point at which departures from Henry's law become noticeable. The only consistent set of experimental data suitable for a general analysis of deviations from Henry's law in polyethylene appear to be those of Rogers, Stannett, and Szwarc (*4*). These authors found that the solubility coefficient $(S = c/p)$ for the 14 organic vapors investigated could be represented by functions of the form $S = S_o \exp (\sigma c)$. These functions imply that Henry's law is obeyed only in the limit $c \rightarrow 0$. Because some substances obey Henry's law at finite concentrations, it is desirable to identify deviations from the law with a characteristic concentration $c_h \neq 0$. Furthermore, it is more convenient to use a pressure $p_S = c_h/S$ than c_h itself, because pressures are more easily measured and because the corresponding states principle is more readily applied.

In order to analyze the data in these terms, p_S was defined as that pressure at which a 5% deviation from the Henry's law solubility would occur. Although this definition is to some extent arbitrary, it is not unreasonable. A deviation of 5% is large enough to be detectable, yet not so large that a meaningful test of Henry's law cannot be made. Thus, with the aid of the 5% criterion $(S/S_o = 1.05)$, values of c_h were calculated using the parameters σ and S_o for amorphous polyethylene; the corresponding values of p_S were then derived. The values of c_h for the vapors investigated range from 1.95×10^{-4} to 3.54×10^{-4}, with an average value $(2.61 \pm 0.31) \times 10^{-4}$ moles solute/g. amorphous polymer/atm. pressure. These values show considerably less variation than the values of the solubility coefficient at unit activity, S_{ao}, given by Rogers, Stannett, and Szwarc, which range from 2.6×10^{-2} to 9.9×10^{-2} cc. solute (as liquid)/cc. amorphous polymer. The values of p_S span two orders of magnitude and are listed in Table 1.

TABLE 1. PREDICTED AND OBSERVED DEVIATIONS FROM PRESSURE INDEPENDENCE IN THE SOLUBILITY AND PERMEABILITY COEFFICIENTS

		S Deviates From S_o by 5% at			
Gas or Vapor	Experimental temperature T (°C.)	Predicted pressure p_S (atm.)	Observed pressure p_S (atm.)	P deviates from P_o by 5% at observed pressure p_P (atm.)	Ref.
helium	0	2.0×10^3		$>5.54 \times 10^1$	(*8*)
	25	2.1×10^3	> 1		(*7*)
	30	2.1×10^3		$>5.54 \times 10^1$	(*8*)
	188.4	2.2×10^3	>20		(*12*)
hydrogen	50	6.0×10^3		$>7.2 \times 10^0$	(*15*)
nitrogen	20.5	1.12×10^3		$>6.5 \times 10^0$	(*16*)
	25	1.18×10^3	> 1		(*7*)
	30	1.24×10^3		$>9.8 \times 10^{-1}$	(*5*)

Gas or Vapor	Experimental temperature T (°C.)	Predicted pressure p_S (atm.)	Observed pressure p_S (atm.)	P deviates from P_o by 5% at observed pressure p_P (atm.)	Ref.
	43	1.43×10^{3}		$>6.5 \times 10^{0}$	(*16*)
	50	1.53×10^{3}		$>6.5 \times 10^{0}$	(*16*)
	188.4	3.9×10^{3}	>20		(*12*)
carbon monoxide	25	1.01×10^{3}	> 1		(*7*)
argon	25	8.7×10^{2}	> 1		(*7*)
	188.4	3.7×10^{3}	>20		(*12*)
oxygen	0	5.5×10^{2}		$>6.5 \times 10^{0}$	(*16*)
	25	8.1×10^{2}	> 1		(*7*)
	42	1.02×10^{3}		$>6.5 \times 10^{0}$	(*16*)
methane	25	2.8×10^{2}	> 1		(*7*)
	33	3.2×10^{2}		$\leqq 9.8 \times 10^{-1}$	(*3*)
				$>9.6 \times 10^{0}$	(*19*)
ethylene	33	3.1×10^{1}		$\leqq 9.8 \times 10^{-1}$	(*3*)
carbon dioxide	0.1	9.8×10^{0}		3.4×10^{0}	this work
	9.1	1.31×10^{1}		6.6×10^{0}	this work
	20.5	1.83×10^{1}		7.1×10^{0}	this work
	25	2.1×10^{1}	> 1		(*7*)
	30	2.4×10^{1}		8.8×10^{0}	this work
	33	2.6×10^{1}		$>1.16 \times 10^{1}$	(*3*)
				$>1.55 \times 10^{1}$	(*22*)
	40.5	3.1×10^{1}		1.22×10^{1}	this work
	51	4.0×10^{1}		3.0×10^{1}	this work
	61	5.0×10^{1}		$>5.4 \times 10^{1}$	this work
	188.4	3.8×10^{2}	>20		(*12*)
ethane	25	1.35×10^{1}	> 1		(*7*)
	33	1.68×10^{1}		$\leqq 9.8 \times 10^{1}$	(*3*)
				$\leqq 2.8 \times 10^{0}$	(*22*)
nitrous oxide	33	2.2×10^{1}		$\leqq 9.8 \times 10^{1}$	(*3*)
sulfur hexafluoride	25	7.1×10^{0}	> 1		(*7*)
propylene	25	2.5×10^{0}	> 1		(*7*)
difluorochloromethane	188.4	8.2×10^{1}	>20		(*12*)
propane	25	2.0×10^{0}	> 1		(*7*)
	33	2.6×10^{0}		$\leqq 9.8 \times 10^{-1}$	(*3*)
				$<4.1 \times 10^{0}$	(*22*)
	34	2.7×10^{0}	1.0×10^{0}		(*13*)
hydrogen sulfide	0	1.54×10^{0}		$>5.7 \times 10^{-1}$	(*2*)
	15	2.7×10^{0}		$>5.6 \times 10^{-1}$	(*2*)
	30	4.6×10^{0}		$>9.6 \times 10^{-1}$	(*2*)
difluorodichloromethane	33	1.68×10^{0}		$\leqq 9.8 \times 10^{-1}$	(*3*)
allene	25	1.31×10^{0}	> 1		(*7*)
methyl chloride	25	9.1×10^{-1}	> 1		(*7*)
isobutylene	−8	1.28×10^{-1}	1.45×10^{-1}	1.5×10^{-2}	(*4*)
	0	1.86×10^{-1}	2.3×10^{-1}	2×10^{-2}	(*4*)
	30	6.3×10^{-1}	3.2×10^{-1}	7×10^{-2}	(*4*)
normal butane	33	5.0×10^{-1}		$\leqq 9.2 \times 10^{-1}$	(*3*)
methyl bromide	−15	2.6×10^{-3}		$\leqq 1.2 \times 10^{-1}$	(*5*)
	0	5.7×10^{-2}	0.93 to 1.20×10^{-1}	1.9×10^{-2}	(*4*)
	20	1.46×10^{-1}		$\leqq 3.5 \times 10^{-1}$	(*5*)
	25	1.81×10^{-1}	1.90×10^{-1}		(*4*)
	30	2.2×10^{-1}	1.96 to 2.8×10^{-1}	5×10^{-2}	(*4*)
	60	6.8×10^{-1}		$\leqq 1.8 \times 10^{-1}$	(*5*)
ethylene oxide	0	7.6×10^{-2}		$\leqq 1.6 \times 10^{-1}$	(*5*)
normal pentane	25	1.08×10^{-1}	6.9×10^{-2}		(*4*)
ethyl bromide	25	7.9×10^{-2}	6.4×10^{-2}		(*4*)
normal hexane	0	9.9×10^{-3}	0.89 to 1.27×10^{-2}	6×10^{-4}	(*4*)
	25	3.5×10^{-2}	2.4×10^{-2}		(*4*)
	30	4.4×10^{-2}	3.2 to 4.5×10^{-2}	4×10^{-3}	(*4*)
chloroform	25	3.2×10^{-2}	2.9×10^{-2}		(*4*)
normal heptane	25	1.31×10^{-2}	7.2×10^{-3}		(*4*)
cyclohexane	25	1.34×10^{-2}	1.39×10^{-2}		(*4*)
carbon tetrachloride	25	1.41×10^{-2}	1.64×10^{-2}		(*4*)
benzene	0	3.3×10^{-3}	4.3×10^{-3}		(*4*)
	25	1.33×10^{-2}	1.46×10^{-2}		(*4*)
	50	5.8×10^{-2}		$\leqq 3 \times 10^{-2}$	(*17*)
normal octane	25	5.4×10^{-3}	3.1×10^{-3}		(*4*)
toluene	25	4.7×10^{-3}	4.6×10^{-3}		(*4*)
para-xylene	25	2.2×10^{-3}	1.53×10^{-3}		(*4*)
ethyl benzene	25	2.2×10^{-3}	1.70×10^{-3}		(*4*)
water	25	5.8×10^{-3}	$>2.9 \times 10^{-1}$	$>2.9 \times 10^{-1}$	(*11*)

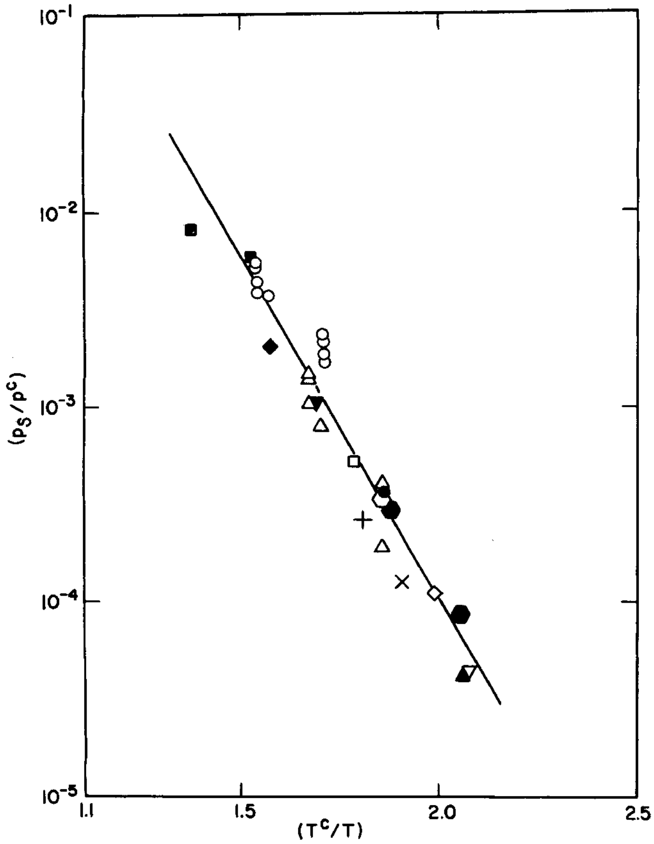

Fig. 5. Correlation of reduced pressure (p_S/p^c) for 5% deviation from Henry's law in polyethylene with reduced temperature (T/T^c). Key to symbols: ■ isobutylene, ○ methyl bromide, ◆ normal pentane, ▼ ethyl bromide, △ normal hexane, □ chloroform, + normal heptane, ⬡ cyclohexane, ● carbon tetrachloride, ⬡ benzene, × normal octane, ◇ toluene, ▲ para-xylene, ▽ ethyl benzene.

The principle of corresponding states was applied in a manner analogous to that used for vapor pressure. A plot of log (p_S/p^c) against (T^c/T) is shown in Figure 5, where p^c is the appropriate critical pressure. Log (p_S/p^c) is a linear function of (T^c/T), and a linear regression of the former variable on the latter yields the equation:

$$\log (p_S/p^c) = 3.025 - 3.50\,(T^c/T)$$

This function correlates not only the values of p_S for different substances, but also the values of p_S for the same solute at different temperatures. Solubility data were obtained at significantly different temperatures with four of the vapors studied by Rogers, Stannett, and Szwarc. As can be seen from Figure 5, the observed temperature dependence for p_S for these solutes is given by the correlation within the limits imposed by the scatter.

In order to test the p_S correlation and assess its value, the predicted departures from Henry's law in polyethylene for solutes other than those studied by Rogers, Stannett, and Szwarc have been compared with available experimental data. Most of these solubility data were obtained at pressures where Henry's law was obeyed, so that experimental values of p_S cannot be derived. However, the maximum pressures employed in these investigations restrict the range of validity for predicted p_S values. That is, the predicted values of p_S should be greater than the maximum experimental pressures.

For the 14 different solutes studied by Michaels and Bixler (*7*) and by Durrill and Griskey (*12*), the predicted p_S values are entirely consistent with the maximum experimental pressures, as is indicated in Table 1. These include data at widely separated temperatures and pressures for the four solutes common to both investigations. In the cases where the experimental boundaries approach the predicted values, allene and methyl chloride at 25°C. and monochlorodifluoromethane at 188.4°C., there is good agreement. Michaels and Bixler mentioned that they studied methyl chloride only at 25°C. and anticipated deviation from Henry's law at lower temperatures for pressures $\leqq 1$ atm. At 15°C., the value of p_S predicted for methyl chloride is 6.2×10^{-1} atm. However, in the case of water vapor, Myers, et al. found that Henry's law was obeyed up to the vapor pressure at 25°C., so that the predicted value of p_S is almost two orders of magnitude too low.

Aside from the data used to derive the p_S correlation, only a few solubility measurements are available that exhibit departures from Henry's law in polyethylene. Unfortunately, not all of these data can be used to test the correlation. From the results of Henley and Souza Neto (*13*) for propane at 34°C. an experimental value of p_S can be obtained, equal to 1.0 atm. This value is in approximate agreement with the predicted p_S value, 2.7 atm. The results of Lundberg, et al. (*14*) for nitrogen and methane at high temperatures and pressures are not suitable for a quantitative check for the reasons given earlier. However, upper limits for p_S may be approximated by estimating the pressure at which the solubility coefficient deviates by 5% from its value at the lowest experimental pressure. As is shown in Table 1, there is poor agreement; the predicted p_S values are about an order of magnitude greater than the values estimated from the data of Lundberg, et al. The results of Eastburn (*10*) for methane and ethane have not been used to test the correlation for the reasons presented earlier and because a value of p_S consistent with its definition cannot be derived from these data.

In summary, the correlation of p_S based on corresponding states provides a satisfactory representation of deviations from Henry's law in polyethylene for the great majority of cases involving twenty-nine different solutes at temperatures in the range 0 to 228°C. The inability to predict a meaningful value for water vapor is not surprising, in view of the limitations of the corresponding states principle discussed earlier. The discrepancies for nitrogen and methane at high temperatures and pressures are somewhat unexpected. However, it is possible that the data of Lundberg, et al. may not be valid tests of the p_S correlation. These data for nitrogen and methane are the only ones for which the solubility in polyethylene decreased with increasing pressure (positive deviations from Henry's law). In contrast, the correlation of p_S is based on data characterized by negative deviations from Henry's law.

DIFFUSIVITY

The purpose of this section is to examine briefly the effect of penetrant concentration on the diffusivity coefficient. Rogers, Stannett, and Szwarc (*4*) cite numerous investigations of diffusion of organic vapors in polymers, and in most of these the diffusion coefficient was found to be strongly dependent on concentration. Particularly interesting is the fact that the diffusivity appears to be more strongly affected by penetrant concentration than the solubility. Thus, it was observed in many cases that the diffusion coefficient was concentration-dependent at penetrant concentrations which were low enough that the solubility still obeyed Henry's law. Since the average penetrant concentration in the membrane depends on the applied pressure, it may be speculated that, as the pressure is increased, the diffusion coefficient would become concentration-dependent before deviations are observed from Henry's law. Consequently, it is possible to define, as in the case of the solubility, a pressure, p_D, at which the mean diffusion coefficient has changed by a specified amount from its value at $p \to 0$. Moreover, it would appear that p_D will be lower than p_S, the pressure at which the solubility will deviate from Henry's law by the same fractional amount.

The available literature for polyethylene is much too scarce to draw any reliable conclusions in this regard. However, the above speculations seem to be substantiated by the data of Rogers, Stannett, and Szwarc (*4*) for methyl bromide at 0 and 30°C., isobutylene at —8, 0, and 30°C., benzene at 0°C., and normal hexane at 0 and 30°C. Values of p_D were calculated for a 5% increase in the diffusion coefficients, that is, for $\overline{D}/D_o = 1.05$, where $\overline{D}$ is the mean diffusion coefficient at a specified pressure, and D_o is the corresponding value at $c \to o$. In all cases, it was found that $p_D < p_S$. A similar behavior is also evident from the data of Lundberg, et al. (*14*) for methane and nitrogen in thermally softened or molten polyethylene, between 125 and 228°C. It should be noted that the diffusivity and the solubility of the organic vapors near ambient temperature increased with increasing pressure, while the opposite trend was reported for methane and nitrogen in the high temperature measurements.

PERMEABILITY

The arguments presented in the preceding sections indicate that p_S may also be considered an upper limit to the pressure range in which the permeability coefficient is essentially independent of pressure. More precisely, p_S defines an upper limit to the pressure range in which the increase in the permeability coefficient with increasing pressure does not exceed a specified value; in the present work, this value has been selected to be within the experimental error of the measurements.

The validity of the above assumption is tested in Table 1 for the permeability of polyethylene to a variety of gases and vapors. The table compares the values of p_S, as obtained from the proposed correlation, with a pressure p_P at which the corresponding permeability coefficients were estimated to have increased by 5% above their values at $p \to 0$. In view of the previous discussions, it is expected that $p_P \lesssim p_D < p_S$. Most measurements were performed at pressures much lower than p_S; the permeability coefficients obtained under these conditions were found to be, as predicted, independent of pressure. Some measurements were made at pressures higher than p_S; the permeability coefficients reported for these cases are pressure-dependent, also in accordance with the predicted behavior. In the few cases where permeability coefficients were determined over a meaningful pressure range it was found that $p_P < p_S$, as suggested previously. The individual measurements are discussed below in detail.

Light Gases

The values of p_S for light gases, such as helium, hydrogen, methane, nitrogen, oxygen, argon or carbon monoxide, are found to be very high (of the order of 10^2 to 10^3 atm.) at temperatures near or above the ambient. Consequently, the permeability coefficients for these gases should be pressure-independent at the temperatures under consideration and in the pressure ranges in which permeabilities are usually measured. This is substantiated by the measurements of Stern, et al. (*8*) for helium at 0 and 30°C. and at pressures up to 54.4 atm; Brubaker and Kammermeyer (*15*) for hydrogen at 50°C. and pressures between 1.4 and 7.14 atm; Stern and Gareis (*16*) for oxygen and nitrogen between 0 and 50°C. and at pressures up to 6.5 atm; and Waack, et al. (*5*), and Myers, et al. (*11*) for nitrogen near ambient temperature and atmospheric pressure.

Carbon Dioxide

In all the cases mentioned above, the measurements were made at pressures which were only a small fraction of p_S and, hence, no values could be obtained for p_P. The present work with carbon dioxide clearly shows that $p_P < p_S$ for all temperatures investigated except the highest (61°C). Generally, it appears that $p_P \lesssim 0.5\ p_S$; the discrepancy at 61°C. requires further investigation, but in any case is not large.

Hydrogen Sulfide

The data of Heilman, et al. (*2*) for hydrogen sulfide are consistent with the assumption that $p_P < p_S$. Unfortunately, these measurements were not extended over a sufficiently wide range of pressures to permit an estimate of p_P. Nevertheless, the trend is definite. The permeation of hydrogen sulfide was measured between 0 and 30°C. at pressures lower than about 0.2 to 0.4 p_S, depending on temperature. As expected, the permeability coefficient was found to be independent of pressure.

Methyl Bromide and Ethylene Oxide

Waack, et al. (*5*) measured the permeation of methyl bromide at —15 and 20°C. at pressures higher than p_S. In accordance with expectations, the permeability coefficient was strongly pressure-dependent. Measurements with methyl bromide at 60°C. and at pressures above about 0.3 p_S also showed that the permeability coefficient was pressure-dependent; these data indicate that at 60°C. $p_P < 0.3\ p_S$. Rogers, et al. (*4*) also found the permeability of methyl bromide at 0° and 30°C. to be strongly pressure-dependent at pressures below 1 atm. The values of p_P calculated from their data show that $p_P < p_D$ and $p_P \approx 0.2 - 0.5\ p_S$.

The permeation of ethylene oxide at 0°C. was measured by Waack, et al. (*5*) at several pressures higher than the predicted value of p_S. The permeability exhibited the expected dependence on pressure, but a reliable value of p_P cannot be determined from the data due to scatter at the lower pressures.

Isobutylene, Hexane, and Benzene

Rogers, et al. (*4*) have measured the permeabilities at pressures below 1 atm. of isobutylene at —8 and 30°C., of normal hexane at 0 and 30°C., and of benzene at 0°C. In all cases strong dependence on pressure was observed. For these vapors, the respective values of p_P and p_D are approximately equal, while $p_P \approx 0.1 - 0.2\ p_S$.

The permeability of benzene at 50°C. was reported by Barrer and Fergusson (*17*) to be strongly pressure-dependent. Their measurements were made at pressures higher than the predicted value of p_S, so that only an estimate of an upper limit of p_P can be derived from the data.

Water

Myers, et al. (*11*) found the permeability of water vapor in polyethylene to be independent of pressure up to the vapor pressure. Their results are contrary to what is predicted from the correlation. As was discussed in the section on solubility, the corresponding states correlation derived for mostly nonpolar materials would not be expected to apply to polar, hydrogen-bonded substances such as water.

The Data of Li and Henley

Li and Henley (*3*) have measured the permeation of carbon dioxide, methane, ethylene, ethane, propane, butane, nitrous oxide, and dichlorodifluoromethane at 33°C. and at pressures up to about 11 atm. Their data are interesting and require a more detailed discussion.

Li and Henley found that the permeability coefficient for carbon dioxide was independent of pressure in the range investigated, but that the permeability coefficients for all other gases were pressure-dependent and could be expressed by an exponential relation similar to Equation (4). The data for the latter gases exhibit two peculiarities. First, the differences in the pressure dependence of these gases, as expressed by the exponent m in Equation (4), are surprisingly small. For example, the values of m vary by a factor of less than two for gases so different in physical properties as methane and dichlorodifluoromethane. Second, the data suggest that the permeability coefficients of all gases, except carbon dioxide, may be pressure-dependent even near atmospheric pressure; this behavior is contrary to the observations of Michaels and Bixler (7), at least for methane, ethane, and propane.

The dependence of the permeability coefficients on pressure is attributed by Li and Henley, very reasonably, to the plasticizing effect of the penetrants on the membrane. They interpreted their results by correlating the difference between the Hildebrand solubility parameter of the gas and the polymer with the exponent m of Equation (4). Unfortunately, the solubility parameters used by these investigators for the gases near their critical temperatures were not calculated by the special methods developed for this purpose (*18*, *19*). Additionally, solubility considerations by themselves cannot explain the striking *dissimilarity* in the effect of pressure on the permeability coefficients of carbon dioxide and of nitrous oxide or ethane, whose critical temperatures are quite close. In fact, the solubilities of carbon dioxide and nitrous oxide in a large number of organic liquids are very similar, as pointed out by Hildebrand and Scott (*20*).

More recently, the permeability of polyethylene to methane (*21*), ethane (*22*), and propane (*22*) at 33°C. has been redetermined by Riley in the general pressure range studied by Li and Henley. He found that the permeability coefficient for methane was independent of pressure, contrary to the results of Li and Henley, while the pressure dependence for ethane was an order of magnitude lower than that reported by the latter investigators. The data of Riley for propane extend the range of pressure and show the same pressure dependence as those of Li and Henley. However, the pressures investigated by Riley are greater than p_S, in contrast to those of Li and Henley. The results of Riley for ethane, on the other hand, suggest that the permeability coefficient of this gas may be measurably pressure-dependent at pressures as low as atmospheric, which is contrary to the findings of Michaels and Bixler.

So far as the corresponding states correlation is concerned, Table 1 indicates agreement with the data of Li and Henley for carbon dioxide and butane, and with the data of Riley for methane, carbon dioxide (*22*), and propane. However, this agreement may be fortuitous, particularly in the case of butane. Clearly, new and more detailed permeability measurements are required before a meaningful comparison can be made with the proposed correlation.

CONCLUSIONS

The principal conclusion that may be drawn from this work is that the generally held views on the effect of pressure on the mechanism of gas and vapor permeation through plastic membranes are somewhat oversimplified. This situation is probably due to the fact that solubility, diffusivity, and permeability measurements have been made, with few exceptions, over limited ranges of pressure and temperature only.

The permeability coefficient for gases and vapors in polyethylene, and probably also in other membranes, is undoubtedly dependent on the applied penetrant pressure. The differences between the effect of pressure on the permeabilities of various gases and vapors are clearly only a matter of degree, as indicated by the corresponding states correlation. When the reduced temperature of the penetrant is low, due to the particular experimental conditions, the pressure dependence of the permeability coefficient could be sufficiently large to be detected even below atmospheric pressure. On the other hand, if the reduced temperature is high, the pressure dependence may be too small to be observed in the range of pressures customarily used in permeability measurements.

This work has also demonstrated the usefulness of the corresponding states principle in correlating the solubilities, within Henry's law limit, of both gases and vapors in polyethylene. This correlation does not appear to be applicable to hydrogen-bonded penetrants, nor is it expected to hold below the glass transition temperature of the polymer. As mentioned previously, similar concepts may be found useful also for other penetrant-membrane systems.

It is obvious that the proposed application of the corresponding states principle must be subjected to stringent tests before its validity can be unambiguously ascertained. It is hoped that reliable experimental data which would permit such tests will become available in not too distant a future.

NOTATION

A = membrane area
a_1 = activity of dissolved vapor
c = concentration of dissolved vapor in membrane
c_h = concentration of solute at which $S/S_o = 1.05$
D = diffusion coefficient for gases
$\overline{D}$ = mean diffusion coefficient for vapors
D_o = diffusion coefficient at $\alpha a_1 = 0$
Δf = fugacity differential across membrane
k = Boltzmann's constant
m = constant in Equations (4) and (5)
p = pressure
Δp = pressure differential across membrane
p_H = value of pressure on high-pressure side of membrane
p_L = value of pressure on low-pressure side of membrane
p_s = pressure of solute at which $S/S_o = 1.05$
p_D = pressure of solute at which $\overline{D}/D_o = 1.05$
p_P = pressure of solute at which $P/P_o = 1.05$
p^o = vapor pressure of pure solute
p^c = critical pressure of pure solute
P = mean permeability coefficient
P_o = permeability coefficient at $\sigma c = 0$ and $\alpha a_1 = 0$ in Equations (9) and (10)
P', P'' = constants in Equations (4) and (5)
q = volumetric rate of gas permeation
S = solubility coefficient, given by c/p
S_o = Henry's law solubility coefficient; value of S at $\sigma c = 0$
S_{ao} = value of solubility coefficient at unit activity
t = membrane thickness
T = absolute temperature
T^c = critical absolute temperature

Greek Letters

α = constant in Equation (7) characterizing the activity dependence of $\overline{D}$
β = constant in Equation (10) characterizing the pressure dependence of P

ϵ = minimum value of intermolecular potential energy

(ϵ/k) = molecular force constant

σ = constant in Equation (6) characterizing the concentration dependence of S

LITERATURE CITED

1. Rogers, C. E., J. A. Meyer, V. Stannett, and M. Szwarc, *Tappi*, **39**, 737, 741 (1956).
2. Heilmann, W., V. Tammela, J. A. Meyer, V. Stannett, and M. Szwarc, *Ind. Eng. Chem.*, **48**, 821 (1956).
3. Li, N. N., and E. J. Henley, *AIChE J.*, **10**, 666 (1964).
4. Rogers, C. E., V. Stannett, and M. Szwarc, *J. Polymer Sci.*, **45**, 61 (1960).
5. Waack, R., N. H. Alex, H. L. Frisch, V. Stannett, and M. Szwarc, *Ind. Eng. Chem.*, **47**, 2524 (1955).
6. Dewar, J., *Proc. Roy. Inst. G. Brit.*, **21**, 813 (1914-16).
7. Michaels, A. S., and H. J. Bixler, *J. Polymer Sci.*, **50**, 393 (1961).
8. Stern, S. A., P. J. Gareis, T. F. Sinclair, and P. H. Mohr, *J. Applied Polymer Sci.*, **7**, 2035 (1963).
9. Lydersen, A. L., R. A. Greenkorn, and O. A. Hougen, *Univ. Wisconsin, Eng. Exp. Sta., Res. Rep.*, No. 4 (Oct. 1955).
10. Eastburn, F. J., MS thesis, Stevens Institute of Technology, Hoboken, N.J., (1963).
11. Myers, A. W., J. A. Meyer, C. E. Rogers, V. Stannett, and M. Szwarc, *Tappi*, 44, 58 (1961).
12. Durrill, P. L., and R. G. Griskey, *AIChE J.*, **12**, 1147 (1966).
13. Henley, E. J., and J. A. de Souza Neto, *ibid.*, 1030 (1966).
14. Lundberg, J. L., M. B. Wilk, and M. J. Huyett, *J. Polymer Sci.*, **57**, 275 (1962).
15. Brubaker, D. W., and K. Kammermeyer, *Ind. Eng. Chem.*, **45**, 1148 (1953).
16. Stern, S. A., and P. J. Gareis, Unpublished data.
17. Barrer, R. M., and R. R. Fergusson, *Trans. Faraday Soc.*, **54**, 989 (1958).
18. Chao, K. C., and J. D. Seader, *AICHE J.*, **1**, 598 (1961).
19. Prausnitz, J. M., and F. H. Shair, *ibid.*, **1**, 682 (1961).
20. Hildebrand, J. H. and R. L. Scott, "The Solubility of Nonelectrolytes," chap. XV, p. 248, Reinhold Pub. Co., New York, (1950).
21. Riley, J. W., Private communication.
22. ———, Ph.D. thesis, Stevens Institute of Technology, Hoboken, N. J. (1965); data reported by E. J. Henley and M. L. dos Santos, AIChE Houston Meeting, (Feb., 1967).

Manuscript received June 16, 1967; revision received December 6, 1967; paper accepted January 10, 1968.

Permeation through Plastic Films

N. N. LI and R. B. LONG

Esso Research and Engineering Company, Linden, New Jersey

Data are presented on the solubility in and permeation through polyolefin films of a number of gases and liquids. The permeation rates are found to be dependent on the type of film, the concentration and the temperature. A classical diffusion model explains the permeation mechanism and other relations serve to correlate the data.

Polymer films can function as remarkably selective membranes, separating mixtures of chemically dissimilar and sterically different compounds (*2, 6, 8, 9, 11, 12*). The process is, however, not well understood. In this work and in the previous work (*5, 6*), permeation of hydrocarbon gases at subcritical and supercritical conditions