

## Polymer Structure and Gas Permeation.

### I. Thermodynamic Interpretation of Permeation

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The possibility that structural changes in polymeric materials (plastic films) could give rise to changes in permeation behavior leads to the intriguing thought that gas permeability data in turn could be used to detect and interpret structural differences. The mechanism of permeation is usually considered to consist of three steps: absorption or adsorption upon the upstream boundary, followed by activated diffusion through the membrane and then dissolution or evaporation from the downstream boundary. Regardless of the mechanism, thermodynamic principles must be considered. Thermodynamically, the polymer system possesses properties such as internal energy,  $E$ , entropy,  $S$ , etc., which are dependent upon the membrane itself.

Over the past twenty years permeability dependence upon temperature has frequently been correlated by means of a linear Arrhenius plot. This correlation is expressed mathematically by:

$$P = P_0 \exp \{ -E_p/RT \} \quad (1)$$

where  $P$  is the permeability constant,  $P_0$  is the permeability constant extrapolated to zero degrees Kelvin,  $R$  is the universal gas constant,  $T$  is absolute temperature, and  $E_p$  is the activation energy of permeation. Values of  $E_p$  and  $P_0$  are unique for each membrane-gas system used.

Attempts to show the interdependence of the several membranes in terms of the  $E_p$  values have been only marginally successful. Perhaps the major difficulty is the strong dependence of polymeric properties upon the film's prior history. The film may appear to be in equilibrium, but this equilibrium may be quite transitory. This is evident in the case of shrinkable films, such as those made of irradiated polyolefins and polyvinylidene chloride copolymers. Since the permeability of films is primarily a function of structural aspects such as crystallinity, it is not surprising that generalizations concerning permeabilities have not been more closely defined.

The conventional mechanism proposed for permeation (absorption, diffusion, and evaporation) has led investigators to place great reliance upon the  $P = DS$  relation. In spite of the interdependence of this relationship,

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the experimental agreement seems convincing. Nevertheless, this approach has not resolved all of the anomalies nor does it fundamentally explain the variety of permeabilities which have been measured of chemically identical films.

On the other hand if one postulates, as did Meares,<sup>1</sup> that permeation "... appears to be governed by the energy required to separate the surrounding medium to give sufficient cross section for the diffusing molecule to pass. . .," a different approach can be taken. The energy "consumed" in permeation suggests a thermodynamic treatment. Since permeability constants are convincingly dependent upon an energy term as in eq. (1), thermodynamics may be helpful in determining the interrelationships of polymeric responses.

The model assumed in this paper concerns the process of "hole formation" within the membrane and its thermodynamic consequences as related to steady-state permeation.

Several assumptions are required in this presentation aside from the major one involving the "hole formation" model. They are as follows.

(1) The membrane-gas system is bounded by the membrane surfaces perpendicular to the flow direction.

(2) The volume of the membrane-gas system under steady-state permeation is constant.

(3) The temperature of the membrane-gas system under the imposed experimental conditions is constant for any particular determination of permeability.

(4) The gas content in the system is negligible with respect to the membrane and hence does not affect the thermodynamic properties. Even if the gas content were to be taken into account, the solubilities are less than 0.1% of the total and would not materially alter the total thermodynamic properties. The gas solubilities in plasticizers are about 10-fold greater than in the unplasticized plastic.

(5) The molecular weight distribution is identical in all portions of the membrane whether crystalline or amorphous, relaxed or stressed, unoriented or oriented.

(6) The expansion of the gas across the membrane is reversible. The model of hole forming does not require a gas continuum from boundary to boundary. The gas expands by an almost infinite number of hole-forming steps and thus the net expansion is approximately reversible.

(7) The permeability constant is directly proportional to the equilibrium constant for the permeation process. The analogy to chemical processes is direct. The greater the negative value of the Gibbs standard free energy,  $\Delta F^\circ$ , in chemical processes or the Helmholtz standard free energy,  $\Delta A^\circ$ , in the permeation process, the more spontaneous the reaction. This concept is fundamental to the thermodynamic treatment. The subsequent mathematical steps illustrate the significance of this assumption.

The maximum work capabilities of any isothermal, isochoric process is called the Helmholtz free energy or work function,  $A$ . This work function

is related to other thermodynamic properties in an isochoric system by eq. (2).

$$A = E - TS \quad (2)$$

The permeability constant,  $P$ , is exponentially dependent upon an energy term and, if  $A$  is that energy term, eq. (1) may be rewritten as follows:

$$P = P_0 \exp \{ -E/RT + S/R \} \quad (3)$$

A consequence of eq. (3) is that the equilibrium constant for the "reaction" is directly proportional to the permeability constant as is shown below. The criterion for equilibrium in an isothermal, isochoric process is:

$$(\Delta A)_{T,V} = 0 \quad (4)$$

Then, by traditional methods the equilibrium constant is found to be:

$$\Delta A_T^0 = -RT \ln K \quad (5)$$

If the standard state is chosen to be  $0^\circ\text{K}$ ., and a constant  $P_0$  is defined at this temperature, then by assumption (7) we may write:

$$A = -RT \ln (P/P_0) \quad (6)$$

Substituting eq. (2) into eq. (6) and exponentiating yields eq. (3).

In statistical thermodynamics the work function can be determined from the partition function. In this case

$$\Delta A = -RT \ln (Q_2/Q_1) \quad (7)$$

where the change in work content  $\Delta A$ , refers to the difference obtained when two thermodynamic states are involved and  $Q_2$  and  $Q_1$  are the partition functions of the system in states 2 and 1, respectively. Similarly, we may relate the change in  $\Delta A$  in terms of permeability constants by use of eq. (6).

$$\Delta A = (E_2 - E_1) - T(S_2 - S_1) = -RT \ln (P_2/P_1) \quad (8)$$

From this analogy it appears that the permeability constant is some function of the partition function. Thus the energy levels, molecular species, etc., are related to permeability. Of course, it would require considerable effort to verify the relationship of  $(P/P_0)$  and  $Q$ , because of the complexity in determining such solid-state partition functions.

### Crystallinity and Permeability

By making use of assumption (5) and eq. (8) the effect of the crystalline content of a plastic film may be estimated.

In this instance, we consider two films as being identical except as to crystalline content. Further, we assume that the crystallinity differences do not alter the internal energy levels and that the internal energy is pri-

marily a function of temperature only. Thus with  $E_2 = E_1$ , eq. (8) can be written as follows:

$$P_2/P_1 = \exp\{(S_2 - S_1)/R\} \quad (9)$$

Many investigators have shown that the gas permeability is reduced by increases in crystallinity. Crystallinity is a manifestation of molecular order and with increases in order the entropy is reduced. Thus eq. (9) fits the general trend that decreased entropy (increased crystallinity) decreases the permeability. The dependence established by eq. (9) is that the permeability is logarithmically dependent upon entropy.

Denoting crystallinity with subscript  $c$  and amorphism with  $a$ , the mole fraction of the crystalline content,  $n_c$ , is related to the mole fraction of amorphous content,  $n_a$  by:

$$n_a + n_c = 1 \quad (10)$$

The total entropies of the two films at the two states are related as follows:

$$S' = n'_a S_a + n'_c S_c \quad (11a)$$

$$S'' = n''_a S_a + n''_c S_c \quad (11b)$$

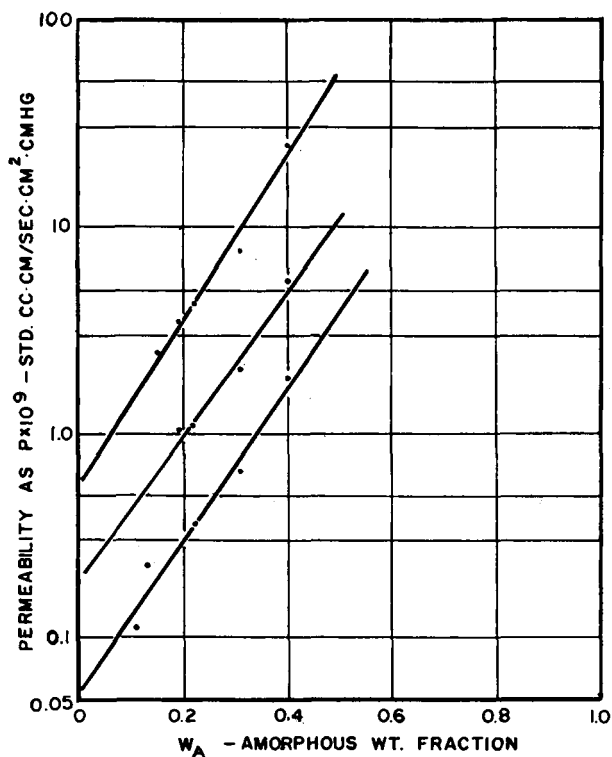


Fig. 1. Permeability dependence on crystallinity of polyethylene.

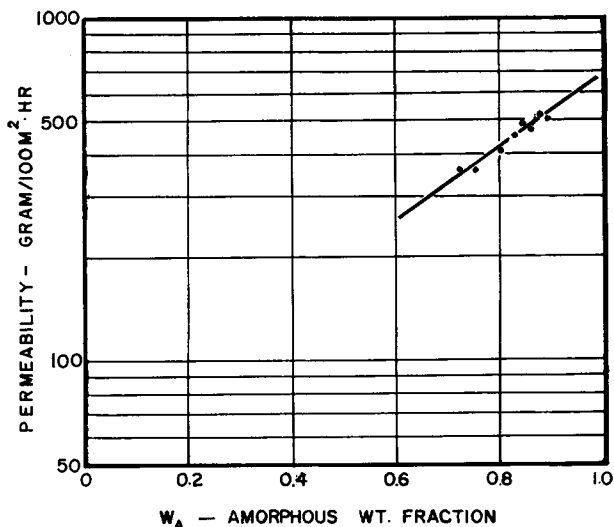


Fig. 2. Water vapor permeability dependence on crystallinity of nylon 610.

Subtracting  $S''$  from  $S'$  and making use of eq. (10) yields:

$$\ln (P'/P'') = (S_a - S_c)(n'_a - n''_c)/R \quad (12)$$

Since the molecular weights of the amorphous and crystalline zones are assumed to be identical, the weight fractions, rather than the mole fractions, may be used to form eq. (13).

$$\ln (P'/P'') = (S_a - S_c)(w'_a - w''_c)/R \quad (13)$$

The quantity  $(S_a - S_c)$ , (subsequently designated as  $\Delta S_{ac}$ ) is the entropy of crystallization and can be found by evaluating the slope of a plot of the logarithm of permeability versus the amorphous weight fraction. The entropy of crystallization should be independent of the gas used. The utility of eq. (13) is evident. If the  $\Delta S_{ac}$  quantity is known for a given material at a particular temperature then the crystalline content of an unknown film may be determined.

The validity of eq. (13) was tested by use of the polyethylene permeability data of Meyers et al.<sup>2</sup> The plot of these data is shown in Figure 1. The linear least squares fit of the data was determined, and  $\Delta S_{ac}$  values were found to be 4.11, 4.36, and 4.68 g. cal/g.-mole<sup>o</sup>K. for oxygen, nitrogen, and carbon dioxide, respectively. From the root mean square of these slopes  $\sigma_{y,z}$ , the standard deviation in the determination of the entropy of crystallization was found to be 0.07, 0.18, and 0.15, respectively.

The data of Lasoski and Cobb<sup>3</sup> for water vapor permeability of nylon 610 are plotted in Figure 2. In this case the value of  $\Delta S_{ac}$  was found to be 1.275 g. cal/g.-mole<sup>o</sup>K. Lasoski and Cobb had previously shown, through use of the  $P = DS$  relation, that the permeability was dependent upon the square of the amorphous volume. The standard deviations of these cor-

relations does not permit rating one correlation method superior to the other. As a by-product of this correlation, a finite permeability was determined at total crystallinity ( $w_a = 0$ ). This is in keeping with the fact that all materials possess some degree of permeability to gases. The permeation of gases through dense crystalline solids has been documented.<sup>4</sup> The recent reporting of the permeability of steel by hydrogen<sup>5</sup> and of quartz by neon<sup>6</sup> gives further evidence that total crystallinity does not lead to zero permeability.

### Orientation and Permeability

Flory<sup>7</sup> has shown that a tensile force imposed upon a rubber increases the internal energy of the material. His analysis of stretched rubber made use of the first law of thermodynamics and included terms which allowed for the work done in stretching. The relationship involving the increase of internal energy,  $E$ , in stretching a membrane is:

$$dE = TdS + XdL - pdv \quad (14)$$

where  $X$  is the tensile force and  $L$  is the distance through which the force acts. Flory has shown further that the  $pdv$  term was insignificant in his studies with rubber, particularly so if the elastic limit was not exceeded. Integrating eq. (14) we find for isothermal and isochoric conditions:

$$\Delta E = T(S^s - S^u) + \int XdL \quad (15)$$

where the superscripts  $s$  and  $u$  refer to the stressed and unstressed states, respectively. By substitution of eq. (14) into eq. (8), the ratio of the permeabilities in two different states may be found from eq. (15):

$$RT \ln (P^s/P^u) = - \int XdL \quad (16)$$

In evaluation of the term  $\int XdL$ , the assumption is made that the membrane remains within elastic range even though it is under stress. The length is usually linearly dependent upon the absolute temperature. Thus, two equations are used:

$$X = k_1(L - L_0) \quad (17a)$$

$$L = L_0 + L_0k_2T \quad (17b)$$

where  $L_0$  is the original length before the stress is applied,  $k_1$  is the spring constant for an elastic material under simple tension, and  $k_2$  is the thermal coefficient. From these equations, the value of the integral becomes:

$$\int XdL = (k_1L_0^2/2) (k_2^2T^2 - 1) \quad (18)$$

Now, by referring to the group  $(k_1L_0^2)/2$  as  $\beta$ , eq. (16) becomes:

$$RT \ln (P^s/P^u) = \beta(1 - k_2^2T^2) \quad (19)$$

The equation for the permeability dependence of a stressed membrane upon temperature is found by adding the equivalent form of eq. (6) to eq. (19) so that:

$$RT' \ln (P^s/P_0) = -E^u + \beta + TS^u - \beta k_2^2 T^2 \quad (20)$$

Equation (20) shows that the permeability response as a function of temperature would not be linear on a semilogarithmic plot. Of course, the non-linearity of such ideal elastic membranes is strongly dependent upon  $\beta$ . If the elastic limit is exceeded, the permeation response becomes even more complicated because of the additional terms which would be necessary in eq. (17a). The various permeation responses of stressed membranes are considered in Part II.<sup>8</sup>

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### Synopsis

A thermodynamic interpretation of the permeation process of gas transport through polymeric membranes is proposed. The mechanism used does not require the usual  $P = DS$  relationship. The dependence of gas permeability upon the crystallinity, strain, etc. is presented, and a method for obtaining values for the entropy of crystallization is suggested. Literature data have been correlated by this approach and values for the entropy of crystallization of polyethylene, polyethylene terephthalate, and nylon 610 were derived.

### Résumé

On propose une interprétation thermodynamique du processus de perméabilité de transport de gaz à travers des membranes polymériques. Le mécanisme employé ne requiert pas la relation habituelle  $P = DS$ . On présente la dépendance de la perméabilité des gaz vis-à-vis de la cristallinité, de la tension, etc. et on expose une méthode pour l'obtention des valeurs de l'entropie de cristallisation. Les données de la littérature sont en corrélation avec cette approximation et on déduit les valeurs pour l'entropie de cristallisation du polyéthylène, du téréphtalate de polyéthylène et du nylon 610.

### Zusammenfassung

Eine thermodynamische Interpretierung des Permeationsprozesses für den Gas-transport durch polymere Membranen wird gegeben. Der verwendete Mechanismus

kommt ohne die übliche Beziehung  $P = DS$  aus. Die Abhängigkeit der Gaspermeabilität von Kristallinität, Verformung u.s.w. wird beschrieben und eine Methode zur Gewinnung von Werten für die Kristallisationsentropie angegeben. Auf diese Weise wurden Literaturangaben ausgewertet und Werte für die Kristallisationsentropie von Polyäthylen, Polyäthylenterephthalat und Nylon 610 abgeleitet.

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