Polymer Structure and Gas Permeation
II. Permeation Studies

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In an earlier paper[1] a thermodynamic interpretation of gas permeation was presented. The permeation transport was postulated as being dependent upon the energy required to form a hole, and this energy was the Helmholtz free energy. The equations developed showed that the variation of permeation of a particular plastic is an exponential function of membrane entropy. Also, it was shown that anomalies in permeation may arise from stressed membranes. Such nonlinear Arrhenius plots have been reported by Barrie and Platt[2] in the case of stressed natural rubber. Aside from explanation of anomalies, permeation studies could serve as indicators of structural properties similar to stress-relaxation studies.

Numerous physical models of the membrane have been proposed to account for permeation transport. Almost without exception, these models involve the concept of a two-phase permeable membrane; one phase amorphous and the other crystalline, the crystalline phase being totally impermeable. Such models have led some investigators to the conclusion that a dead volume exists and, on other occasions, that a continuum of pores is present. This paper does not intend to reconcile these viewpoints but instead presents some experimentally induced anomalies and other tentative explanations of them in terms of molecular structure.

Cellulose Acetate Butyrate

Initial experiments in this research were directed toward the permeation of nitrogen through cellulose acetate butyrate which previously had shown very anomalous behavior.[3] Although exact confirmation of the previous work was not obtained, an anomaly was detected in the range of 14–19°C. as shown in Figure 1.

The lack of linearity of the permeability plots, as in Figure 1, has been used to confirm the temperature transitions of membranes.[4,5] The inflections in Figure 1 are weak when compared to those of the glass transition of polyvinyl acetate.[5]

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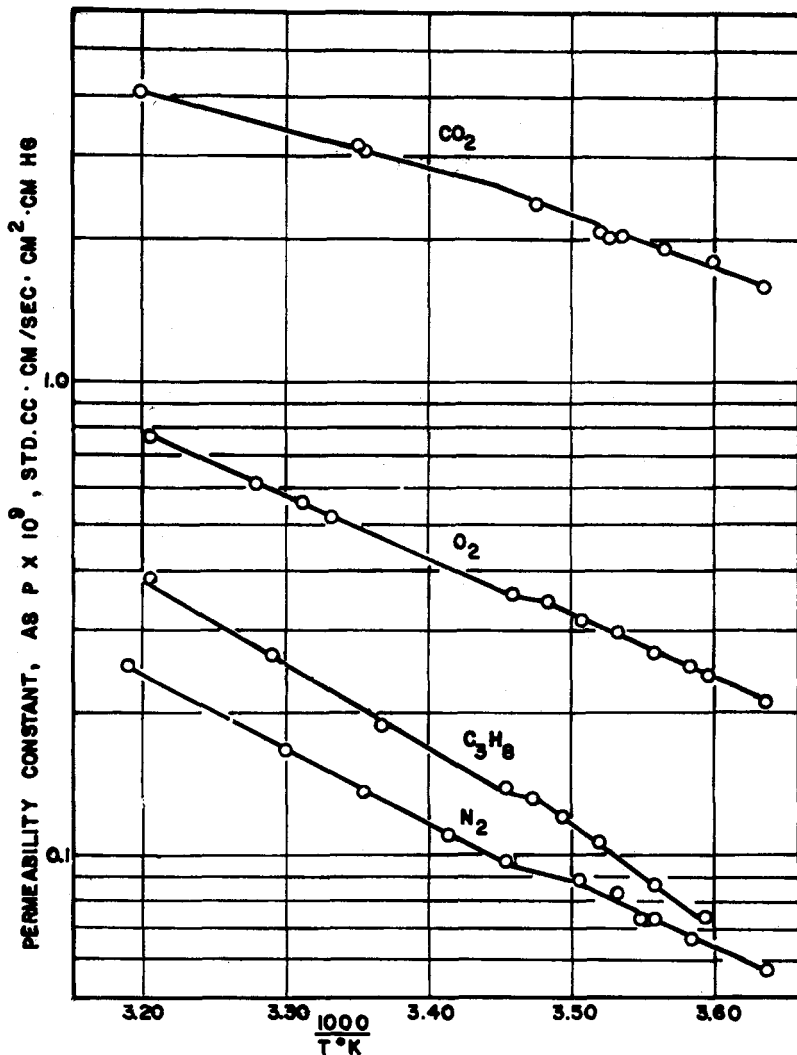
Fig. 1. Temperature dependence of permeability of cellulose acetate butyrate.

Explanation of this anomaly is not certain. Meares[5] found a minor transition at 16–17°C. in his gas permeation studies of polyvinyl acetate in addition to the glass transition point at 25°C. The coincidence of the cellulose acetate butyrate transition at the same temperature as the unexpected one found in polyvinyl acetate suggests an acetate group response. To say the least, this is highly conjectural.

The presence of a plasticizer could be the cause of the apparent transition. The reversibility of the response permits a limited solubility interpretation, and also a phase change of the plasticizer itself could be the reason. The plasticizer is known to be a high boiling phthalate, and melting points of

these compounds may be as high as 18°C., depending upon the exact species which is, however, unknown.

Ethyl Cellulose

Experiments with solution-cast ethyl cellulose films confirm that a molecular arrangement caused by a difference of solvents–polymer equilibria significantly affected gas permeation. Such differences were previously reported by Doolittle.[6]

The films were cast from 10% solutions of 95% ethanol, tetrahydrofuran, and toluene at a temperature about 10°C. lower than the boiling point of
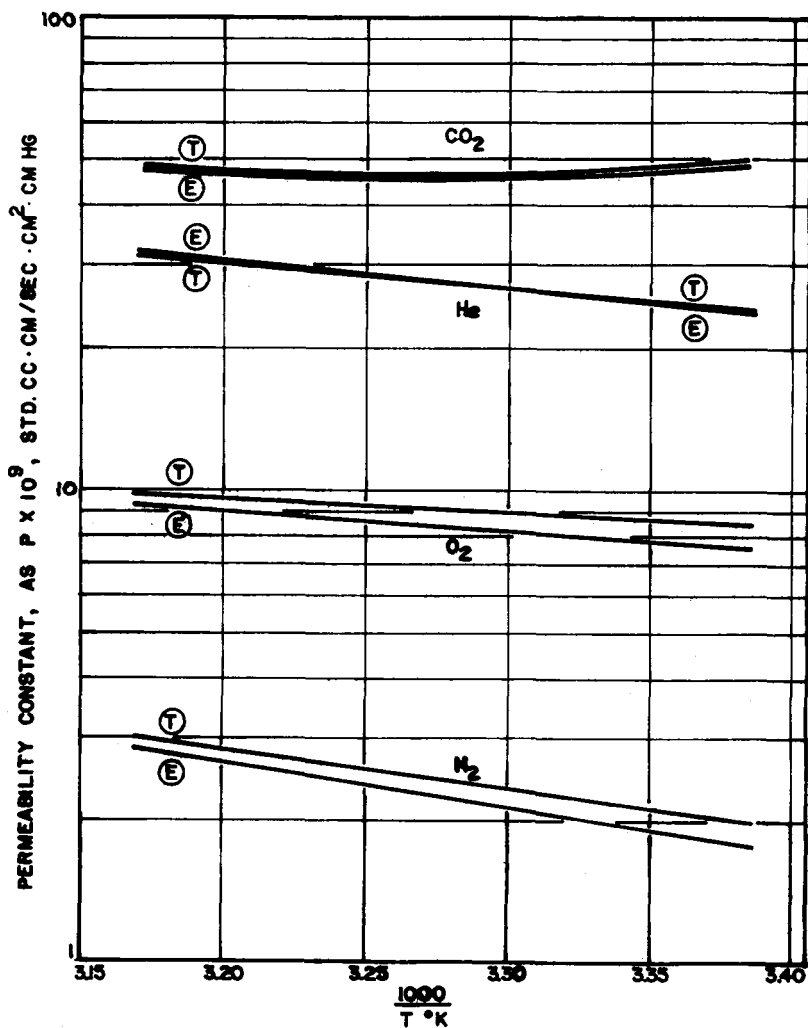

Fig. 2. Temperature dependence of permeability of ethyl celluloses cast from tetrahydrofuran (T) and ethyl alcohol (E) solutions.
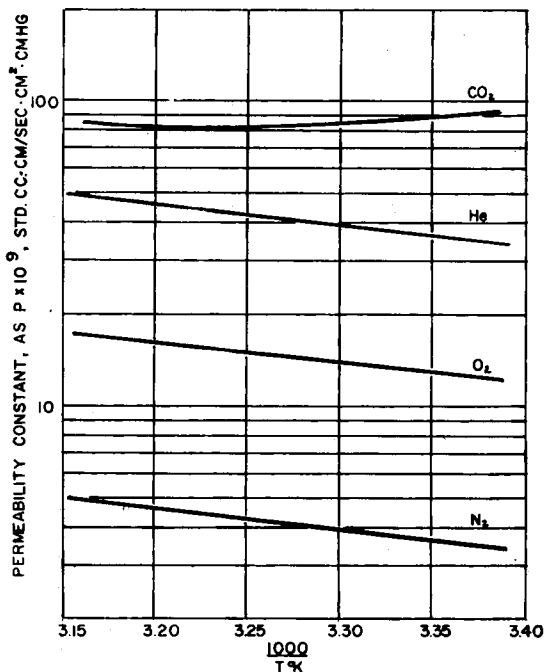
Fig. 3. Temperature dependence of permeability of ethyl cellulose cast from toluene solutions.

the pure solvent. The films were baked at 60°C. for 24 hr. and stored under identical conditions.

Permeability constants of nitrogen, oxygen, and helium were determined in duplicate runs of at least six determinations per run and at 5°C. intervals. A plot of these data is shown in Figures 2 and 3. Clearly the films cast from toluene exhibit greater permeability than do either of the films prepared from the tetrahydrofuran and ethyl alcohol solutions. Also, the film from tetrahydrofuran was more permeable than the film obtained with alcohol, as determined by appropriate statistical means.

In addition, the slopes of the several gas–film systems were evaluated in terms of the activation energy of permeation, E_p. The values are shown in Table I.

TABLE I
Activation Energy of Permeation E_p of Ethyl Cellulose Films[a]

	E_p, kcal./g.-mole		
Solvent	He	O_2	N_2
Toluene	3.21	3.11	3.70
Tetrahydrofuran	2.61	2.44	3.70
Ethyl alcohol (95%)	2.90	2.91	4.36

[a] Dow Ethocel (100 cpoise).

These data tend to support the physical model of Michaels et al.[7]   The permeability constants increased as the solubility parameter, δ, increased. This amplifies the concept that molecular order as characterized by end-to-end distances or randomness has a pronounced effect upon permeation. It appears that permeation is increased with poorer solvents.   Physically, the interpretation of Michaels et al., as it pertains to permeation may be extended as follows: (1) good solvents promote greater extension of the molecules and greater molecular freedom; (2) as the good solvent is removed, the film forms a more dense (more interwoven) network with more polymer–polymer interaction zones; (3) the increased number of these polymer unions inhibit transport, similar to crystalline zones.
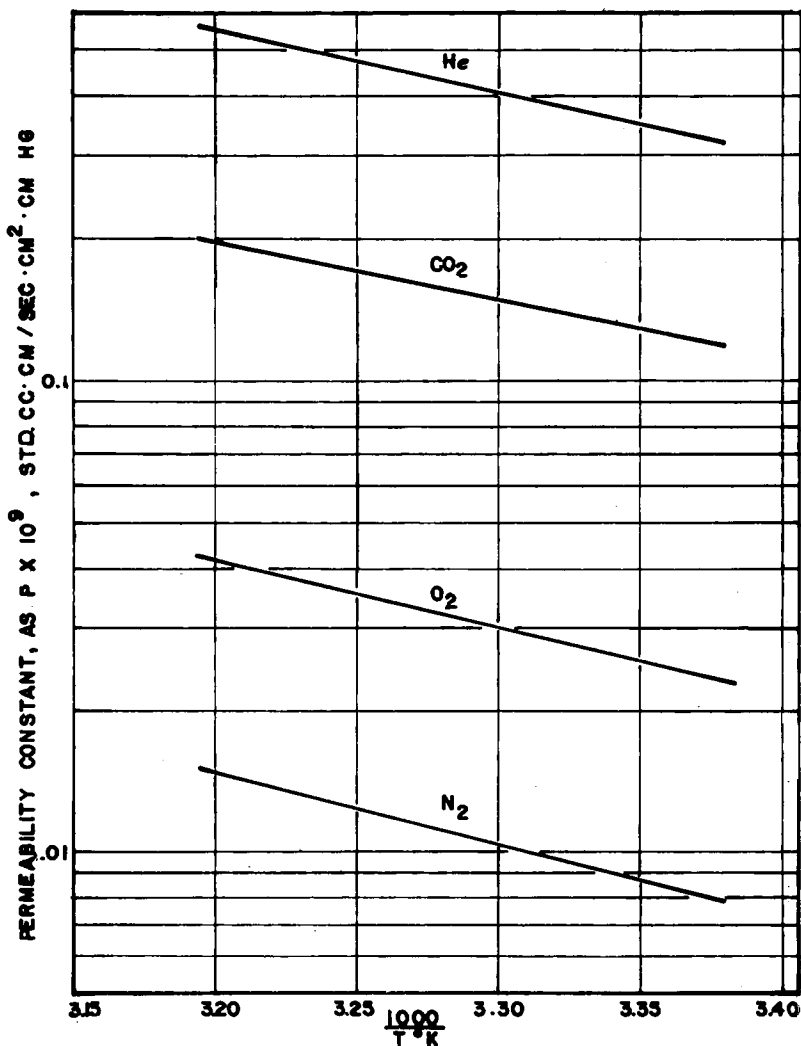

Fig. 4. Temperature dependence of permeability of unplasticized polyvinyl chloride.

Polyvinyl Chloride

A series of experiments was conducted to evaluate the permeation response of stressed polyvinyl chloride (PVC) films with varying plasticizer concentrations. The films were cast from tetrahydrofuran solutions at relatively low temperatures (20–25°C.). The plasticizer used was di-2-ethylhexyl phthalate (DOP). The orientation in the films was induced by mechanical means at room temperature. The data of these runs are summarized in Table II and Figures 4–6.

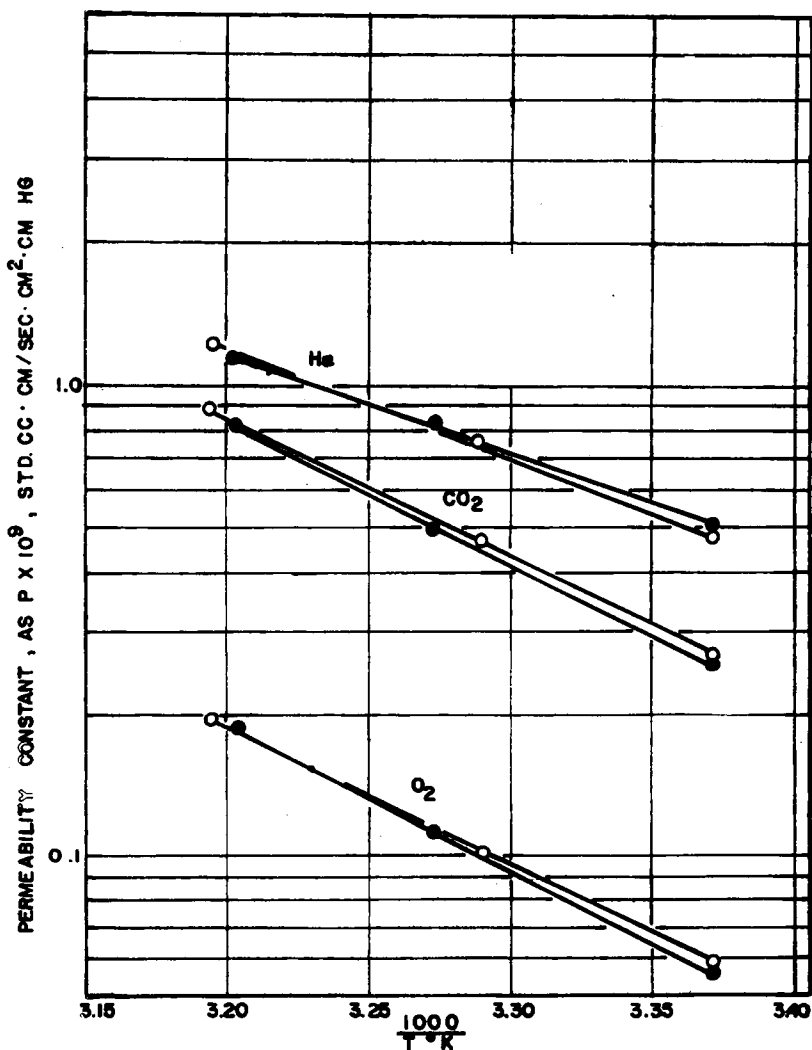The effect of orientation upon the polyvinyl chloride films was much

Fig. 5. Temperature dependence of permeability of plasticized polyvinyl chloride (16.8% DOP): (●) oriented 30%; (O) unoriented.

TABLE II

Activation Energy of Permeation E_p of Various Polyvinyl Chloride Films

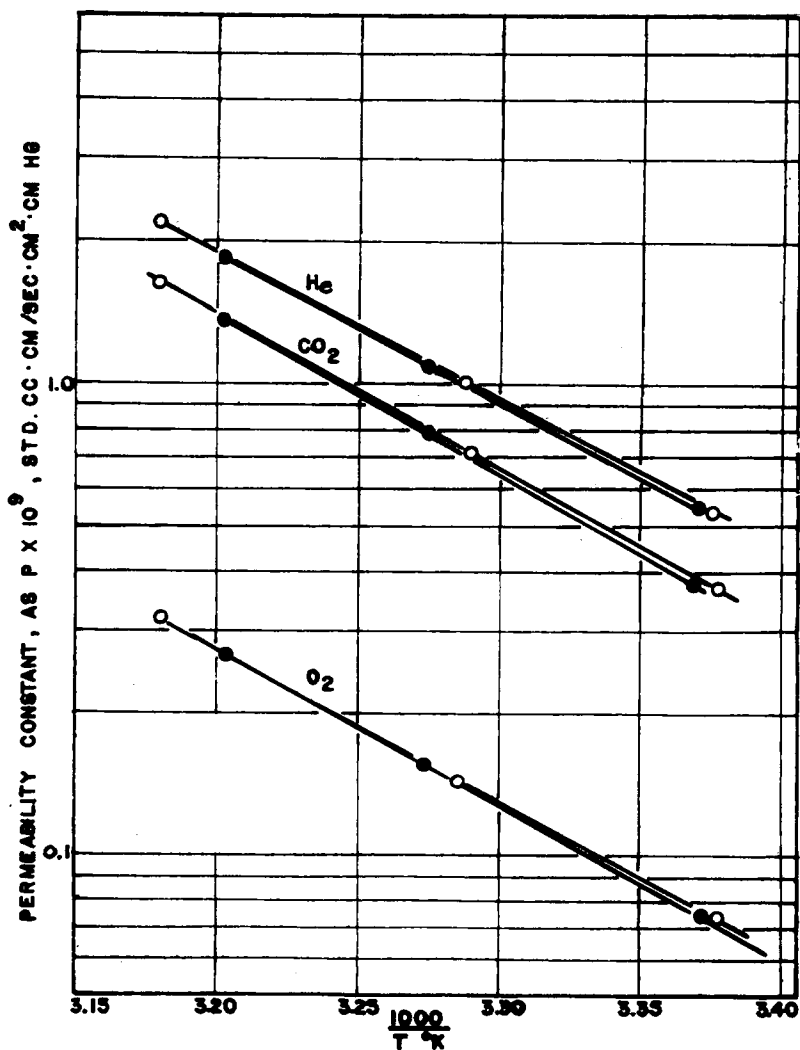| Elongation, %	Plasticizer (DOP), wt.-%	E_p, kcal./g.-mole			
		He	CO_2	O_2	N_2
0	0	6.33	5.76	6.62	7.202
0	16.8	10.56	12.92	13.73	—
30	16.8	10.03	13.73	14.23	—
0	19.3	14.17	14.92	14.70	—
30	19.3	13.58	14.47	14.47	—

Fig. 6. Temperature dependence of permeability of plasticized polyvinyl chloride (19.3% DOP): (●) oriented; (O) unoriented.

less pronounced than upon polyethylene as will be shown later.   Since the orientation was attempted at temperatures below the glass transition temperature of PVC, little if any effect was noted in the permeation response.
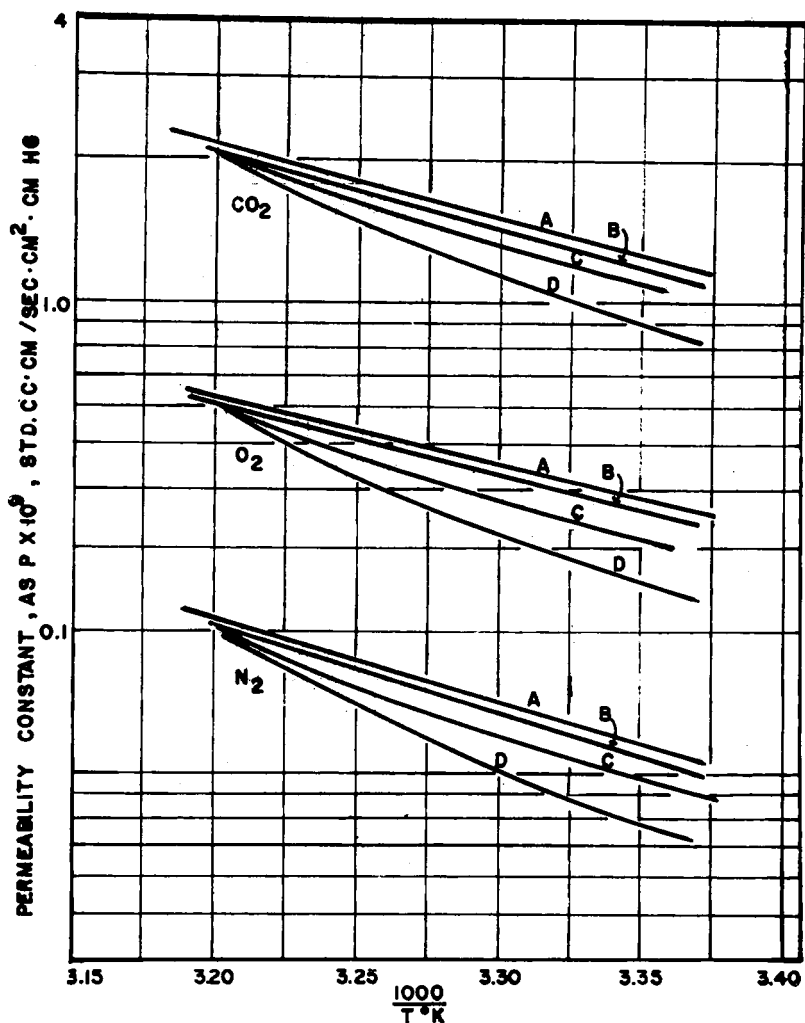

Fig. 7. Temperature dependence of permeability of polyethylenes: (*A*) melted and annealed; (*B*) commercial monoaxial; (*C*) 30% elongation; (*D*) 90% elongation.

The lack of plasticization in one sample prevented any measurable extension without breaking, whereas the plasticized samples were stretchable.

Previously[1] it was proposed that the permeation is dependent upon the internal energy and the entropy of the membrane as follows (eq. 3 of Part I[1]):

$$R \ln (P/P_0) = -(E/T) + S \tag{1}$$

In the light of this relationship, qualitative evaluation of the polyvinyl chloride permeation responses can be made.   The two plasticized samples showed that the stress in the film not only increased the internal energy, but also marginally altered the entropy.   Unfortunately, these data are likewise confounded with stress relaxation.   This is because the permeability constants were obtained with increasing temperature.   Thus the greatest displacement of the oriented sample from the unoriented sample occurred at the lowest temperature.   This makes the response of oriented samples appear to intersect the unoriented plot at the higher temperature. Because of the finite time required in measurement and the time between each temperature point the approach of the oriented plot to that of the unoriented is also a function of time.   Thus it is uncertain whether the slopes of these curves do, in fact, reflect a constant activation energy of permeation or internal energy shift.   If the value obtained at time zero ($\sim$ 20°C.) is considered, it is apparent that orientation does reduce permeation, even in the case of noncrystalline polymers.   Thus, amorphous ordering rather than a phase change is the cause.   The fact that permeation is reduced by ordering is compatible with the thermodynamic interpretation, since an increase in order decreases the entropy.

The effect of plasticization is to increase the permeation.   Relating this to the thermodynamic interpretation, the increased intercept of the plot indicates that the entropy was higher.   The increased entropy was probably due to increased randomness, which in turn is probably caused by the partial solution of the plastic in the plasticizer.   It is also true that the internal energy and entropy of the membrane are altered because of the sizeable quantity of plasticizer.   It is at present not possible to discern whether molecular configuration alone is responsible for the shift in permeation rate.

Generally speaking, plasticization increases the slope of the temperature response plot, whereas orientation decreases the slope.   Thus, orientation decreases the permeation rate whereas plasticization increases it.

Polyethylene

The effect of stresses in modifying the permeation response of polyethylene as a function of temperature is shown in Figure 7.   The correlation with temperature, labeled B is the permeation response of the monoaxially produced commercial film on an "as is" basis.   Plot A was obtained with a sample of the same film after a thermal treatment which erased the previous history.   This involved heating the film to 10°C. above its crystalline melting point for 30 min. and a subsequent quick chill in air.

It is interesting that the slope of the A and B plots are the same.   In light of eq. (1), the internal energies of these films are the same, but the displacement of A with respect to B indicates a shift in entropy.   The destruction of the extruder-induced order, or orientation, by the thermal treatment increased the entropy.   The loss of orientation was confirmed by birefringence evaluation.

Curves C and D represent permeation responses obtained in the case of the films under stress. Unfortunately, the measured responses are complicated by simultaneous stress relaxation phenomena. Nevertheless, these curves do show that stressed films give anomalous results in comparison with the usual Arrhenius-type plots. Assuming that the temperature
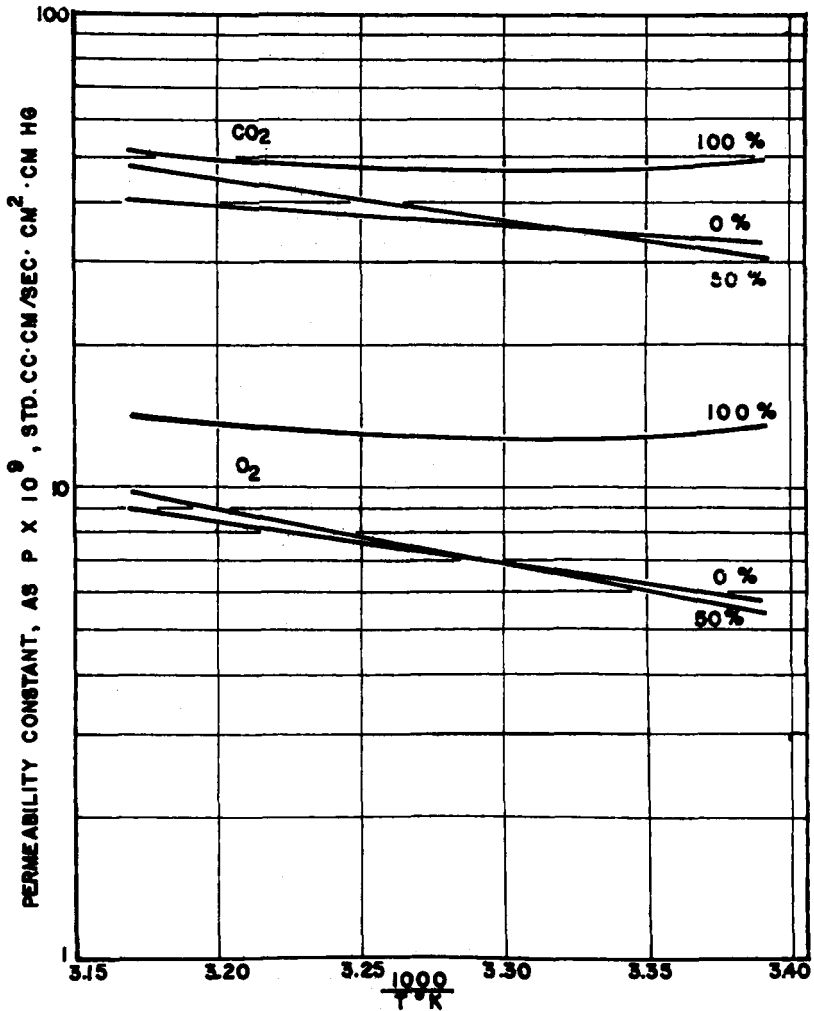

Fig. 8. Temperature dependence of permeability of LS-63 silastic silicone rubber.

coefficient of expansion is quite small, the curves reflect a substantial change in the membrane's entropy, caused by amorphous ordering when the membrane is stressed beyond the elastic limit. No doubt, some of the change in slope with temperature is also caused by the increase in internal energy, which is a function of applied stress.

Silicon Rubber

In the case of permeability studies of stressed and unstressed silicone rubber (LS-63 Silastic) another type of an anomaly appeared as seen in Figure 8.   Increased stress in the membrane did, in fact, increase the temperature dependence of permeability, whereas only a minor change was noted in the magnitude of the permeability constant.

The absolute thickness of a sample is critical in establishing the permeability constant.   The thickness of the "rested" sample was measured by a micrometer.   The change in thickness with per cent elongation herein defined as 100 $(L - L_0)/L_0$, was determined by means of x-ray attenuation.

The sample was placed on a solid aluminum plate and x-ray diffractions were obtained by the sample at several elongations.   The relative thickness
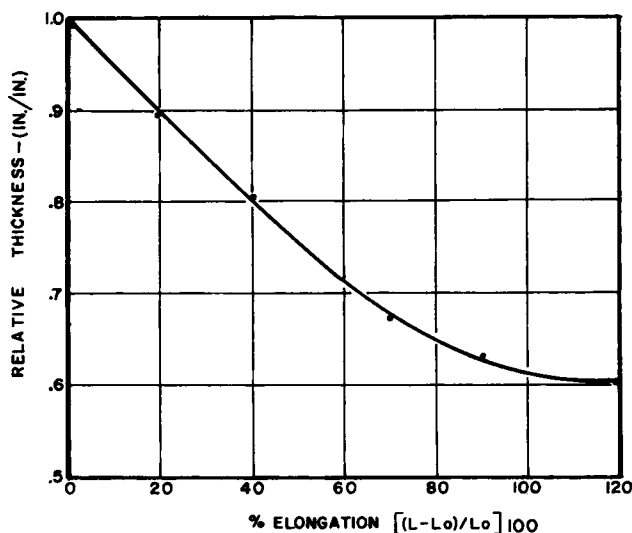

Figure 9.

was determined by noting the relative aluminum peak heights and were plotted as a function of elongation (see Fig. 9).   This indicates that elastic behavior is limited to the range of 0–70% elongation.

The permeability experiment was conducted by clamping the stretched sample at 30°C. in the permeability cell.   The thickness used in the calculations was that obtained from the relative thickness plot.   The intersection of the 0% and 50% elongation plots near 30°C. suggests that no increase in entropy was obtained but that the internal energy was altered.

The previous paper[1] showed that the permeability of stressed films was dependent upon temperature as follows (eq. 20 of Part I[1]):

$$P_s = P_0 \exp \left\{ (1/RT)(-E^u + \beta + TS^u - \beta k_2 T^2) \right\} \qquad (2)$$
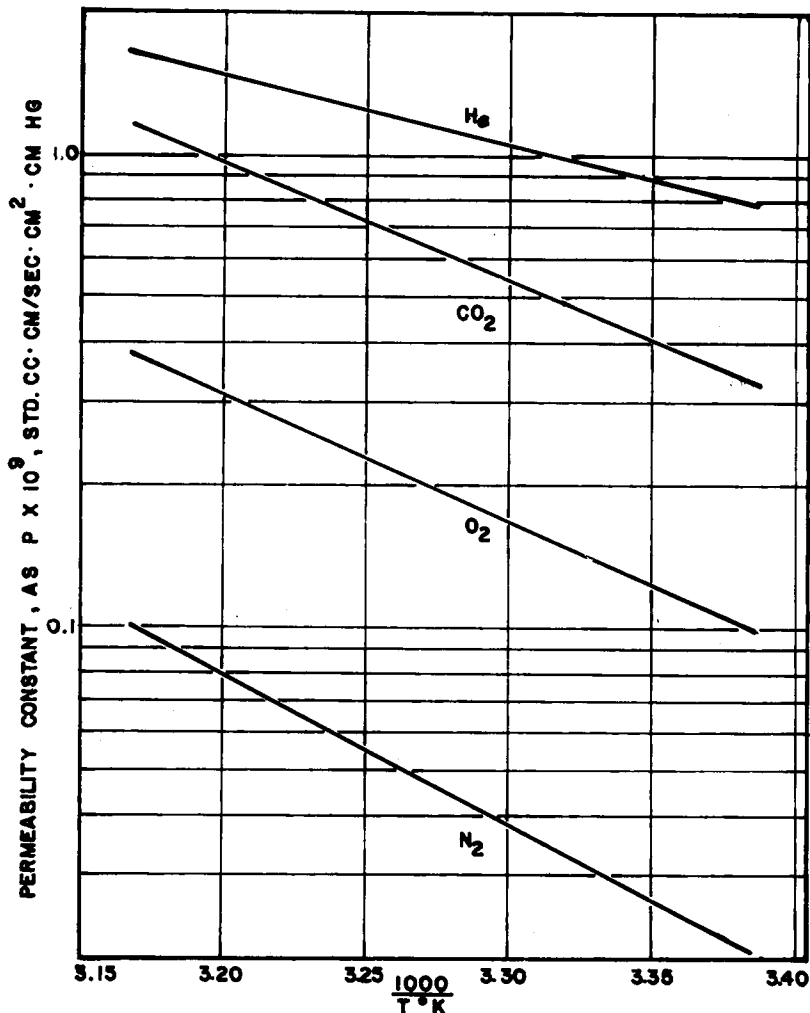
Fig. 10. Temperature dependence of permeability of monoaxial polypropylene.

The above equation is limited to the elastic region. The curvature of plots at 100% elongation, being in the inelastic region, reflects the dependence of permeability upon several terms. Much of the curvature may also be the result of the elongation not being linearly dependent upon the stress. The increase in the magnitude of permeation is probably due to the effect of β in eq. (2). The remarkable increase in permeability at 100% elongation is probably due to the destruction of order of the molecules at high stress.

Polypropylene

An extensive investigation of monoaxial and biaxial polypropylene film was undertaken to evaluate the interrelation of orientation and crystal-
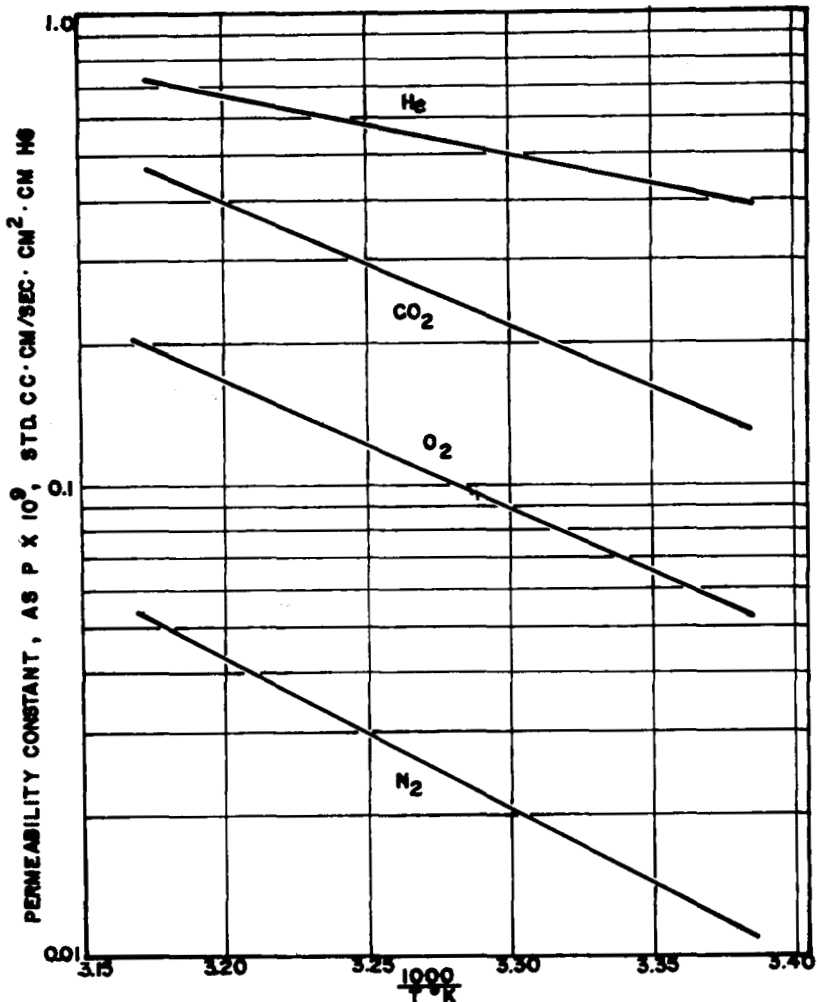
Fig. 11. Temperature dependence of permeability of biaxial polypropylene.

lization. This study was important in attempting to verify the suspicion obtained in the silicone rubber experiment that orientation and crystallization effects are but two facets of the same phenomenon.

A sample of each orientation type was analyzed by gas permeation and x-ray diffraction as a function of the original machine direction of the film. The evaluation of the orientation was qualitatively determined by polarization. Clearly, the monoaxial sample showed much less polarization than did the biaxial sample. The crystalline content was determined by the method proposed by Johnson[8] with the exception that a correction factor for thickness as shown by Kakudo and Ullman[9] was employed. The gas permeation runs for these samples in the relaxed state are shown in Figures 10 and 11.

The crystalline content of the biaxial film was 82% and that of the mono-axial was 42%. From these data the molar entropy of crystallization ΔS_{ac} at 30°C. was found to be 3.11 ± 0.1 g.cal./g. mole °K.

Measurements were made of the crystalline content while the film was under stress. In this case the stress was induced by clamping the sample in one direction and shrinking the sample by heating. The increase in thickness of the sample was monitored by noting the attenuation of the first two aluminum peaks at $2\theta = 38.5$ and 45°. From these evaluations at right angles for each film it is apparent that the "crystalline" content varied quite erratically. In no way was it possible to infer the usual constancy of crystallinity at moderate temperatures, as has been claimed.[10] The effect of the induced stress was also noted in the splitting of the poorly defined peak of the monoaxial sample into the several peaks which characterize the usual crystalline film. This rearrangement was not observed in the biaxial samples which gives credence to the proposition that an amorphous ordering took place in the case of the monoaxial samples. This ordering was reflected by a pseudo-crystallinity increase. Krimm and Tobolsky[11] noted similar effects at high extensions of polyethylene. The inference can be made that in stressed films the crystalline content as determined by the usual methods reflects amorphous ordering. This ordering is detectable in permeability studies and can be discriminated from the "rested" crystalline content by the shift of the permeabilities at a given temperature.

Conclusion

The changes observed in permeation responses by plastic films reflect changes in molecular structure. The permeabilities of chemically identical but structurally different films vary logarithmically with the entropy of the film. The entropy level of a film is dependent upon the orientation, induced strain, and the crystalline content.

The measurement of the entropy of crystallization by means of permeability opens new vistas for thermodynamic treatment of polymeric materials.

References

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Synopsis

A series of gas permeability studies of plastic membranes demonstrated the strong dependence of gas transport on structural aspects of the membrane.   Films of cellulose acetate butyrate, silicone rubber, polyethylene, polypropylene, and vinyl chloride, were used in these studies.   The effect of elastic and nonelastic stretching, orientation, plasticization, and phase changes were shown to be detectable by gas permeations.   Interpretation of the permeation response, as a function of temperature, is compatible with a thermodynamic appraisal of the permeation process.

Résumé

Un série d'études de la perméabilité aux gaz de membranes plastiques montre une étroite dépendance entre le transport gazeux et la structure de la membrane.   Des films d'acétobutyrate de cellulose, de caoutchouc siliconé, polyéthylène, polypropylène et de chlorure de polyvinyle, ont été utilisés pour cette étude.   Les effets de l'étirement élastique et non-plastique, de l'orientation, la plastification et du changement de phase, peuvent être détectés par perméabilité gazeuse.   L'interprétation de la réponse à la perméabilité, en tant que fonction de la température, est compatible avec une évaluation thermodynamique du processus de perméabilité.

Zusammenfassung

Eine Reihe von Gaspermeabilitätsmessungen an Polymermembranen zeigte die starke Abhängigkeit des Gastransportes von der Struktur der Membranen.   Bei diesen Untersuchungen wurden Cellulosebutyrat-Acetat-, Silikonkautschuk-, Polyäthylen-, Polypropylen- und Vinylchloridfolien verwendet.   Der Einfluss von elastischer und nichtelastischer Dehnung, Orientierung, Weichmachung und Phasenumwandlungen lässt sich an der Gaspermeation verfolgen.   Das Permeationsverhalten lässt sich in Abhängigkeit von der Temperatur mit einer thermodynamischen Betrachtung des Permeationsprozesses in Einklang bringen.