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APPENDIX

$$h_o = \sqrt{k\rho\, C_p\, S_o}$$

For fully developed turbulent flow in a pipe

S_o proportional to $\dfrac{v^*\, N_{Re}{}^{0.8}}{D}$

$$\therefore h_o = \sqrt{k\rho\, C_p \left[\frac{\beta v^*\, N_{Re}{}^{0.8}}{D}\right]}$$

where β = constant of proportionality

$$h_o \sqrt{\frac{D}{k\rho\, C_p}} = \sqrt{\beta}\,\sqrt{v^*}\, N_{Re}{}^{0.4}$$

For fully developed turbulent pipe flow from reference *16*

$$v^{*2} = \frac{0.0396\, \overline{V}^{7/4} \nu^{1/4}}{D^{1/4}}$$

$$\therefore h_o \sqrt{\frac{D}{k\rho\, C_p}} = C_1\, N_{Re}{}^{0.4} \frac{\overline{V}^{1/2}}{N_{Re}{}^{1/16}}$$

where

$$C_1 = \sqrt{\beta}\,(0.0396)^{1/4}$$

$$\therefore \frac{h_o D}{k} = C_1\, N_{Re}{}^{0.838}\, N_{Pr}{}^{0.5} \qquad (A1)$$

McAdam correlation reference *17*

$$\frac{h_o D}{k} = 0.023\, N_{Re}{}^{0.8}\, N_{Pr}{}^{0.4} \qquad (A2)$$

valid in range $10{,}000 \leqq N_{Re} \leqq 120{,}000$

$$0.7 \leqq N_{Pr} \leqq 120$$

The results from (*A*1) and (*A*2) agree to within 6% when $C_1 = 0.0162$ and $N_{Pr} = 0.73$ for the range $10{,}000 \leqq N_{Re} \leqq 120{,}000$; a slight divergence in results occurs with increasing N_{Re}.

Manuscript received November 13, 1966; revision received March 13, 1967; paper accepted March 15, 1967.

Permeation of Vapors Through Polymers at Low Temperature and Elevated Pressures

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The permeation of propane, propylene, ethane, and ethylene through 0.0051-cm. thick polyethylene films was measured at temperatures between 25° and —30°C. Plots of *P* vs. 1/*T* for C_3H_8, C_3H_6, and C_2H_6 were saucer shaped, the activation energies changing from positive (endothermic) to negative (exothermic) over a narrow temperature range. This change is attributed to a plasticization-condensation phenomenon and a change in intermolecular potentials.

Membrane permeation is a diffusional process which, to a first approximation, follows Fick's law:

$$N = -D\frac{dC}{dz} \qquad (1)$$

If *D* is independent of concentration, Equation (1) can be integrated with ($z = 0, C = C_1, z = z, C = C_2$) to

$$N = \frac{D}{z}(C_1 - C_2) \qquad (2)$$

Assuming the solubility constant S is only a function of temperature and not pressure and $C = Sp$, we have

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$$N = DS\,(p_1 - p_2)/z = P\,(p_1 - p_2)/z \qquad (3)$$

The temperature dependence of the diffusion and solubility processes is usually expressed in terms of the activation energies ΔH_p, ΔH_D, and ΔH_S

$$D = D_o e^{-\Delta H_D/RT} \qquad (4)$$

$$S = S_o e^{-\Delta H_S/RT} \qquad (5)$$

where ΔH_S is usually negative, and $\Delta H_p = \Delta H_D + \Delta H_S$.

The temperature dependence of the permeation constant therefore is, to a first approximation, given by an Arrhenius relationship, the basic premise being that the activation energies for permeation and diffusion are independent of the temperature. Confirming data have been obtained by numerous investigators at temperatures above the critical points of the gases, and the glass transition temperatures of the polymers. Pertinent literature citations are given in recent reviews (*1* to *4*).

MATERIALS, APPARATUS, AND PROCEDURE

The polyethylene film furnished by Union Carbide was 0.00255 cm. thick, and had an ASTM 793-50 density of 0.92. Two layers of film were used in the majority of runs, *P* not being a function of the number of layers.

The gases furnished by Petrobrás were analyzed chromatographically with the following results:

Gas/ percent	C_2H_4	C_2H_6	CH_4	C_3H_6	C_3H_8
C_2H_6	0.18	99.82	—	—	—
C_2H_4	97.85	1.30	0.85	—	—
C_3H_6	—	—	—	98.87	1.13
C_3H_8	—	—	—	0.91	99.09

The stainless steel diffusion cell shown in Figure 1 was mounted inside a mechanically refrigerated enclosure. The gas cylinders were outside the enclosure but there were approximately 100 cc. of holdup volume inside the enclosure upstream of the membrane to ensure thermal equilibrium. In addition to the pressure gauge on the cylinder, one each was mounted on the upstream and downstream sides of the cell. Gas flows rates were obtained by measuring the volume displaced by a moving soap film in a calibrated burette.

RESULTS

Figure 3 gives the permeation constant of ethane and ethylene as a function of temperature. The downstream pressure in both cases was 1 atm. Figure 2 shows the corresponding data for propane and propylene, the downstream and upstream pressures being 1 and 1.97 atm respectively, in both cases.

Activation energies for the high-temperature portion of the curves are given in Table 1 along with Ti, the temperature at the inflection point in the curve of *P* vs. $1/T$, and *Tc*, the critical temperature of gas.

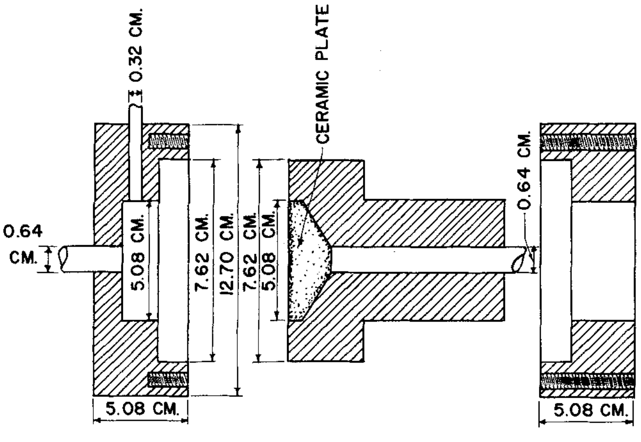

Fig. 1. Diffusion cell.

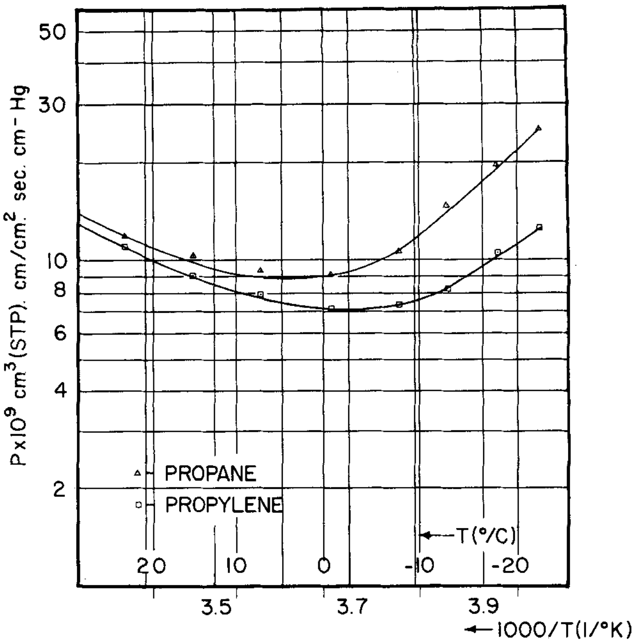

Fig. 2. Permeability of propane and propylene as a function of temperature.

The values of *P* and the initial slopes of Figures 2 and 3 are in agreement wtih literature values. At temperatures between 25° and −5°C., for instance, the activation energy for ethane is not a function of temperature. This is in rough agreement with the data of Brand (*5*), who reported ΔH_D's of from 10.6 to 15.4 kcal./mole and heats of solution ΔH_S = 2.65 kcal./mole (also independent of temperature). The value of ΔH_p obtained here, 7.35 kcal., is somewhat lower, an effect which can be attributed to the higher pressure employed.

DISCUSSION OF RESULTS

The most striking feature of the experimental results is the dramatic change in ΔH_p within a narrow temperature span (>10,000 cal./mole in less than 20°C. for ethane, propane, and butane). One might attribute this to morphological changes in the polymer, a change in ΔH_D, a change in ΔH_S, or condensation and plasticization phenomenon.

Morphological Changes

Tg for polyethylene is about −20°C. (*6*). Although *Ti* for ethane is below the glass transition point, the *Ti*'s for propane and propylene are not. Furthermore, the permeation rates for ethylene do not seem to vary with the temperature in the region in question.

Changes in ΔH_D

Quantitative models to account for the effect of temperature on diffusion may be based on such theories as

Table 1. Activation Energies, Critical Temperatures, Inflection Points

	T_c, °C.	Ti, °C.	ΔH_p, cal./mole	$\alpha/\alpha C_2H_6$
C_2H_4	9.7	> −30	8,200	
C_2H_6 (5.44 atm.)	32.1	−27	7,300	1
C_2H_6 (8.44 atm.)	32.1	−22	6,200	1.08
C_3H_6	92.3	−2	3,780	1.2
C_3H_8	96.8	−2	3,160	1.35

the zone theory of Barrer (*7*) or the transition state theory of Eyring (*8*). The Barrer equation is

$$D = \frac{1}{6}\sigma d^2 \exp - \Delta H_D/RT \sum_{f=1}^{m} \left(\frac{\Delta H_D}{RT}\right)^{f-1} \frac{1}{(f-1)!} \quad (6)$$

The Eyring model is

$$D = K(kT/h)d^2 e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (7)$$

As has been demonstrated by Van Amerongen (9) both Equations (6) and (7) will, for small temperature differences, reduce to a linear form

$$\Delta H_D = \Delta H^o{}_D + a\Delta T \quad (8)$$

where a is a small negative constant $(f-1)$ in the zone theory) and $\Delta H^o{}_D$ is a temperature insensitive activation energy. It is apparent therefore that the temperature effects observed here cannot be explained on the basis of a change in ΔH_D.

Changes in ΔH_S

An analysis of the factors entering into ΔH_S show this term to be a very weak function of temperature. ΔH_v for propane, for instance, changes only by 600 cal. between 20° and −30°C. (from 3,800 to 4,400 cal./g.-mole).

Condensation and Plasticization Phenomena

The dependence of P on penetrant concentration for the case of a strongly plasticizing penetrant has been shown to be of the form

$$P = P_o e^{\alpha C} \quad (9)$$

At or near condensation regions, one would expect C, the concentration of penetrant in the polymer, to be a strong reciprocal function of T. This is in rough agreement with the experimental solubility of methyl bromide in polyethylene (*10*). If this is to be the case, the permeation equation becomes

$$P = D_o S_o e^{-\Delta H_D/RT}\, e^{-\Delta H_S/RT}\, e^{\alpha/RT^6} \quad (10)$$

where a sixth-power temperature dependence is postulated.

If, to a first approximation, ΔH_D and ΔH_S are not functions of temperature, we have

$$P = A\, e^{-\Delta H_p/RT}\, e^{\alpha/RT^6} \quad (11)$$

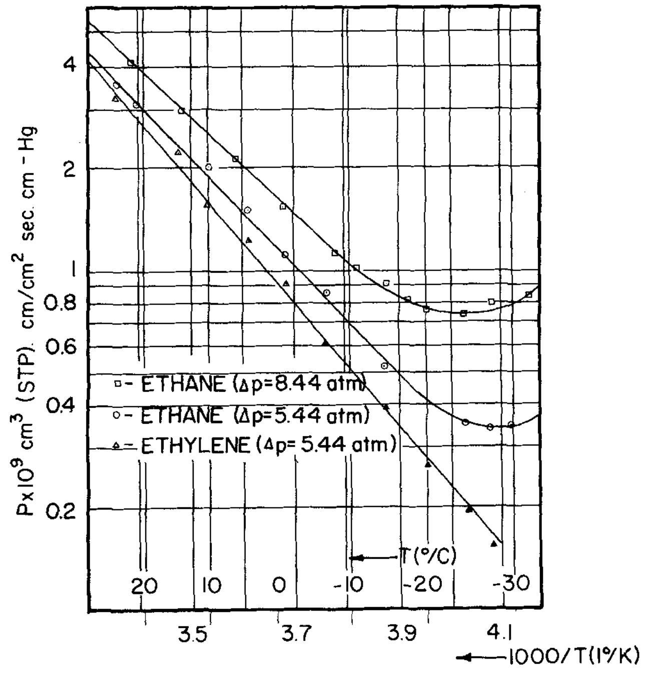

Fig. 3. Permeability of ethane and ethylene as a function of temperature.

thus

$$\frac{dP}{dT} = \frac{P}{RT^2}\left[\Delta H_p - \frac{6\alpha}{T^5}\right] \quad (12)$$

dP/dT is a minimum at Ti, hence

$$\alpha = \frac{\Delta H_p Ti^5}{6} \quad (13)$$

The relative α's calculated via Equation (13) given in Table 1 are in the inverse order of the solubility parameter differences between the permeants and polyethylene and in general (order of magnitude) agreement with the α's obtained by Li and Henley (*11*) and Riley (*12*) from Equation (9). More data (particularly solubility data) are needed to verify this, but the results obtained here strongly suggest that, in addition to their potential application to membrane separation processes, low-temperature permeation studies represent a possible way of studying intermolecular force constants in polymers.

NOTATION

a = constant
C = concentration
d = distance
D = diffusivity
f = degrees of freedom
h = Plank's constant
ΔH = activation energy
k = Boltzman constant
K = transmission coefficient
N = mass transfer rate, moles/(time)(area)
p = pressure
P = permeation constant
R = gas constant
S = solubility constant
ΔS^* = entropy of activation
t = time
T = temperature
z = film thickness
α = constant
σ = frequency

Subscripts

P = permeation
S = solubility
D = diffusion
o = temperature and concentration independent
v = vaporization

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Manuscript received September 30, 1966; revision received March 2, 1967; paper accepted March 3, 1967. Paper presented at AIChE Houston meeting.