The Pressure Dependence of Permeation Constants

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An effect of total pressure on the permeability of gases through polyethylene membranes was reported by Li and Henley in 1963 (*1*). If one assumes that Fick's law applies to the diffusion process

$$N = -D\frac{dC}{dx} \tag{1}$$

and that Henry's law can be used to relate the concentration of the gas in the polymer with that in the gas phase

$$C = Kp \tag{2}$$

we arrive, after substituting (2) into (1) and inserting the appropriate boundary conditions, at

$$N = \frac{DK\Delta p}{Z} = \frac{P\Delta p}{Z} \tag{3}$$

P, the permeation constant, was found to be a strong function of total pressure at constant Δp and Z (*1*). The question now arises of whether this is due to an increase of *K* or to an increase of *D* with total pressure.

The meager gas solubility data to be found in the literature indicate that the dependence of *K* on pressure is rather small, and that the more pressure-dependent variable is probably *D* (*2*, *3*). Unfortunately, the solubility data available up to now were not of sufficient integrity to allow one to say this unequivocably.

In a study recently concluded, we measured gas solubilities at elevated pressures by a newly developed, direct volumetric technique. The polymer film was placed in the sample space shown in Figure 1. Gas was introduced through the inlet, the system was equilibrated, and the amount of gas in the system (with and without polymer) was measured volumetrically.

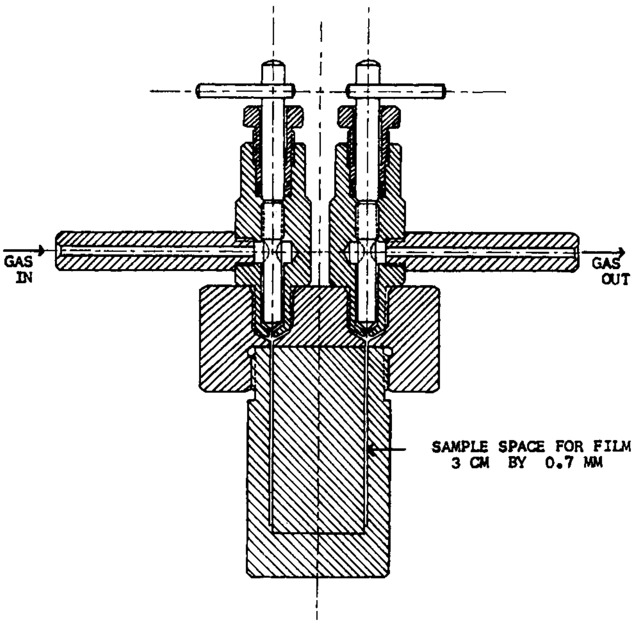

Fig. 1. Pressure cell for gas solubility measurements.

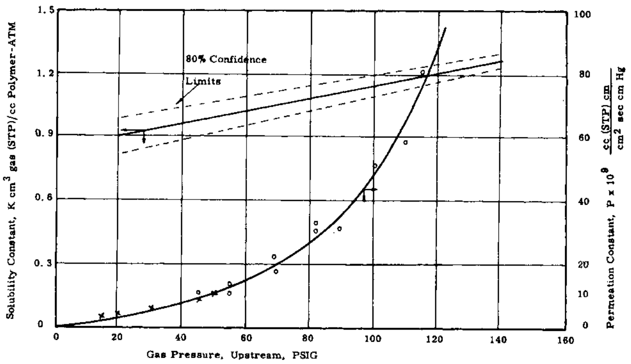

Fig. 2. Solubility and permeation constants as functions of pressure. x = data of Li and Henley (*1*); o = data of Riley (*4*). Propane-polyethylene system at 34°C.

Figure 2 shows the measured solubility of propane in 1-mil. thick low density (0.929) polyethylene. As is to be expected, the 80% *t* test confidence limits indicates that the accuracy of the technique increases with pressure. Shown also in Figure 2 is the permeability constant for the same system as measured by Li and Henley (*1*) and by Riley (*4*).

It is to be noted that over the range of pressure in which *K* increases only 20%, *P* increases by a factor of 8. Similar, although less pronounced effects were noted for methane and ethane gas diffusing through polyethylene.

The foregoing indicates that for relatively strongly interacting polymer-penetrant systems, the plasticization enhances diffusivity to an appreciably greater extent than solubility.

ACKNOWLEDGMENT

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LITERATURE CITED

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NOTATION

C = concentration in molar units
D = diffusivity
K = Henry's law solubility, cc. gas (STP)/cc. polymer
N = mass transfer rate, moles/(time)(area)
P = differential permeation constant
p = gas pressure
p = gas pressure difference across membrane
Z = film thickness