

NOTES

Helium Separation by Cellulose Acetate Membranes

The mechanism of permeation of gases through porous polymeric membranes at high pressures is of interest for the recovery of gases such as helium from natural gas. In highly shrunk porous cellulose acetate membranes the pore diameters¹ are of the order of 10 Å. At ordinary pressures the mean free paths of most gases are much larger than such pore diameters and thus the permeation would seem to follow Knudsen's law of molecular effusion. However, since the length of the pores are considerably greater than their diameters the flow of a gas through such barriers does not follow the simple equation of orifice diffusion except at such pressures where the mass flow is so small that the equilibrium Maxwell distribution is undisturbed due to the flow through the orifice.

We have measured the pure gas permeabilities of helium, nitrogen and methane through a cellulose acetate membrane at pressures up to 70 atm. The experimental method has been described.²

The volume rate of permeation v of a gas of molecular weight M measured at T absolute temperature at a pressure P_2 is, on the basis of Knudsen orifice flow, given by

$$v = (\rho_1/\rho_2)A\sqrt{RT/2\pi M}$$

where ρ_1 and ρ_2 are the densities at pressures P_1 and P_2 , A is the area of the film, P_1 is the pressure on the high-pressure side at temperature T . Thus for an ideal gas

$$v = (k/\sqrt{M})(P_1/P_2)$$

where

$$k = A\sqrt{RT/2\pi}$$

so that in Knudsen flow the measured permeabilities should be linear in P_1/P_2 and the slope of the straight lines obtained should be in inverse proportion to the square roots of their molecular weights.

A plot of v versus P_1/P_2 is shown in Figure 1. Here v is measured at ambient temperature (23–25°C). It will be seen that for $D/\lambda \geq 0.1$ (points beyond those indicated by the arrows), where D is pore diameter and λ is the mean free path, the graph is not linear, and observed permeabilities are much higher than Knudsen values even for helium. However, the ratio of the slopes for different gases obtained by extrapolating the $D/\lambda \leq .1$ region closely correspond to the Knudsen relationships.

The departure from Knudsen flow at $D/\lambda > 0.1$ has been discussed by Liepmann³ as a function of Reynolds number. However, in our range of Reynolds number (0.05–1.6) the departure from Knudsen flow should not exceed by 10–12% if one has an orifice length/orifice diameter $\ll 1.0$, a condition definitely not satisfied in membrane permeation.

The theory of solubility according to Henry's law followed by Fick's law diffusion has been widely accepted to govern gas permeation in polymers.^{4–6} In this theory one would expect permeation to be linearly proportional to the applied pressure differential. The observed permeation is found to exceed this significantly in the case of our data.

For a compressible fluid and small pressure differentials Poiseuille flow is given by⁷

$$v = K(P_1^2 - P_2^2)$$

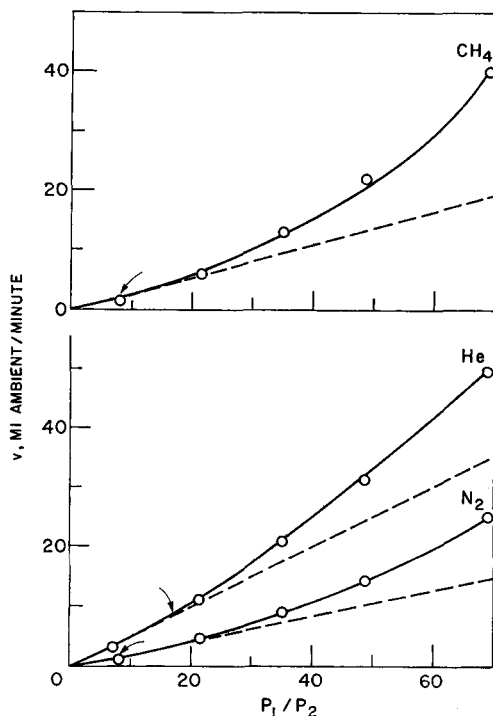


Fig. 1. Deviation from Knudsen flow in membrane permeation.

where K is a constant. If $P_2 = 1$ and $P_1/P_2 \gg 1$,

$$v \approx K \left(\frac{P_1}{P_2} \right)^2$$

A plot of $\log v$ versus $\log P_1/P_2$ shown in Figure 2 is a straight line but the slopes of these lines are always less than 2.0. Let us recall that for true Knudsen flow the slope should be 1.0. Thus the experimental value of 1.3–1.5 indicates a flow intermediate between the two regions. The flow also exceeds the Euler limit of Liepmann,³ evidently due to appreciable "lip thickness" of the orifice.

A number of experiments was done on helium separation in mixtures of methane, helium, and also natural gas samples as a function of pressure. The analysis of the permeant was done by gas chromatography. A 13X, 14–30 mesh molecular sieve column gave sufficient resolution and excellent detection limits for helium when operated at 40°C using argon as the carrier gas and a thermal conductivity-type cell detector. The natural gas contained about 0.05% helium and 2.0% nitrogen. The synthetic mixtures contained no more than 1.8 per cent helium. All compositions are in terms of volume per cent. In all cases the product rates corresponded closely to that for pure methane. Table I gives the permeability constant A_g for the pure gases expressed in the usual units of cm^3 (STP) $\text{cm}/\text{cm}^2\text{-sec}$ (cm of Hg). The film thickness was taken as 0.25μ ,⁸ and the area of the film was 9.6 cm^2 . The α 's are the separation factors obtained by dividing A_g for a pair of gases. The experimental separation factors $\alpha_{\text{He-CH}_4}^{\text{Expt}}$ agreed satisfactorily with those based on the pure gas permeabilities, at all but low pressures where due to the low permeation rates the errors may be significant.

The present method will give a product rate of about 190 l. (ambient)/hr-ft² with

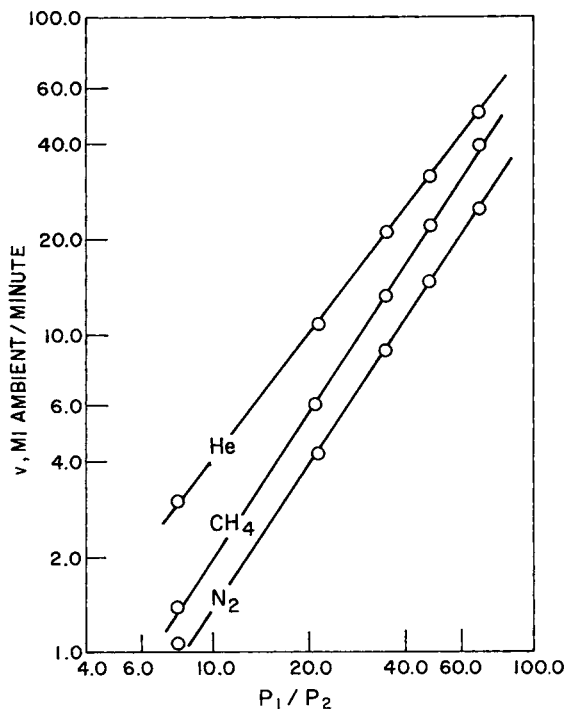


Fig. 2. Effect of pressure ratio on gas permeation.

TABLE I
Permeability Constants A_g for Gases on a Cellulose Acetate Membrane

Pressure P_1 , lb/in. ²	$A_g \times 10^{10}$, CH ₄	cm ³ (STP) cm cm ² sec/(cm of Hg)		$\alpha_{\text{He-N}_2}$	$\alpha_{\text{He-CH}_2}$	$\alpha_{\text{He-CH}_4}^{\text{Expt}}$
		He	N ₂			
100	1.27	2.69	0.95	2.83	2.10	1.78
300	1.64	2.91	1.16	2.53	1.78	1.58
500	2.09	3.32	1.40	2.37	1.59	1.52
700	2.49	3.54	1.65	2.14	1.42	1.41
1000	3.11	3.90	1.96	1.99	1.25	1.30

$\alpha_{\text{He-CH}_4} = 1.35$ as compared with 3.6 l. (ambient)/hr-ft² and $\alpha_{\text{He-CH}_4} = 7.5$ by Stern et al.⁴ at 900 psig but different operating temperatures. Owing to its high product rate the present method is expected to be useful for upgrading pre-enriched natural gas.

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