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Surface Diffusion of Deuterium and Light Hydrocarbons in Microporous Vycor Glass

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Summary

The significance of the surface diffusion of helium through a microporous Vycor glass is emphasized, and the experimental evidence is presented. New permeability data of D_2, CH_4, C_2H_6, and C_3H_8 are reported over a wide temperature range, and the results are analyzed numerically. Interesting comparisons are made for D_2-H_2 and C_3H_8-CO_2 systems. Finally, the separation factors for CO_2-C_3H_8 and CH_4-C_3H_8 systems are discussed.

All the experimental work has been carried out with porous Vycor glass as the microporous medium. However, there is good reason to believe that the basic findings will hold for any other microporous barrier. Differences will only be a matter of magnitude and will be determined by the adsorption interaction of the respective gas-solid system.

The use of microporous membranes in separation by means of gaseous diffusion has been well established. Although the process goes back in principle to the use of Graham's law and Knudsen flow, the effect of surface diffusion has been effectively recognized in recent years, and the strong influence of this phenomenon upon separation behavior is receiving increasing attention. A very recent publication (*8*) has shown that there is a pronounced temperature effect which up to now has not been recognized.

In that paper (*8*), new findings were reported for the surface diffusion behavior of He, Ne, H_2, Ar, O_2, N_2, and CO_2 in flow through microporous Vycor glass. It was pointed out that the use of total helium permeability to predict the gas-phase flow is in principle incorrect, because helium also exhibits a considerable amount of surface flow. Consequently, a simple equation was proposed to separate the surface diffusion from the observed total flow.

There are several recent reports (*2,5,6,12,13*) on the same subject, but none of them contains a discussion of the possible surface flow of helium. The purpose of this paper, therefore, is to clarify the present status and to extend the previous work.

The commonly accepted reasons for using helium as a reference gas can be stated as follows:

1. The amount of helium adsorption at ordinary temperatures and pressures is very small.
2. The permeability of helium is independent of the average pressure.
3. The product of the permeability and the square root of temperature shows little variation with temperature.

These contentions lead to the hasty conclusion that helium obeys the Knudsen equation. The actual state of affairs is quite different, however, because:

1. Even though the amount of adsorption is very small, if the mobility of the adsorbed molecules is great, then the contribution of surface flow could be appreciable. Also, there is some experimental evidence that helium is adsorbed on solid surfaces, especially at low temperatures (*3,4,14–16*).
2. If the surface flow rate is independent of the pressure in the low-pressure range, the total flow rate should be independent of the pressure, and this is the case, as pointed out previously (*8*).
3. A careful experimental study shows that the value of $Q(MT)^{1/2}$ for helium decreases as temperature decreases. The maximum difference of $Q(MT)^{1/2}$ between the lowest and the highest temperatures is more than 10% which cannot be considered an experimental error. The same result was reported by Ash et al. (*1*) for the permeability of helium through a microporous carbon. These authors found a decrease of as much as 15% with decreasing temperature. But apparently they did not realize that the deviations were due to the surface flow. Since this fact is new and so significant, the flow measurements for helium were repeated several times, so as to reproduce the data within the range of experimental error of ±1%. A typical set of data is shown in Fig. 1. This phenomenon signifies a serious conflict with the Knudsen law; furthermore, it indicates that neither the value of $Q(MT)^{1/2}$ at the highest temper-

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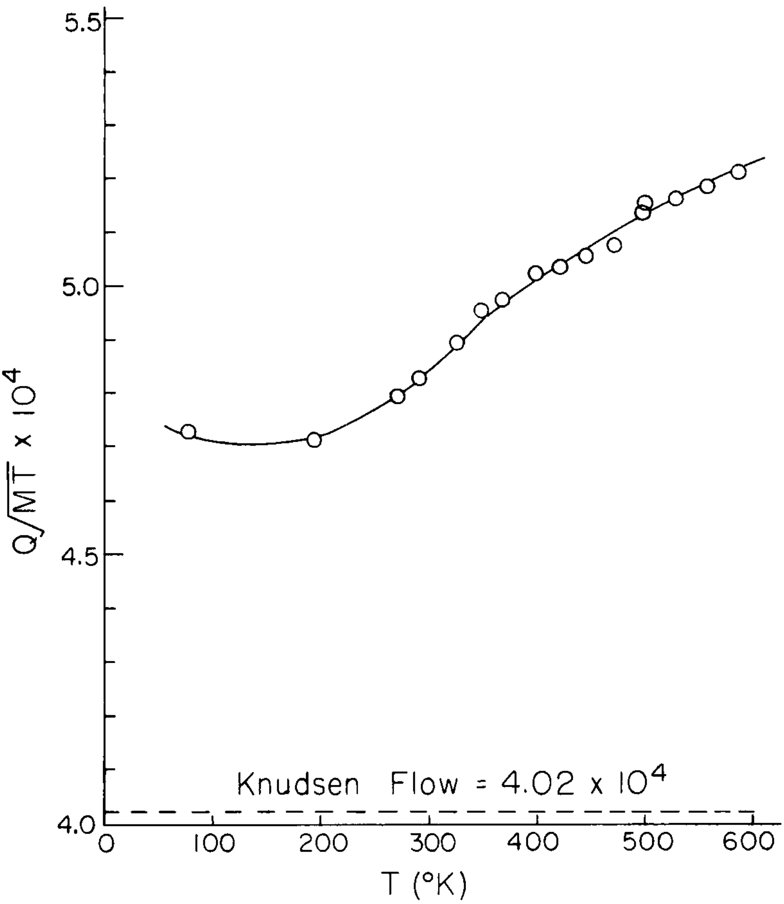

FIG. 1. Deviation from Knudsen law for helium.

ature nor the value of $Q(MT)^{1/2}$ at the lowest temperature should be used as the Knudsen level.

4. Kammermeyer and Rutz (9) first reported that the observed permeability of hydrogen is slightly less than the predicted value based on helium permeability; the same behavior was confirmed by Kaser (*11*). The previous paper (*8*) reinforced this fact by presenting data for neon, oxygen, and argon; and the present study contains additional evidence of analogous behavior for deuterium and methane.

Summing up, helium cannot be considered an ideal gas which

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obeys the Knudsen equation. Rather, it should be treated in the same manner as other gases. The previous analysis (8) reported that the fraction of surface diffusion for helium varies from 0.247 at 600°K to 0.133 at 130°K.

Experimental

The experimental apparatus and conditions were described in

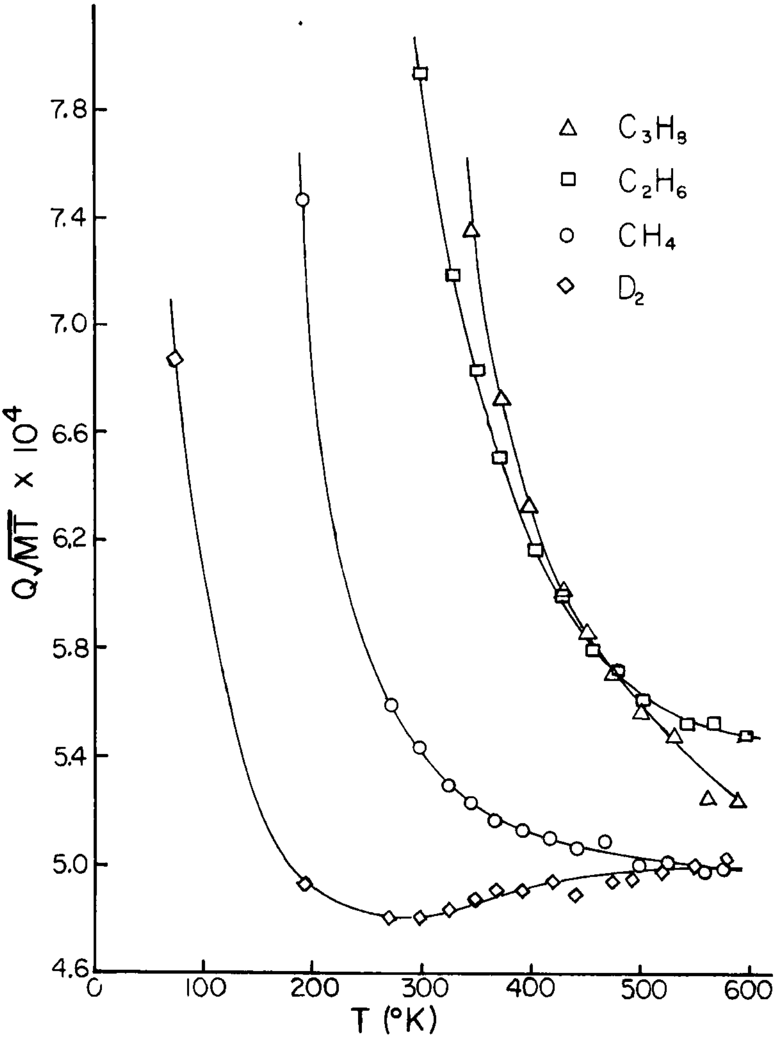

FIG. 2. Deviations from Knudsen law for D_2, CH_4, C_2H_6, and C_3H_8.

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(*8*). The change of permeability with respect to temperature is shown in Fig. 2 for D_2, CH_4, C_2H_6, and C_3H_8. This graph pictures how the deviation from the Knudsen law varies with temperature.

CORRELATIONS OF SURFACE FLOW

The permeability equation derived in the previous paper (*8*), Eq. (1), is again used to correlate the experimental data.

$$Q(MT)^{1/2} = A + BTe^{\Delta/T} \tag{1}$$

The constant A represents the Knudsen flow or gas-phase flow. Since the results were obtained with the same porous medium as before, this value $A = 4.02 \times 10^{-4}$ would not be changed. Consequently, the numerical evaluation of other constants, B and Δ, is much simplified. The computer results of the least-squares method to fit the experimental data are shown in Table 1 and plotted in Fig. 3. A similar plot for gases is shown in Fig. 7 of (*8*).

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TABLE 1

Values of A, B, Δ, and Σ

$A = 4.02 \times 10^{-4}$ (for all gases)[a]

Gas	$B \times 10^7$	Δ, °K[b]	$\Sigma \times 10^{4(c)}$
D_2	1.103	272	0.0244
CH_4	0.515	676	0.0716
C_2H_6	0.451	1003	0.1866
C_3H_8	0.188	1397	0.2946

[a] $\left(\frac{\text{std cc-cm}}{\text{sec-sq cm-cm Hg}}\right)\left(\frac{\text{g-°K}}{\text{g mole}}\right)^{1/2}$.

[b] Note that these values represent the locations of the minima.

[c] Σ: standard deviation of $Q(MT)^{1/2}$.

Deuterium

If Knudsen flow alone were to exist, the only possible change of the permeability for different gases would be due to a change in molecular weight. But if there is any adsorbed flow, or surface flow, at all, many factors besides the molecular weight can be conceived to cause a change in permeability. Since adsorption is

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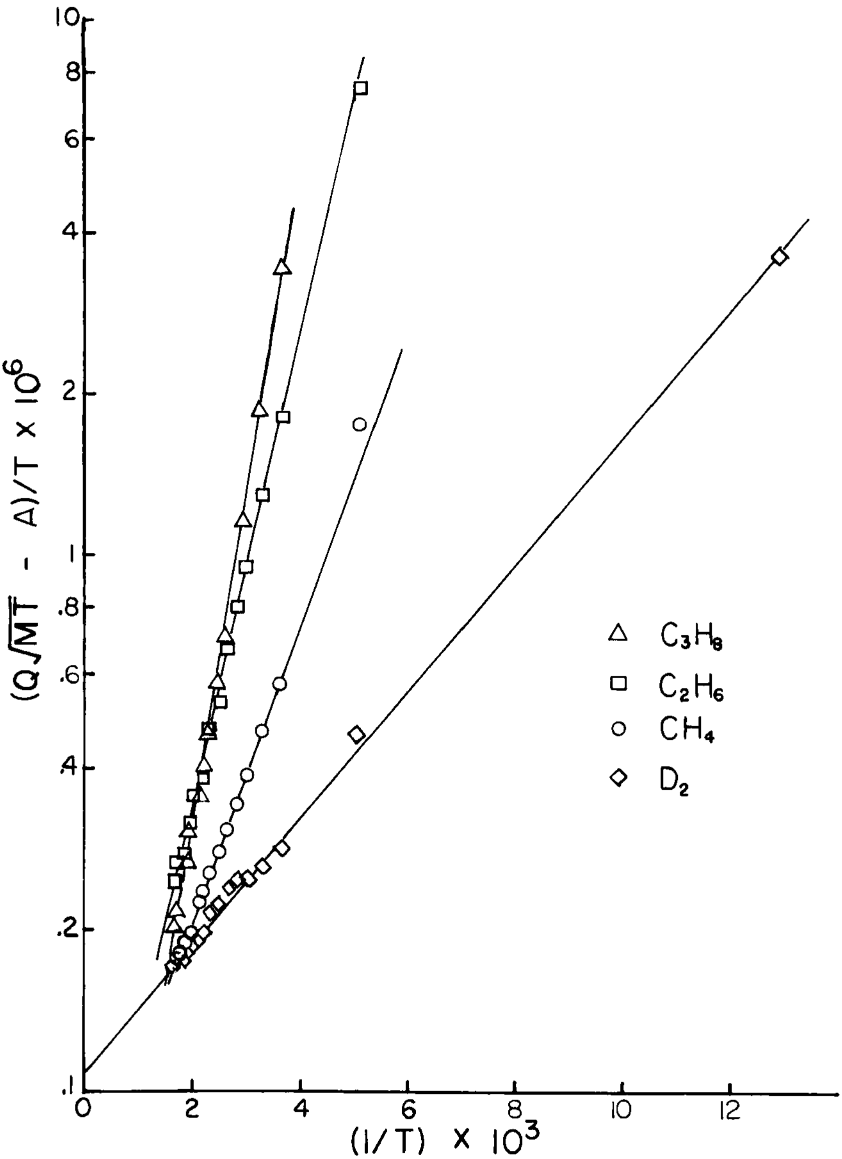

FIG. 3. Correlations of surface diffusion for D_2, CH_4, C_2H_6, and C_3H_8.

a phenomenon of gas-solid interaction, all the molecular properties would exert an influence on it.

To see if this is the case, deuterium was chosen. The molecular weight of deuterium is 4.03, which is quite close to that of helium 4.003, but all other molecular properties are essentially the same as those of hydrogen.

Needless to say, the behaviors of deuterium and hydrogen are alike, but quite different from that of helium. The experimental results are shown in Fig. 4. Deuterium exhibits greater deviation

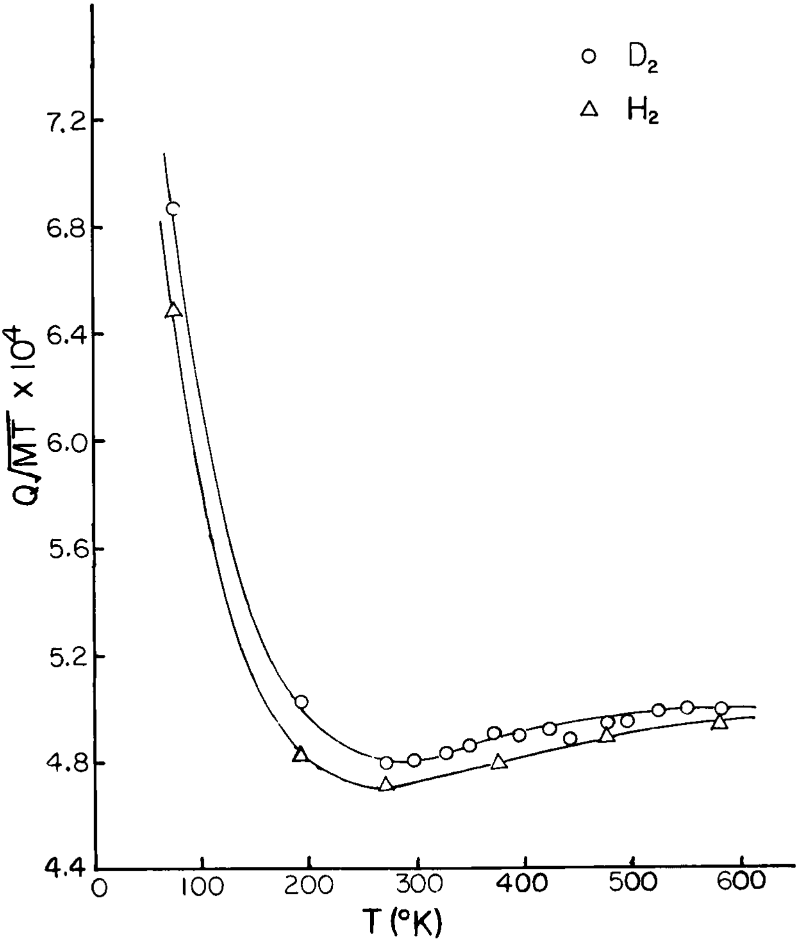

FIG. 4. Comparison of H_2 and D_2.

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from Knudsen flow than hydrogen does, and this fact is quite understandable.

Propane

Another interesting system which elucidates this view is propane and carbon dioxide. Their molecular weights are 44.094 and

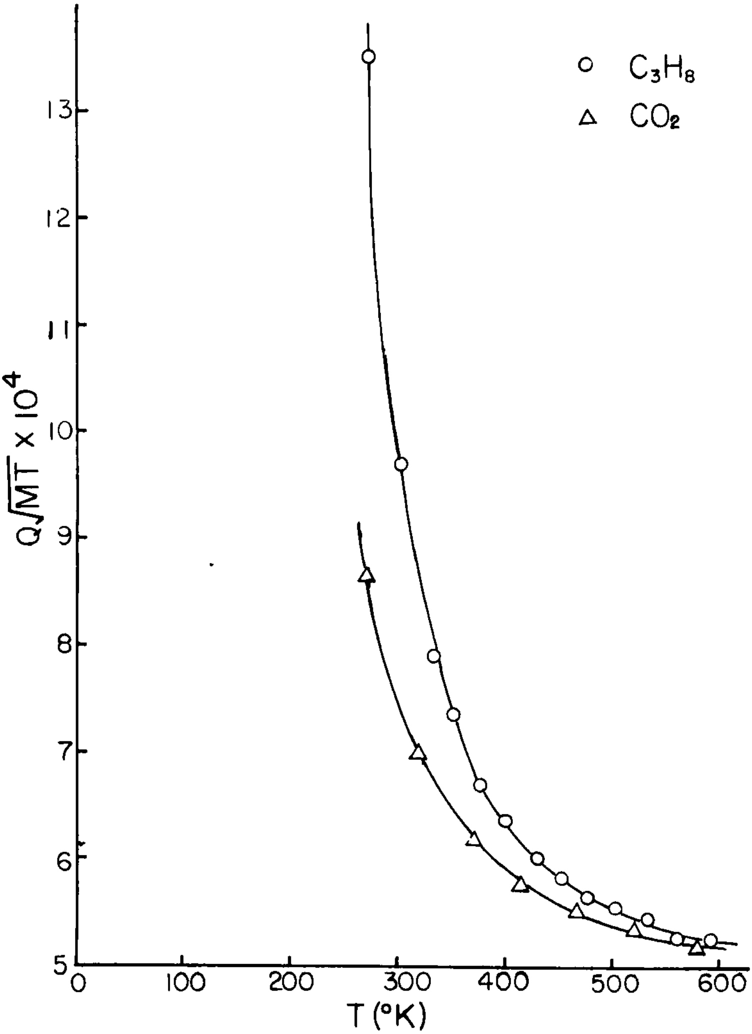

FIG. 5. Comparison of CO_2 and C_3H_8.

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44.010, respectively. But other molecular properties, such as critical temperatures, polarizabilities, magnetic susceptibilities, or molecular sizes, are far different. One would naturally expect that these differences in molecular properties should result in different amounts of surface flow, thus giving rise to a discrepancy in the observed permeabilities.

Present data for this system are shown in Fig. 5. Propane exhibits higher permeability than carbon dioxide at all temperatures. This agrees with literature reports (*7,10*).

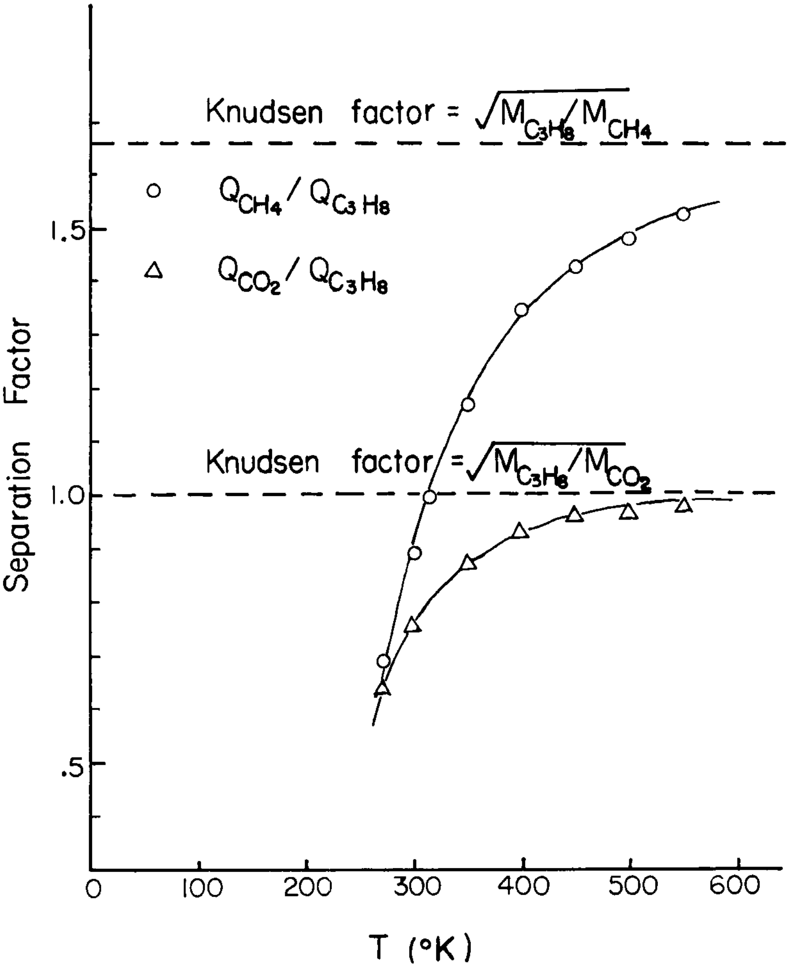

FIG. 6. Separation factors for CO_2-C_3H_8 and CH_4-C_3H_8.

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Methane and Ethane

For the study of hydrocarbons, methane and ethane were employed. As shown in Fig. 3, the experimental data points can well be represented by Eq. (1).

Separation Factor

For the purpose of illustration, two systems are selected to estimate the ideal separation factors based on the permeability data of pure components. The actual systems of mixtures of gases are now under investigation.

The first system is propane–carbon dioxide. The lower curve on Fig. 6 tells how the surface diffusion plays an important role in separation and how it varies with temperature.

The second system is methane–propane, which is of importance in natural-gas purification. As shown in Fig. 6 (upper curve), either gas can be enriched in the diffused stream, depending on the operating temperature. At 315°K there exists an azeotropic point which gives no separation. This temperature could be shifted to the left or right for an actual mixture, as mentioned in the previous paper (*8*).

In either case, the ideal separation factor approaches the Knudsen value as temperature rises.

Nomenclature

Q	$\dfrac{\text{(std cc)(cm)}}{\text{(sec)(sq cm)(cm Hg)}}$
M	molecular weight
T	absolute temperature, °K
A	constant representing Knudsen or gas flow
B	surface-flow coefficient determined experimentally
Δ	a function of potential-energy difference; see (*8*)

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