

Temperature-Dependence of the Diffusion Constants of Rigid, Closed-Cell Foams

It has been shown¹ that the diffusion of gases in rigid, closed-cell foams obey Fick's Law and that the diffusion coefficient D_t can be predicted from the following expression

$$D_t = (3RT/M)(\rho_0/\rho)P_e \quad (1)$$

where D_t is the diffusion coefficient of the foam, P_e is the permeation constant of the solid polymer-gas system, ρ_0 is the density of the solid polymer, ρ is the density of the foam, T is the absolute temperature, M is the molecular weight of the diffusing gas, and R is the gas constant. The validity of this equation was confirmed at room temperature from experimentally measured values of D_t as a function of ρ .

By using eq. (1), it should also be possible to evaluate D_t at any temperature from the knowledge of the temperature dependence of P_e , which is known² to obey an Arrhenius relation

$$P_e = P_{e0} \exp\{-\Delta H_p/RT\} \quad (2)$$

where ΔH_p is the activation energy of permeation. Substituting eq. (2) into eq. (1) and rearranging results in

$$\ln(D_t/T) = -(\Delta H_p/RT) + \ln(3R\rho_0 P_{e0}/M\rho) \quad (3)$$

Inasmuch as the ratio ρ_0/ρ is temperature-independent, the last term is a constant, and hence a straight-line relationship between $\ln D_t/T$ and $1/T$ is predicted.

In Table I are given values of D_t obtained at four temperatures for a rigid, closed-cell (>95%) polyurethane foam of density 4.5 lb/ft³ (Emerson and Cuming, Incorporated, Eccofoam FPH/12/6H). The experimental details have been reported previously.¹ The data which are plotted in Figure 1 as $\ln D_t/T$ versus $1/T$ show a reasonably good straight line relationship. The slope yields for ΔH_p a value of 7.4 kcal/mole. This value is in excellent agreement with the usual 6–12 kcal/mole range for the activation energies for diffusion processes in polymers.²

For the particular case of the permeation of CO₂ through a rigid polyurethane, no data were found in the literature. However, some data³ were found for a rubbery polyurethane, and these are given in Table II. The activation energy for permeation ΔH_p was found to be 9.4 kcal/mole, and this compares favorably with the value of 7.4 kcal/mole. Further, it is expected that ΔH_p for the rigid polyurethane should be lower than that for the rubbery polyurethane, since it has been adequately verified² that the activation energy of a polymer above its T_g is higher than that value obtained when the polymer is below its T_g . Hence the 9.4 kcal/mole corresponds to a polyurethane above T_g , whereas the 7.4 kcal/mole is for a polyurethane below T_g .

TABLE I
Diffusion Constants of a Polyurethane Foam at Various Temperatures

Temperature, °C	$D \times 10^6$, cm ² /sec	$D/T \times 10^9$, cm ² /sec °K	$1/T$, °K $\times 10^3$
22	1.76	5.96	3.39
41	3.34	10.6	3.18
61	9.57	28.6	2.99
81	13.7	38.7	2.82

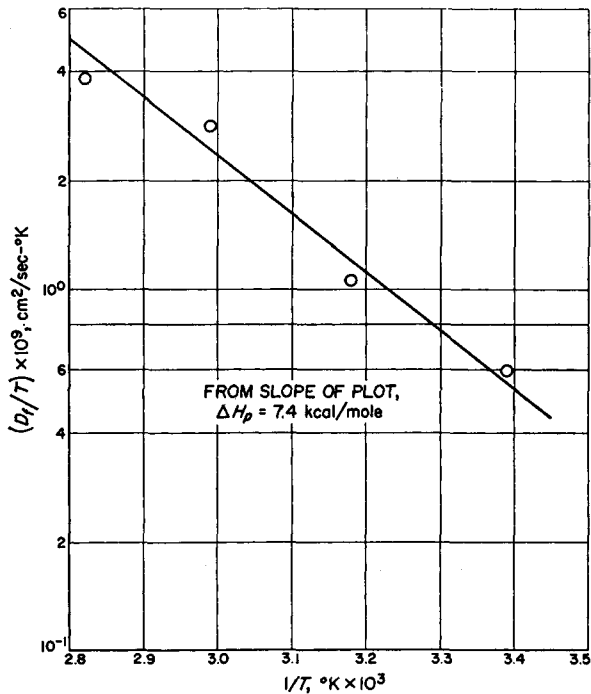


Fig. 1. Temperature dependence of the diffusion coefficient for a CO_2 -filled rigid polyurethane foam, density 4.5 lb/ft³.

TABLE II
Results for CO_2 Permeation Through a Rubbery Polyurethane^{a,b}

Temperature, °C	$P_s \times 10^6,$ cm ³ STP-mm/ cm ² -sec-cmHg	$D \times 10^6,$ cm ² /sec	Solubility, cm ³ STP/cm ³ -atm
25	1.85	0.094	1.50
50	6.34	0.440	1.10

^a Data for Vulcaprene polyurethane rubber.³

^b Activation energies: $\Delta H_p = 9.4$ kcal/mole (for permeation); $\Delta H_d = 11.7$ kcal/mole (for diffusion); $\Delta H_s = -2.3$ kcal/mole (for solubility).

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References

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