# COMMUNICATIONS TO THE EDITOR

## On Negative Temperature Coefficients for Surface Diffusion

**J. M. SMITH**
**University of California, Davis, California**

Gupta and Douglas (*1*) have presented interesting data showing the importance of surface migration for the hydration of isobutylene to tertiary butyl alcohol by using a cation exchange resin as catalyst. They have identified the major intraparticle transport process as migration of adsorbed isobutylene through the negative temperature coefficient of the effective diffusivity. They further provide a brief review of the literature in which surface diffusion is related to heterogeneous catalysis (*3*) and they conclude that the isobutylene hydration work provides definite experimental evidence for the occurrence of surface diffusion, and the associated negative coefficient, in a reaction rate study. It may be helpful to point out that recently the same negative coefficient was observed experimentally by Masamune and Smith (*2*) in studies on the adsorption of ethyl alcohol on silica gel. In that work the overall transport from the bulk gas stream to the adsorption site was found to be determined by intraparticle diffusion (predominantly surface diffusion) and the adsorption resistance at the site. It was shown that the effective diffusivity decreases with temperature (Figure 8) because of the decrease in fraction of surface covered by adsorbed molecules. Both references correctly note that the activation energy for the surface migration is positive, despite the negative temperature coefficient of the diffusivity, measured in terms of fluid rather than surface concentrations. Gupta and Douglas referred to the direct proportionality between effective diffusivity and adsorption equilibrium constant but did not point out the required assumption; that is, that the adsorption step is very rapid (occurs at near equilibrium conditions) with respect to surface migration. Hence in heterogeneous catalysis where the adsorption step at the site has a significant resistance with respect to intraparticle diffusion, the direct proportionality would not apply. When the assumption is valid it has been shown (*3*) that the observed effective diffusivity $D_e$ is related to the surface diffusivity $D_s$, and the adsorption equilibrium constant $K$, and catalyst density $\rho_p$, by the relation:

$$D_e = D_p + \rho_p \; KD_s \tag{1}$$

Equation (1) has been applied (*3*) to the physical adsorption of nitrogen on Vycor, where the assumption is justified. However for chemisorption and heterogeneous catalytic reactions, such as that studied by Gupta and Douglas, the direct proportionality between $KD_s$ and $D_e$ may not be true.

### LITERATURE CITED

1. Gupta, V. P., and W. J. M. Douglas, *AIChE J.*, **13**, 883 (1967).
2. Masamune, S., and J. M. Smith, *ibid.*, **11**, 41 (1965).
3. *Ibid.*, **10**, 246 (1964).