Modification to the Higashi Model for Surface Diffusion

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The model introduced by Higashi, Ito, and Oishi in 1963 (HIO model) was an important advance in the understanding of surface diffusion. It attempted to explain the dependence of surface diffusion rates on adsorbed species and agreed reasonably well with experimental data at surface coverages up to about 60% of a monolayer, that is, up to $\theta = 0.6$. At higher values of θ, the values predicted became greater than those measured. In fact, at $\theta = 1$ the model indicated that the surface diffusion coefficient would be infinite. In this note we propose a modification of the model which reduces the discrepancy between theory and experiment at all coverages. It also provides for a finite value of diffusion coefficient at $\theta = 1$.

THE ORIGINAL MODEL

The HIO model is based on a random walk of molecules from adsorption site to adsorption site on the solid surface. It assumes that the transit time between sites is negligible relative to a residence time τ at each site given by

$$\frac{1}{\tau} = \nu \cdot e^{-\Delta E/RT} \tag{1}$$

where ν is the vibration frequency of the bond holding the molecule to the site and ΔE is the effective energy of that bond, that is, the difference in energy between the states corresponding respectively to adsorption at the ground vibrational level of the bond and to free mobility on the surface.

The surface diffusion coefficient is thus obtained by the Einstein equation

$$D_s = \frac{\lambda^2}{2\tau} \tag{2}$$

where λ is the average distance between sites.

It is further assumed that when a molecule encounters a site occupied by another molecule it immediately bounces off and continues without stopping until it finds an unoccupied site at which to rest. The average number of jumps for a molecule to find an empty site at surface coverage θ was calculated to be $\eta_\theta = \sum_{k=1}^{\infty} k(1-\theta)\theta^{k-1} = 1/(1-\theta)$. Thus, the following relation is obtained:

$$\frac{D_{s,\theta}}{D_{s,\theta=0}} = \frac{\eta_\theta}{\eta_{\theta=0}} = \frac{1}{1-\theta} \tag{3}$$

MODIFIED MODEL

The assumption of zero residence time for a diffusing molecule at an occupied site implies no attractive force or bonding between the molecule and the site or the molecule adsorbed on the site. A further implication is the impossibility of adsorbing more than one monolayer on a surface. But multilayer adsorption is well known and, in fact, can begin to occur even before a complete monolayer has been formed. (Gregg and Sing, 1967). We suggest, therefore, that it would be more reasonable to assume an attractive force capable of forming a bond between a diffusing molecule and an occupied site since at minimum we expect a van der Waals interaction during collision with the adsorbed molecule. We can then allow for a finite residence time τ_2 at such a site in accordance with Equation (1) by suitable choice of values for ΔE and ν. Under this assumption the molecule makes $(\eta_\theta - 1)$ stops with holding time τ_2 at each stop before it occupies an empty site. Therefore, the average time τ for covering distance d in the random walk model of Higashi et al. (1963) should be replaced by τ_a where τ_a is given by

$$\tau_a = \frac{\tau_1 + (\eta_\theta - 1)\tau_2}{\eta_\theta} \tag{4}$$

If we indicate an unoccupied site by subscript 1 and an occupied site by subscript 2 and substitute $\eta_\theta = 1/(1-\theta)$ into Equation (4), we obtain

$$\tau_a = \tau_1\left(1 - \theta + \theta \cdot \frac{\nu_1}{\nu_2} e^{-(\Delta E_1 - \Delta E_2)/RT}\right) \tag{5}$$

Replacing τ in the random walk model by τ_a from Equation (4), we obtain the following expression:

$$D_{s,\theta=0} = \frac{\lambda^2}{2\tau_1} \cdot \frac{1}{1 - \theta + \theta \cdot \frac{\nu_1}{\nu_2} e^{-(\Delta E_1 - \Delta E_2)/RT}} \tag{6}$$

or

$$\frac{D_s}{D_{s,\theta=0}} = \frac{1}{1 - \theta + \theta \cdot \frac{\nu_1}{\nu_2} e^{-(\Delta E_1 - \Delta E_2)/RT}} \tag{7}$$

COMPARISON WITH EXPERIMENTAL DATA

In principle, the activation energies ΔE_1 and ΔE_2 can be evaluated experimentally; however, data on heats of adsorption are easier to measure and are more readily available. Therefore, we approximate the value of $\Delta E_1 - \Delta E_2$ by the difference in heats of adsorption for the first and

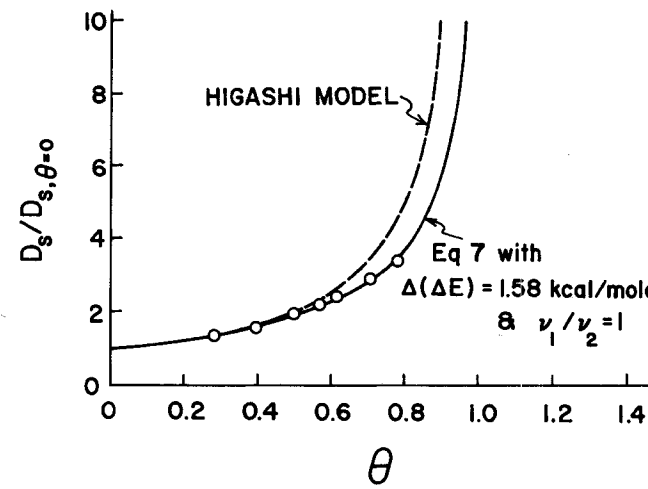

Fig. 1. Surface diffusion of propane on silica glass at 35°C (data points from Higashi et al., 1963).

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second layers. The quantity ν_1/ν_2 is more difficult to determine. We expect that it should be of order unity and for our present consideration we have assumed a value of unity except when otherwise indicated.

Higashi et al. (1963) measured the surface diffusion of propane on silica. Their results are shown on Figure 1 as a plot of $D_{s,\theta}/D_{s,\theta=0}$ versus θ. The solid line is Equation (7) assuming $\nu_1/\nu_2 = 1$ and $\Delta E_1 - \Delta E_2 = 1.58$ kcal/mole. The dashed line is the HIO model [Equation (3)]. Clearly in this case the experimental results favor the modified model.

One deficiency of the original HIO model is its indication that $D_{s,\theta}/D_{s,\theta=0}$ should be independent of temperature. Our modification suggests a fairly strong temperature dependence by way of the exponential term in Equation (7). Moreover, it is likely that ν_1/ν_2 will also be temperature dependent, but to an extent which would be hard to predict. The experimental results of Ross and Good (1956) show a definite dependence of $D_{s,\theta}/D_{s,\theta=0}$ upon temperature. Their data for *n*-butane on carbon black (Spheron 6 – 2700°C) at 30°C and 41.7°C are shown on Figure 2. They also measured heats of adsorption and found values of 8 kcal/mole in the monolayer region and 5.9 kcal/mole at $\theta = 1.2$. We used the difference, 2.1 kcal/mole, as an estimate for $\Delta E_1 - \Delta E_2$ in the solid line plots of Equation (7) in Figure 2. For the 30°C case ν_1/ν_2 was assumed to be unity. To obtain a proper fit we found that a value of 1.5 was required for the data at 41.7°C. The dashed line again represents the HIO model.

Carman and Raal (1951) measured diffusion rates of CF_2Cl_2 on Carbolac over a wide enough temperature range to obtain activation energies for diffusion by means of Arrhenius plots. They found that the activation energy was 3.3 kcal/mole in the monolayer region and about 2 kcal/mole between θ values of 1.2 and 1.8. The solid curve in Figure 3 is based on the resulting value of 1.3 kcal/mole for $\Delta E_1 - \Delta E_2$. It clearly provides a better approximation of the data than the unmodified HIO model.

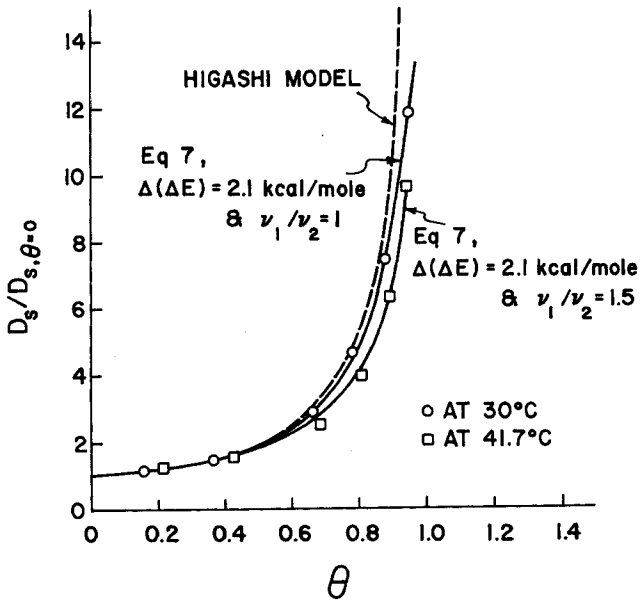

Fig. 2. Surface diffusion of butane on Spheron 6 (data points from Ross and Good, 1956).

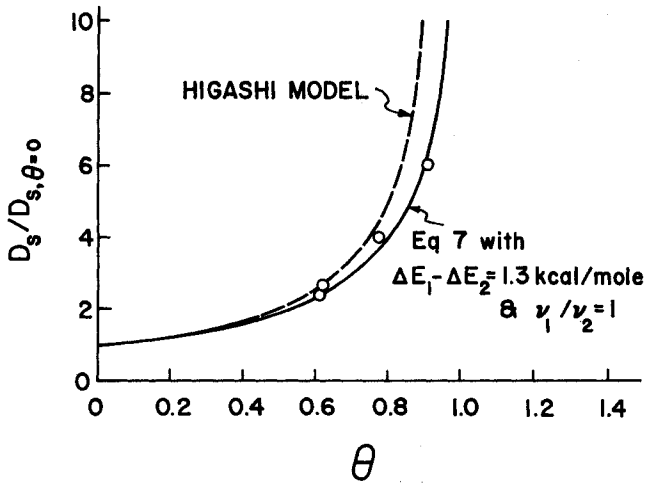

Fig. 3. Surface diffusion of CF_2Cl_2 on Carbolac matrix at –21°C (data points from Carman and Raal, 1951).

CONCLUSIONS

This test of our modification to the HIO model by comparison with some experimental data has been by no means exhaustive. Even so we feel that it supports the physical credibility of allowing for the possibility of attraction between a diffusing molecule and an occupied site. This simple extension provides better agreement with experiment and more insight with respect to the actual process.

ACKNOWLEDGMENT

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NOTATION

d = distance between adjacent surface sites
$D_{s,\theta}$ = surface diffusion coefficient, D_s at θ
E = energy level of adsorbed molecules referred to the gas phase
ΔE = activation energy for surface diffusion = $\Delta E_1 - \Delta E_2$
n = average number of jumps to find an empty site
R = gas constant
T = absolute temperature

Greek Letters

ν = frequency of oscillation of the adsorbed molecule with respect to the normal to the surface
θ = fractional surface coverage in the first layer
τ = residence time of the molecule on a site

Subscripts

1 = first adsorption layer
2 = second adsorption layer

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