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Surface Diffusion of Adsorbable Gases Through Porous Media

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An activated diffusion, or site-hopping, mechanism is used to describe surface diffusion of gases through porous media. This analysis provides a useful and accurate method for correlating data at submonolayer coverages on energetically heterogeneous surfaces. The data needed to use this correlation are surface area and pore structure of the adsorbent, adsorption isotherms at two or more temperatures, and the activation energy for migration. The former quantities are easily determined from Knudsen diffusion and adsorption measurements, while the activation energy can be found from a single permeability measurement. Predictions made in this way show excellent agreement with experimental data.

Surface diffusion plays an important role in the transport of gases through beds of porous and nonporous solids. It has been measured for a number of gases to (*1* to *10*), and attempts to find a mathematical description of this phenomenon have been made. An excellent review of early developments in adsorption and surface diffusion studies is presented by Dacey (*11*). Our objective is to find a plausible explanation for the fundamental surface transport mechanism and to use this model to correlate data covering broad ranges of temperature, surface properties, and gas-solid systems.

THEORY

The activated, or site-hopping, mechanism is commonly used to describe submonolayer surface diffusion (*1*, *4*, *12* to *14*). It postulates that an adsorbed molecule must partially desorb to migrate from one localized site to another. At room temperature, an adsorbed molecule may make as many as 6,000 jumps before completely desorbing (*15*). If one assumes a migrating molecule is more likely to readsorb at a vacant site than at an occupied site (*16*), a net flux of hopping molecules in the direction of decreasing surface concentration results.

Weaver and Metzner (5) derived an expression that relates the rate of surface diffusion to the pressure gradient within a cylindrical porous pellet. Their result is

$$I = \frac{s\rho}{2\pi j^2}\left[r\frac{\partial\overline{\lambda^2}}{\partial P} + \frac{\pi}{2j}\overline{\lambda^2}\frac{\partial r}{\partial P}\right] \qquad (1)$$

Here s is the specific surface area of the solid, j is the tortousity factor, ρ is the adsorbate density, $\overline{\lambda^2}$ is the average value of the square of the migration distance, r is the rate of migration, P is pressure, and I the permeability. This expression can be used to correlate experimental data or predict surface diffusion rates if the quantities $\overline{\lambda^2}$, $\frac{\partial\overline{\lambda^2}}{\partial P}$,

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r, and $\frac{\partial r}{\partial P}$ are known. This problem is considered here.

A transition state estimate of the number of activated (hopping) molecules that cross the potential energy barrier between adsorption sites per unit area of surface per unit time is (*17*)

$$r = \frac{x}{s}\left(\frac{q^*}{q}\right)\frac{kT}{h}\exp\left(\frac{-E^*}{RT}\right) \tag{2}$$

where x is the concentration of adsorbed molecules, q and q^* are partition functions of adsorbed and activated molecules, and E^* is the activation energy for hopping. We now use

$$\frac{\partial r}{\partial P} = \frac{1}{s}\left(\frac{q^*}{q}\right)\frac{kT}{h}\exp\left(\frac{-E^*}{RT}\right)\left[\frac{\partial r}{\partial P} - \frac{\partial E^*}{\partial P}\frac{x}{RT}\right] \tag{3}$$

$$k_r = \frac{1}{s}\left(\frac{q^*}{q}\right)\frac{kT}{h}$$

$$\theta = x/x_m \tag{4}$$

and

$$\frac{\partial}{\partial P} = \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial P}$$

to obtain the final transport equation

$$I = \frac{s\rho k_r x_m}{2\pi j^2}\left[\theta\frac{\partial\overline{\lambda^2}}{\partial\theta}\frac{\partial\theta}{\partial P} + \frac{\pi\overline{\lambda^2}}{2j}\left[\frac{\partial\theta}{\partial P} - \frac{\theta}{RT}\frac{\partial E^*}{\partial\theta}\frac{\partial\theta}{\partial P}\right]\right]\exp\left(\frac{-E^*}{RT}\right) \tag{5}$$

The quantities $\overline{\lambda^2}$ and $\frac{\partial\overline{\lambda^2}}{\partial\theta}$ were computed by Monte Carlo simulation (*18*). We surmised that if one could observe a surface containing mobile adsorbed molecules, he would see them hopping in what seemed to be a random way from one site to another. At submonolayer coverages, it is unlikely that a molecule would hop to an occupied site, also the probability of a hop of length λ is expected to decrease exponentially as λ increases (analogy with the mean free path concept of the kinetic theory of gases). These observations were simulated on a computer.

Before detailing the simulation, consider why it must be used to find $\overline{\lambda^2}$. The concept of localized adsorption forces the length of a hop to conform to discrete site spacings. The counting process requires a choice of site arrangement; we assumed a square lattice of sites with lattice spacing l. For any average coverage θ, some sites will be unoccupied, so there may be 0, 1, 2, 3, or 4 empty (available) sites at distance l from an activated molecule; 0, 1, 2, 3, or 4 empty sites at distance $\sqrt{2}l$, etc. Each molecule has a distinct environment and migrates according to the configuration of available sites around it. Now, admittedly, if we look at a large number of lattice configurations, each with average coverage θ, the *average* number of available sites at distance l is $4(1-\theta)$. Unfortunately the averages over discrete available sites and over configurations do not commute! Consequently, one must first average over hop lengths for a given configuration, and then average over configurations, rather than averaging over hop lengths in an average configuration. The fact that the two averages do not commute gives rise to the coverage dependence of the average hop distance.

For the simulation, a matrix of 2,500 sites was set up in a computer. For each value of coverage θ, an appropriate number of adsorbed molecules (filled sites) was distributed among the adsorption sites in a random manner (*18*). Each migration was simulated by randomly selecting a "jumper" from the surface, scanning the region within four lattice spacings to determine the likelihood that the migrating molecule would hop there, and then making the hop. Probabilities for each site around the jumper decreased exponentially with distance; occupied sites were assigned zero probability. The readsorption site was determined by a random selection using the assigned probability distribution. Sufficient jumps (5,000 to 15,000) were made at each coverage to insure convergence of the averaging process. The calculation was repeated for additional values of θ so a plot of $\overline{\lambda^2}$ versus θ, Figure 1, could be made and $\frac{\partial\overline{\lambda^2}}{\partial\theta}$ evaluated from that curve. Values of $\overline{\lambda^2}$ and $\frac{\partial\overline{\lambda^2}}{\partial\theta}$ were then related to the diffusion experiments by assuming that each site was occupied at BET monolayer coverage, x_m. Hopping distance, in units of lattice spacings, was then correlated with experiment by multiplying $\overline{\lambda^2}$ by the expression

$$a^2 = \left[\frac{s}{x_m\, 6.023\times 10^{16}}\right] \tag{6}$$

We recognize the crudeness of this last assumption, but note that meaningful refinements can be made only when better surface site descriptions are found. It should be noted, however, that site spacings calculated in this manner (about 9.5Å for vycor glass) are of the correct order of magnitude (*19*). By this method an average hopping distance of about 40Å was calculated for a coverage of 0.1, a very plausible result!

The only parameters still unspecified are partition functions q and q^* and the energy of activation E^*. E^* was determined experimentally, while q^*/q was estimated from statistical mechanics (*17*).

EXPERIMENTAL DATA

Surface transport through porous media has been measured (*7* to *10*) for a number of gases and adsorbent materials. Knudsen flow measurements reported there were used to calculate the tortuosity factor, j. BET surface area s and pellet density ρ were also given.

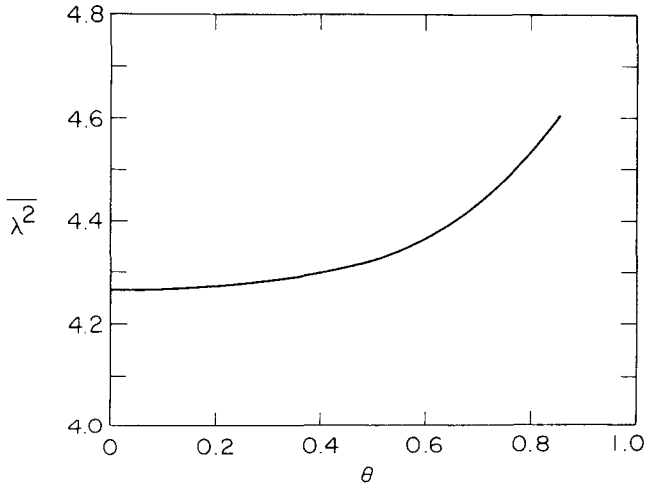

Fig. 1. The average value of $\overline{\lambda^2}$, in units of lattice spacings, as a function of coverage as computed from our simulation.

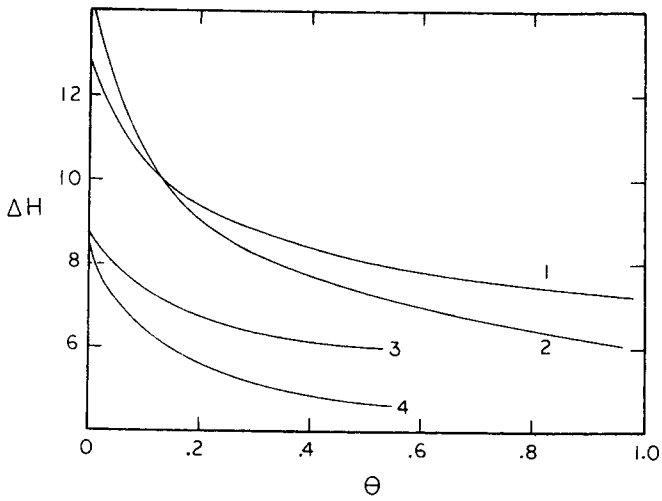

Fig. 2. The heat of adsorption, ΔH, in kcal./g.mole, as a function of coverage θ, as computed from reported adsorption isotherms. Curve 1 was computed from the data in reference 10, curve 2 from reference 6, curve 3 from reference 9, and curve 4 from 7.

The quantities x_m, θ, $\frac{\partial\theta}{\partial P}$, and the heat of adsorption were calculated from reported adsoption isothems, so isotherms were selected carefully. Least square fits of Freundlich, Langmuir, and BET isotherms (*20*) were found for each set of data in an effort to achieve an accurate fit. The BET equation best fit all data studied here, and provided a fit well within reported experimental accuracy. Once the isotherm was found, θ and $\frac{\partial\theta}{\partial P}$ were computed directly. Since calorimetric data were not available, isoteric differential heat of adsorption, ΔH, was calculated from the Clausius-Clapyron equation (*21*). Values for ΔH as a function of coverage are given in Figure 2.

CALCULATIONS AND RESULTS

Surface diffusion data of Russell (*4*), Perkinson (*6*), Carman and Raal (*9*) and Weaver (*5*) were compared to this theory. We first treated E^* as an adjustable parameter to determine if it was simply related to the heat of adsorption. A relationship between E^* and θ was assumed so $\frac{\partial E^*}{\partial\theta}$ could be evaluated. Each permeability data point and its corresponding value of $\frac{\partial E^*}{\partial\theta}$ (evaluated from the assumed relationship, with θ determined from the pellet's average pressure) were used in Equation (5) to obtain an improved E^* versus θ relationship. The procedure was repeated until the assumed and calculated values of E^* agreed. The ratio of E^* to the heat of adsorption ΔH,

$$R = E^*/\Delta H$$

was then tabulated in Table 1. R was found to be nearly constant for each system. This is a pleasing result, for while we are not able to predict the effect of surface heterogeneities on either the heat of adsorption or the energy of activation, it is likely that they are related. Tabulated values show E^* fell between 0.169 and 0.394 of the heat of adsorption for these systems. Unfortunately, no a priori method to determine its value could be suggested.

In order to illustrate the usefulness of the method of correlation presented in this paper, we have used Equation (5), together with the results of the computer simulation, to estimate gas-solid permeabilities. Here we used R equal to 0.28 and 0.32 for the high and low temperature data of Perkinson for the sulfur dioxide-glass system, 0.21 and 0.23 for the data of Russell for the isobutane-glass system, 0.365 and 0.39 for the data of Carman and Raal for the dichlorodifluoro-methane-silica system, and 0.19 for the data of Weaver for the isobutane-glass system. Experimental data and theoretical predictions are plotted in Figure 3. In all cases there is agreement between them. This is significant because earlier attempts such as Russell's test of the Carman and Raal data (*9*), and Perkinson's attempt to correlate Russell's data (*6*) failed to yield such a good correlation. The shape of our curves corresponds to the data, and numerical values never differ by more than a factor of two, even though the data span a range of more than two orders of magnitude.

Two curves (labeled 1 and 2) in Figure 3 illustrate the extent to which the choice of R influences our predictions of Russell's high temperature experiments. Curve 1 corresponds to the choice $R = 0.29$, while curve 2 repre-

TABLE 1. ACTIVATION ENERGIES CALCULATED FROM EXPERIMENTAL DATA

Solid-gas system	T, °C.	x, mg. moles g. solid	E^*	$R = E^*/\Delta H$
Perkinson	30.0	0.353	2256	0.291
		0.453	2137	0.289
SO_2 on glass		0.577	1955	0.278
		0.625	1882	0.273
		0.757	1742	0.262
		0.768	1738	0.261
		0.819	1729	0.259
	15.0	0.494	2381	0.332
		0.511	2354	0.329
		0.538	2309	0.325
		0.685	2151	0.310
		0.761	2050	0.301
		0.810	1941	0.290
		0.811	1892	0.286
		0.871	1887	0.285
Weaver	25.0	0.0122	1429	0.183
		0.0281	1404	0.188
iC_4 on glass		0.0312	1399	0.189
		0.0686	1337	0.198
		0.1396	1191	0.202
		0.1649	1127	0.199
Carman & Raal	−21.5	0.3013	2676	0.353
		0.4075	2634	0.361
CF_2Cl_2 on silica		0.5677	2560	0.369
		0.7288	2484	0.374
		1.0224	2381	0.372
	−33.1	0.5737	2724	0.394
		0.8528	2556	0.392
		1.082	2447	0.385
Russell	25.0	0.013	1794	0.169
		0.025	1787	0.173
iC_4 on glass		0.089	1735	0.193
		0.184	1618	0.214
		0.185	1617	0.214
		0.231	1553	0.217
		0.301	1464	0.216
		0.309	1455	0.216
		0.364	1409	0.213
		0.437	1418	0.215
	0.0	0.068	1961	0.212
		0.074	1955	0.215
		0.122	1906	0.231
		0.233	1764	0.248
		0.352	1620	0.240

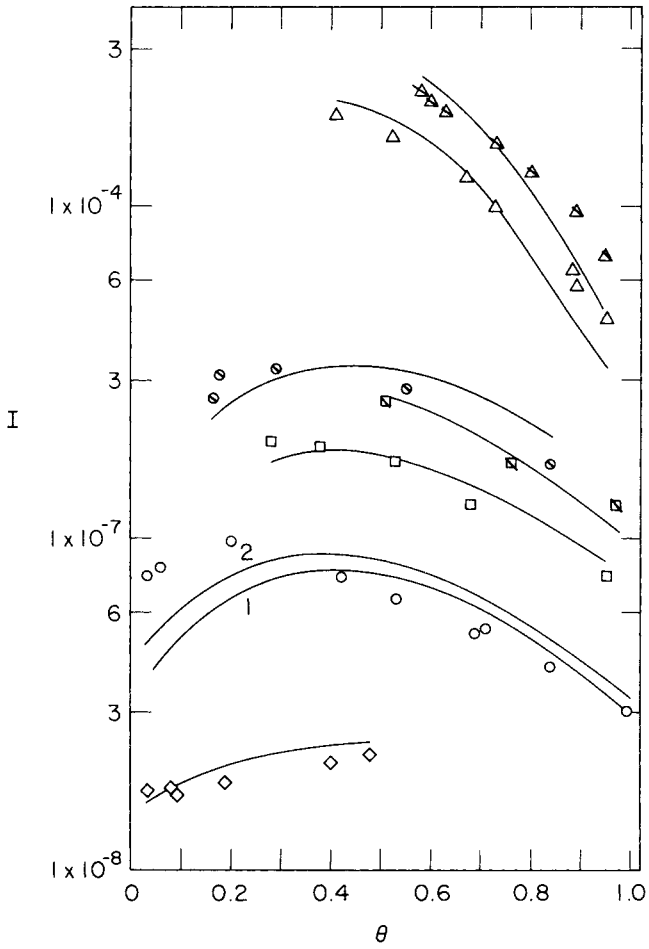

Fig. 3. The predicted and measured permeabilities, in units of mg.moles/(sec.)(cm)(mm)(Hg) as a function of coverage. Here ○ and ◐ are the data of reference 4, for isobutane on glass at 25° and 0°C.; respectively; △ and ◭ are the data of reference 6 for SO_2 on glass at 30° and 15°C.; □ and ◪ are the data of reference 9 for CF_2Cl_2 on silica at −21.5° and −33.1°C.; and ◇ is the data of reference 7 for isobutane on glass at 25°C.

sents $R = 0.28$. Either value gives reasonable agreement. The choice of R influences only the position of the curve, not its shape.

The shapes of the curves presented in Figure 3 are interesting because they predict permeability increases at low coverages, but decreases at higher coverages. This can be explained by the interrelation of two competing effects present in surface diffusion. First, as seen from Figure 2, the heat of adsorption decreases with increasing coverage, particularly at low coverages. Consequently, the energy of activation for migration decreases with coverage, reducing the intersite barrier to hopping. As the adsorption isotherms level off at increased coverage, $\frac{\partial \theta}{\partial P}$ decreases. Therefore, a higher pressure gradient is needed to retain the diffusion driving force. Otherwise the apparent permeation decreases. Since the decrease of activation energy is significant only at low coverages, and the saturation behavior of the isotherm important only at moderate and high coverages, the overall behavior of the permeability is first to increase and then decrease as coverage increases.

CONCLUSIONS

For the first time, a single transport equation has successfully correlated the experimental data of several investigators for a broad range of temperatures, surface properties, and gas-solid systems. The success of this work supports the site hopping mechanism for surface diffusion at adsorbate concentrations below monolayer coverage.

The computer simulation of surface diffusion gave a unique jumping distance-coverage relationship for a square arrangement of adsorption sites. The square arrangement is apparently not overwhelmingly important in the analysis, since it is unlikely that the porous solids used in the experimental studies had such a regular site arrangement.

Activation energy for surface diffusion was found to be nearly a constant fraction of the heat of adsorption. This proportionality factor varied from system to system, however, and no a priori method of calculating it was found. Since some questions about the model we used remain unanswered, particularly a justification for the assumption of a mean-free-path like distribution of hopping length, we did not consider methods to predict R. Nevertheless, with only one experimental permeability measurement to establish R, one can now predict the contribution of surface diffusion to the total gas flow through a bed of solid media.

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