Connectivity Effects for Surface Diffusion of Adsorbed Gases

Nonlocal models for the surface transport of adsorbed gases on solids are proposed and compared to experimental data. These models take into account connectivity effects due to heterogeneous adsorption potential surfaces and introduce a more realistic calculation of the surface mean free path.

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SCOPE

Several models exist that describe the surface flux of adsorbed gases in solids to various degrees of accuracy. However, there are two aspects that have not been taken into account in the literature:

1. The cooperative nature of the effects of the surface adsorptive potential's heterogeneity, which means that the activation energy needed for a molecule to migrate through a distance R is determined not only by the adsorptive potential at a point but also by what we call the energetic topography of the surface within a distance R.
2. The fact that a migrating molecule stops contributing to the surface flux not only when it is readsorbed on a site, but also when it evaporates from the surface into the gas phase. This particularly affects the calculation of the mean free path.

The objective of this study is to develop a general surface diffusion model that is based on the connectivity concept of percolation theory and that takes these two aspects into account.

CONCLUSIONS AND SIGNIFICANCE

By developing a close analogy of the surface diffusion of adsorbed gases on a heterogeneous surface with the conduction of electrons in an amorphous semiconductor, we were able to take into account the cooperative nature of the phenomenon and arrive at a remarkably simple equation for the surface permeability, Eq. 35: $l_s = l_o \exp\{-(T_o/T)^{1/3}[f(\theta)]^{-2/3}\}$.

We concluded our work by improving the calculation of the mean free path $\lambda(\theta)$ by including the evaporation contribution to it. We show that the model fits the experimental data for several gas-solid systems very well and that the parameters obtained are fully significant.

In short, we have developed a model that leads to a very simple equation for the surface permeability, one that takes into account more physical facts than previous models and that fits experimental data at least as well as other models.

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Introduction

Several models to describe the surface flux of adsorbed gases on solids have been developed and tested during the past three decades (Babbit, 1950; Gilliland et al., 1958, 1974; Higashi et al., 1963; Horiguchi et al., 1971; Weaver et al., 1966; Smith et al., 1964; Roybal et al., 1972; Sladeck et al., 1974; Ponzi et al., 1977; Horas et al., 1980).

In general, most of these models show the following common characteristics:

1. They are local models, ones in which everything is determined from what happens at any point on the surface, without taking into account the energetic topography of the surface.
2. The calculation of the mean free path for diffusion of adsorbed molecules does not take into account that such a molecule may stop contributing to the surface flux by evaporating from the surface.

However, some efforts have been made toward a description of migrating molecules on heterogeneous surfaces. For example, Gilliland et al. (1974) and Sladek et al. (1974) take into account the energetic heterogeneity of the solid through the dependence of the isosteric heat of adsorption with surface coverage, and Horas et al. (1980) introduce a two-point correlation function for the surface diffusion coefficient on the basis of the generalized Gaussian model for adsorption (Ripa and Zgrablich, 1975).

In the present paper we discuss some new ideas toward a more detailed understanding of transport phenomena for adsorbed gases, describing the cooperative nature of the surface heterogeneity and proposing a more realistic calculation of the mean free path.

Adsorptive Potential Surfaces: Effect on Surface Migration of Adsorbed Molecules

In practice most solids used for adsorption and catalytic processes are energetically heterogeneous. This means that the adsorption potential $V(x, y)$ changes from one point (x, y) to another on the surface according to some probabilistic distribution.

We could say that, for a particular sample, the adsorptive potential surface $V(x, y)$ would look like a mountainous landscape whose contour lines, or constant potential lines, could, for example, be like those represented in Figure 1.

Surface migration of adsorbed molecules takes place in an activated state in such a way that molecules continue under the influence of adsorption forces of the solid, which are of short range. The probability for an adsorbed molecule to make a transition to the activated state decreases exponentially with the activation energy needed. Then, if a molecule migrates, say, from site A to site B, it is much more probable that it does it through a "valley" C (dashed line) and not through a "mountain" D (dotted line). Besides, if the molecule migrates through D, it probably acquires enough activation energy to desorb and would not contribute to the surface flow.

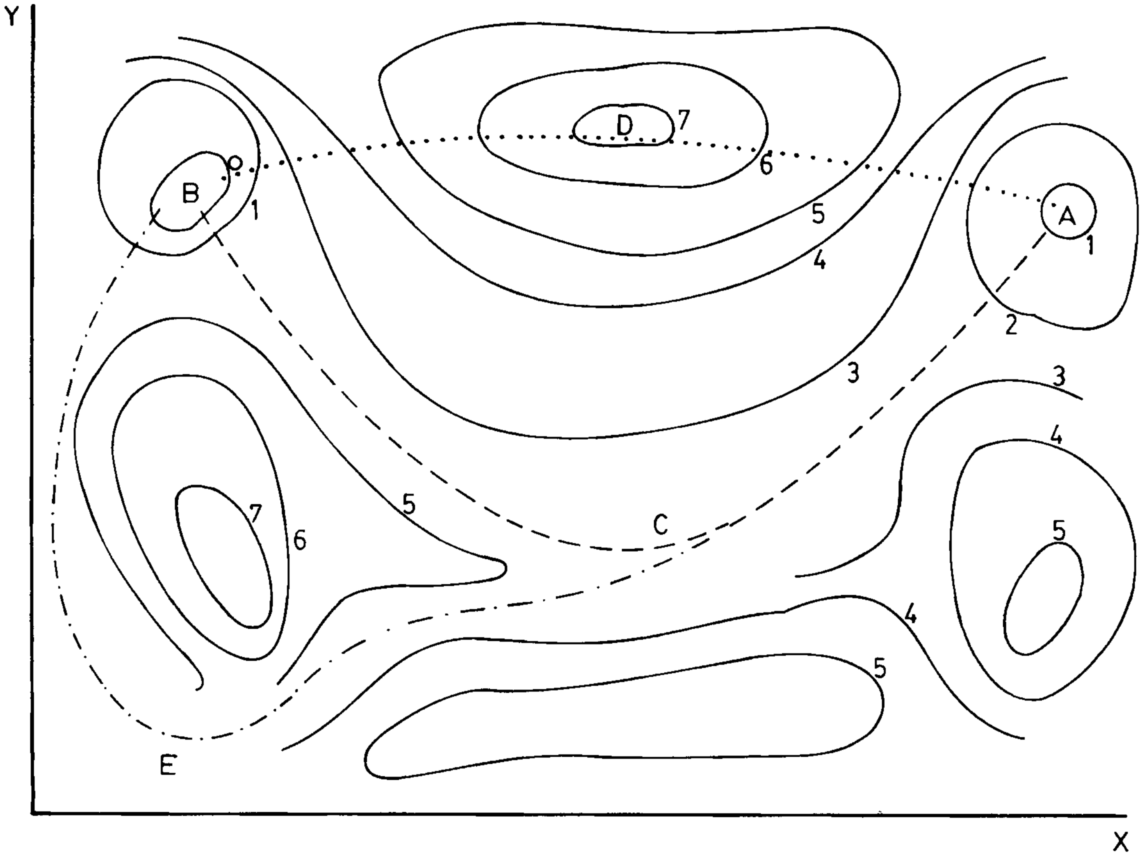

Figure 1. Typical configuration of contour lines of adsorptive potentials surface.

Furthermore, there could be other competing easy paths to get to B, for example through E (point-and-dash line).

We see, then, that the energetic heterogeneity of the solid brings about the problem of the "connectivity" of the potential surface and this introduces the nonlocal nature of surface diffusion.

We shall discuss how the surface transport problem can be mathematically described in such a way as to take into account these features, first in a global and simple way and then in a more detailed description.

A Simple Model

Let $P(R)$ be the probability per unit time for an adsorbed molecule to migrate through a distance R on the solid surface. Then we can write

$$P(R) = \nu_o \exp(-R/\lambda) \exp(-\Delta E/kT) \qquad (1)$$

where ν_o is a characteristic frequency of the gas-solid system, λ is the one-dimensional mean free path, ΔE is an activation energy, k the Boltzmann constant, and T the temperature.

If we suppose a constant probability distribution for adsorptive potentials, then the number of energy states between E and $E + \Delta E$ within a distance R is proportional to R^2 and we can substitute ΔE by a mean activation energy $\langle \Delta E \rangle$ given by

$$\langle \Delta E \rangle = A_o W/R^2 \qquad (2)$$

where A_o is a characteristic area of the gas-solid system and W is the width of the constant probability distribution of adsorptive potentials.

From Eqs. 1 and 2 we get

$$P(R) = \nu_o \exp(-R/\lambda) \exp(-A_o W/kTR^2) \qquad (3)$$

The easiest way in which we can account for connectivity effects is to suppose that the most efficient transport mechanism is the one that maximizes $P(R)$. Then we obtain the condition

$$\frac{\partial}{\partial R}\left[\frac{R}{\lambda} + \frac{A_o W}{kTR^2}\right] = \frac{1}{\lambda} - 2\frac{A_o W}{kTR^3} = 0 \qquad (4)$$

From here we get

$$R = (2A_o W\lambda/kT)^{1/3} \qquad (5)$$

and

$$P_m(R) = \nu_o \exp\left\{-\frac{3}{2}\left[\frac{2A_o W}{kT}\right]^{1/3} (\lambda)^{-2/3}\right\} \qquad (6)$$

From this we can calculate the surface diffusion coefficient D_s through

$$D_s = \lim_{t\to\infty} \frac{\langle[\vec{R}(t) - \vec{R}(o)]^2\rangle}{t} \qquad (7)$$

where $\langle\ \rangle$ means time average.

If ν is the number of migrations per unit time, during a time t there will be νt migrations. If $\vec{S}_i$ is the displacement vector for ith migration, then:

$$\vec{R}(t) - \vec{R}(o) = \sum_{i=1}^{\nu t} \vec{S}_i \qquad (8)$$

Therefore,

$$\begin{aligned}\langle[\vec{R}(t) - \vec{R}(o)]^2\rangle &= \left\langle\sum_{i=1}^{\nu t} |\vec{S}_i|^2\right\rangle + \left\langle\sum_{i\neq j} \vec{S}_i \cdot \vec{S}_j\right\rangle \\ &= \left\langle\sum_{i=1}^{\nu t} |\vec{S}_i|^2\right\rangle = \sum_{i=1}^{\nu t} R^2 = \nu t\, R^2 \end{aligned} \qquad (9)$$

Now, ν is just $P_m(R)$; then from Eqs. 6, 7, and 9 we finally obtain

$$D_s = \nu_o \left(\frac{2A_o W\lambda}{kT}\right)^{2/3} \exp\left\{-\frac{3}{2}\left[\frac{2A_o W}{kT}\right]^{1/3} \lambda^{-2/3}\right\} \qquad (10)$$

We leave the discussion of the mean free path λ to a later section. For the time being we remark only that λ is a function of the surface coverage θ and can be described as

$$\lambda = \lambda_o f(\theta) \qquad (11)$$

Then Eq. 10 takes the form

$$D_s = \nu_o \lambda_o^2 \left[2\frac{T'_o}{T} f(\theta)\right]^{2/3} \cdot \exp\left\{-\frac{3}{2}\left[2\frac{T'_o}{T}\right]^{1/3} [f(\theta)]^{-2/3}\right\} \qquad (12)$$

where we introduced $T'_o = A_o W/(k\lambda_o^2)$. This, according to Eq. 2, means that T'_o is a characteristic temperature of the gas-solid system such that kT'_o is the mean activation energy for migration.

We see that the predominant temperature (energy) and coverage (space) dependences, in the exponential factor of D_s, carry the power $-1/3$ and $-2/3$, respectively. This behavior is intimately related to the fact that the relevant phase space for surface diffusion is essentially three-dimensional, namely, one dimension for energy and two dimensions for the surface.

The more detailed discussion in the following section will show this relation again in a sharper way.

General Nonlocal Model

We are interested in surface diffusion at surface coverage below the monolayer. In such a case, the mean coverage at a site i, θ_i, can be described as a Fermi–Dirac-like distribution

$$\theta_i = \frac{1}{1 + \exp[\beta(E_i - \mu)]} \qquad (13)$$

where E_i is the energy of the molecule at site i and μ is the chemical potential

$$\beta\mu = \ln(\beta p \Lambda^3) \qquad (14)$$

with

$$\Lambda = \left(\frac{h^2\beta}{2\pi m}\right)^{1/2}; \quad \beta = \frac{1}{kT} \qquad (15)$$

where h is the Planck constant and m the molecule mass. This is equivalent to saying that the adsorption isotherm for sites of energy E_i is a Langmuir isotherm, even though the global isotherm for the whole heterogeneous surface cannot be described by such an equation.

At equilibrium, let ϕ_{ij}^{eq} be the number of molecules that migrate from i to j, separated by a distance Rij, per unit time.

We suppose that a molecule gets (or loses) energy through absorption (or emission) of phonons. Let P_a and P_e be the probabilities for absorption or emission, respectively, of a phonon. Then

$$\phi_{ij}^{eq} = \phi_o \quad \theta_i(1-\theta_j)\begin{Bmatrix} P_e & \text{for} & E_i > E_j \\ P_a & \text{for} & E_i < E_j \end{Bmatrix}\exp(-R_{ij}/\lambda) \qquad (16)$$

Now, the energetic behavior for diffusion at low coverage should not depend strongly on θ, whose main contribution will come from $\lambda(\theta)$, to be calculated later. Then, for the time being, we can assume very low surface coverage where $\beta(E_i - \mu) \gg 1$.

With this in mind, we can write

$$\theta_i \simeq \exp[-\beta(E_i - \mu)] \qquad (17)$$

$$P_e \propto N_p + 1 = \frac{\exp(\beta E_p)}{\exp(\beta E_p) - 1} \simeq 1 \qquad (18)$$

$$P_a \propto N_p = \frac{1}{\exp(\beta E_p) - 1} \simeq \exp(-\beta E_p) \qquad (19)$$

where N_p = number of phonons and $E_p = |E_i - E_j|$.

From these approximations and Eq. 16 we obtain

$$\phi_{ij}^{eq} = \phi_o \exp(-R_{ij}/\lambda)\exp(\beta\mu) \cdot \exp\left[-\frac{\beta}{2}(|E_i| + |E_j| + |E_i - E_j|)\right] \qquad (20)$$

which clearly shows that $\phi_{ij}^{eq} = \phi_{ji}^{eq}$, and there is no net transport.

When a pressure gradient is applied, then a net transport will arise, given by

$$\psi_{ij} = \phi_{ij} - \phi_{ji} = \phi_{ij}^{eq}\,\frac{p_i - p_j}{p} \qquad (21)$$

where p is the pressure mean value.

Equation 21 can be put in the form

$$\psi_{ij} = \frac{\phi_{ij}^{eq}}{p}\frac{\Delta p}{\Delta\theta}\Delta\theta = -G_{ij}\Delta\theta \qquad (22)$$

This equation is completely equivalent to the one that would describe the electric current in a circuit with conductance G_{ij} between two points with an electric potential difference $\Delta\theta$.

By this analogy we shall take into account the nonlocality, or connectivity effects, of adsorption potential surfaces, following arguments from percolation theory that have been applied with success to the problem of electrical conductivity in amorphous solids (Ambegaokar et al., 1971).

Different points of the three-dimensional space $(\vec{R}, E)$ are connected by resistances whose conductance values G_{ij} are probabilistically distributed. This is so because the surface is energetically heterogeneous. If we take resistances from that distribution, one by one in decreasing order of conductance values, and assign them randomly to pairs of sites on the surface, then we will achieve a critical conductance G_c equal to the total conductance of network, when a path crossing the entire surface has been built, Figure 2.

At this point we say that a completely connected component has been obtained, and there will be conduction of current. Now if more resistances are added there will appear new paths, but the total conductance will not increase appreciably because only big resistances (small conductance values) are left and the current will remain approximately constant.

Then if σ is the conductivity of the sample, we can put

$$\sigma = gG_c = D_s \qquad (23)$$

where g is a geometrical factor. In our problem σ is just the surface diffusion coefficient D_s, and g has units of area. The problem now reduces to finding G_c.

The condition for conduction is

$$G_{ij} = \frac{\phi_{ij}^{eq}}{p}\frac{\Delta p}{\Delta\theta} > G_c \qquad (24)$$

or, using Eqs. 20 and 14

$$\frac{R_{ij}}{\lambda} + \frac{1}{2}\beta[|E_i| + |E_j| + |E_i - E_j|] < \ln\left(\frac{G_c}{\beta\Lambda^3\phi_o}\frac{\partial\theta}{\partial p}\right)^{-1} \qquad (25)$$

Let us consider the three-dimensional space $(\vec{R}, E)$ in Figure 3. Any given point i is surrounded by a conducting region determined by all $\vec{R}$ and E values that satisfy the condition

$$\frac{|R - R_i|}{\lambda} + \frac{1}{2}\beta[|E_i| + |E| + |E_i - E|] < \ln\left(\frac{G_c}{\beta\Lambda^3\phi_o}\frac{\partial\theta}{\partial p}\right)^{-1} \qquad (26)$$

These regions are three-dimensional polyhedra in the $(\vec{R}, E)$ space as shown in Figure 3. These polyhedra have a maximum spatial dimension (which results when $E_i = E = 0$ in Eq. 26)

$$\Delta R_{max} \simeq \lambda \ln\left(\frac{G_c}{\beta\Lambda^3\phi_o}\frac{\partial\theta}{\partial p}\right)^{-1} \qquad (27)$$

and a maximum energy dimension (which results when $|\vec{R} - \vec{R}_i| = 0$ in Eq. 26)

$$\Delta E_{max} \simeq \frac{1}{\beta}\ln\left(\frac{G_c}{\beta\Lambda^3\phi_o}\frac{\partial\theta}{\partial p}\right)^{-1} \qquad (28)$$

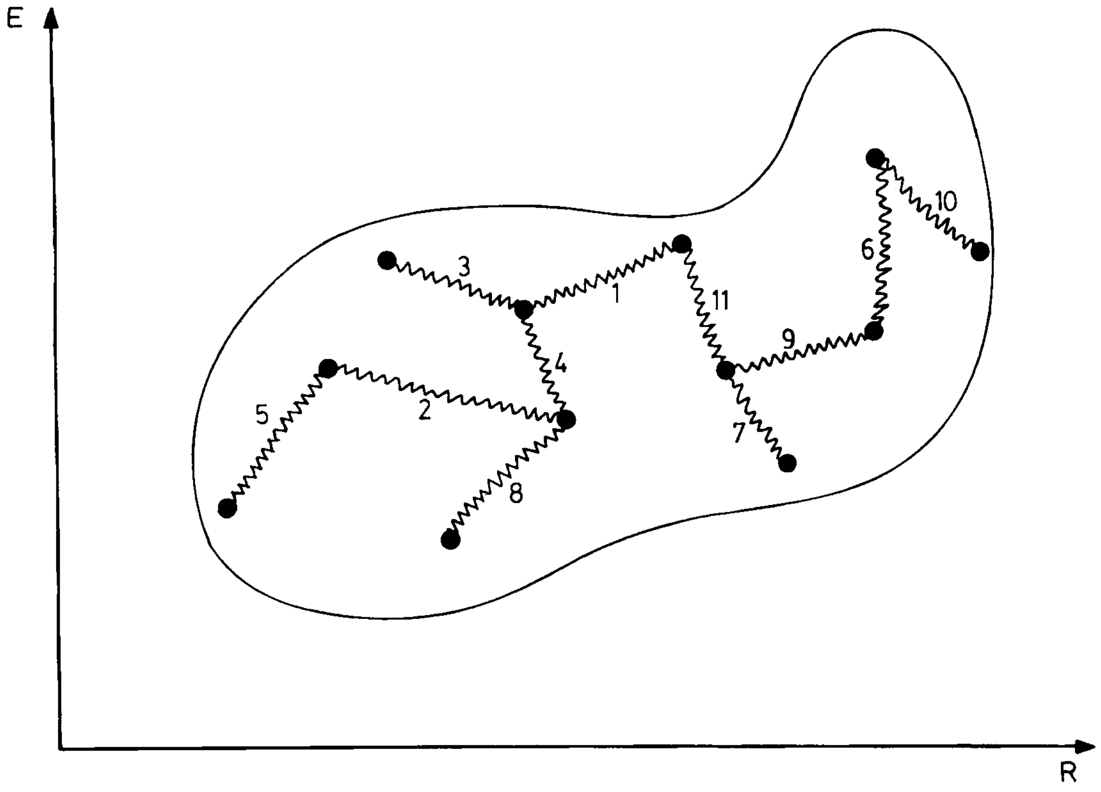

Figure 2. Representation of a "completely connected component."

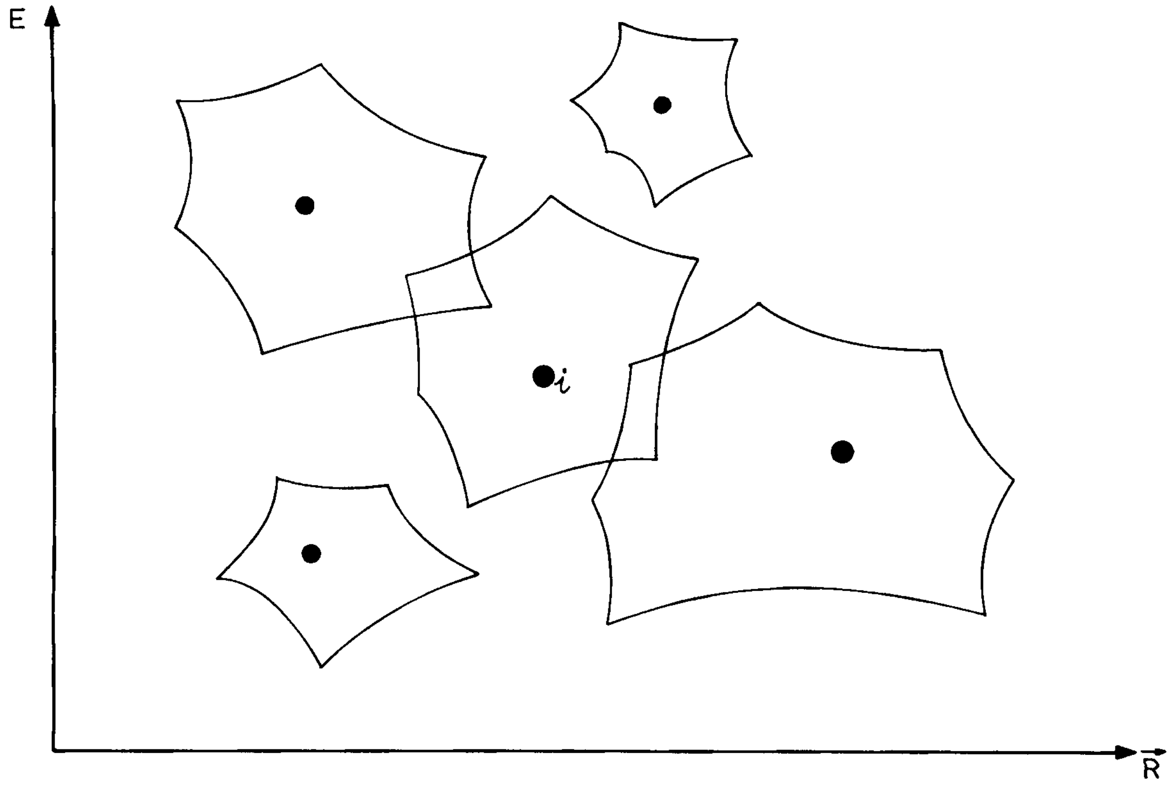

Figure 3. Conducting polyhedra in the three-dimensional ($\vec{R}$, E) space.

Table 1. Parameter Values Obtained in Fitting Experimental Data

Gas	Temp. K	Parameter $T_oa_o^2$ K	 $I_o\sqrt{MT}$*	 a_1/a_o	 a_2/a_o	Ref.
Freon 12	268	315.0	0.075	2.94	0.72	Ponzi et al. (1977)
	283	312.0	0.053	3.41	−0.52	
	313	294.0	0.030	5	−9.4	
1,3-butadiene	283	229.0	0.300	2.16	1.49	Marchese et al. (1982)
	298	240.0	0.292	4.8	−1.2	
	323	235.0	0.133	2.21	0.619	
	348	292.0	0.071	1.45	0.32	
	403	216.5	0.028	0.186	0.66	
n-butane	283	297.5	0.274	1.417	1.37	Marchese et al. (1982)
	298	193.1	0.162	1.05	1.56	
	323	262.5	0.105	1.16	0.814	
	358	216.6	0.050	2.09	−0.83	
	413	273.4	0.024	2.27	−1.75	
Ethylene	194	170.8	0.226	1.28	1.30	Horas et al. (1980)
	206	138.5	0.135	0.2	1.45	
	225	202.5	0.125	1.04	0.445	
	248	175.9	0.043	−0.73	1.09	
	278	126.0	0.023	−1.5	1.81	

*$I_o\sqrt{MT} = 10^{11}$ (kmol · K · kg)$^{1/2}$/m · s · Pa.

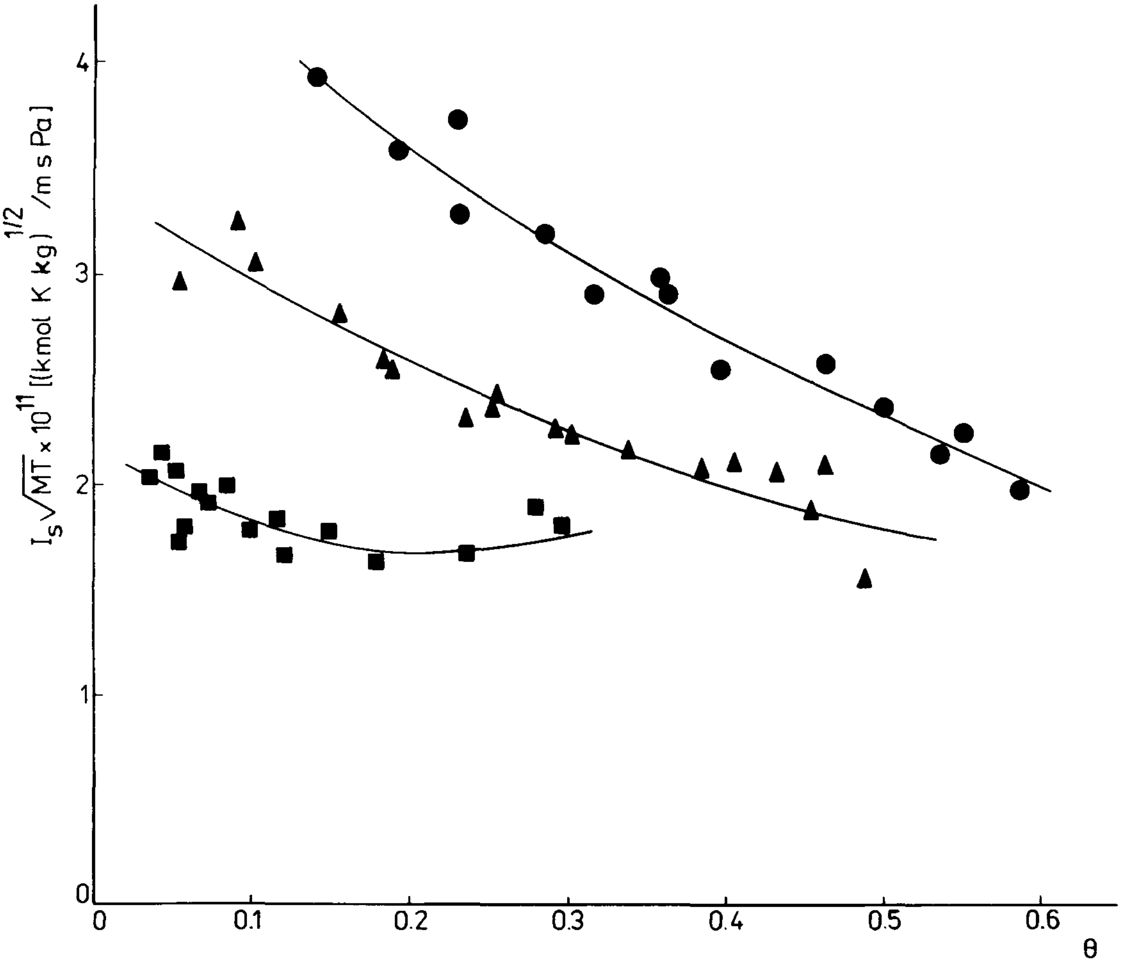

Figure 4. Surface permeabilities for Freon 12 on Carbon Regal 660.
● 268 K; ▲ 288 K; ■ 313 K.

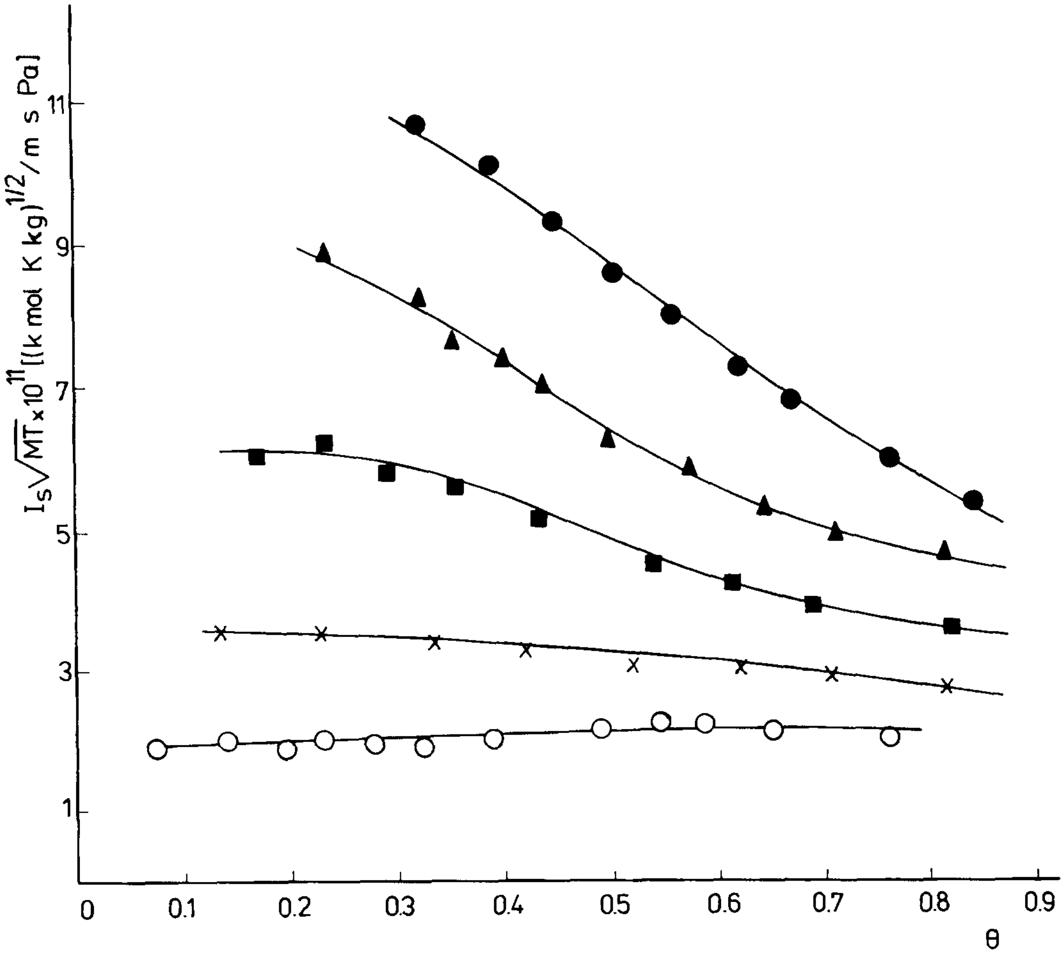

Figure 5. Surface permeabilities for 1,3-butadiene on Carbon Regal 660.
● 283 K; ▲ 298 K; ■ 323 K; X 348 K; O 403 K.

Then, a typical volume for these polyhedra is

$$\Omega = (\Delta R_{max})^2 \cdot (\Delta E_{max}) \tag{29}$$

To obtain conduction, these polyhedra must touch one another in such a way as to form a completely connected component. This will happen when the total volume of conducting polyhedra reaches some fraction of the total space (according to percolation theory, this is about 15% of total space: Ambegaokar et al., 1971).

If we assume a constant density ρ_o in the $(\vec{R}, E)$ space (this is equivalent to assuming constant probability distribution for adsorptive potentials), then the condition for having a completely connected component will be

$$\rho_o \Omega = \delta \tag{30}$$

From here, and using Eqs. 23, 27, 28, and 29 we obtain at once

$$D_s = g \frac{\Lambda^3 \phi_o}{kT} \frac{\partial p}{\partial \theta} \exp\left[-\left(\frac{\delta}{kT\rho_o}\right)^{1/3} \lambda^{-2/3}\right] \tag{31}$$

We find, again, the power $(-1/3)$ for temperature and $(-2/3)$ for the mean free path in the exponential factor in analogy to Eq. 10. Now we clearly see that this is due to the three-dimensional characteristic of the $(\vec{R}, E)$ space and to Eq. 29.

If we put, as before, $\lambda = \lambda_o f(\theta)$ and define

$$T_o = \frac{\delta}{k\rho_o\lambda_o^2} \tag{32}$$

then Eq. 31 becomes

$$D_s = g \frac{\Lambda^3 \phi_o}{kT} \frac{\partial p}{\partial \theta} \exp\left\{-\left(\frac{T_o}{T}\right)^{1/3} [f(\theta)]^{-2/3}\right\} \tag{33}$$

Again, T_o is a characteristic temperature of the gas-solid system, such that kT_o is the mean activation energy for diffusion, as can easily be seen from the definition of parameters in Eq. 32.

In contrast to Eq. 12, Eq. 33 shows explicitly the dependence of D_s on the adsorption isotherm through its derivative $\partial p/\partial \theta$ in the preexponential factor.

For the analysis of experimental measurements it is easier to work with the surface permeability I_s. D_s is related to I_s through the equation

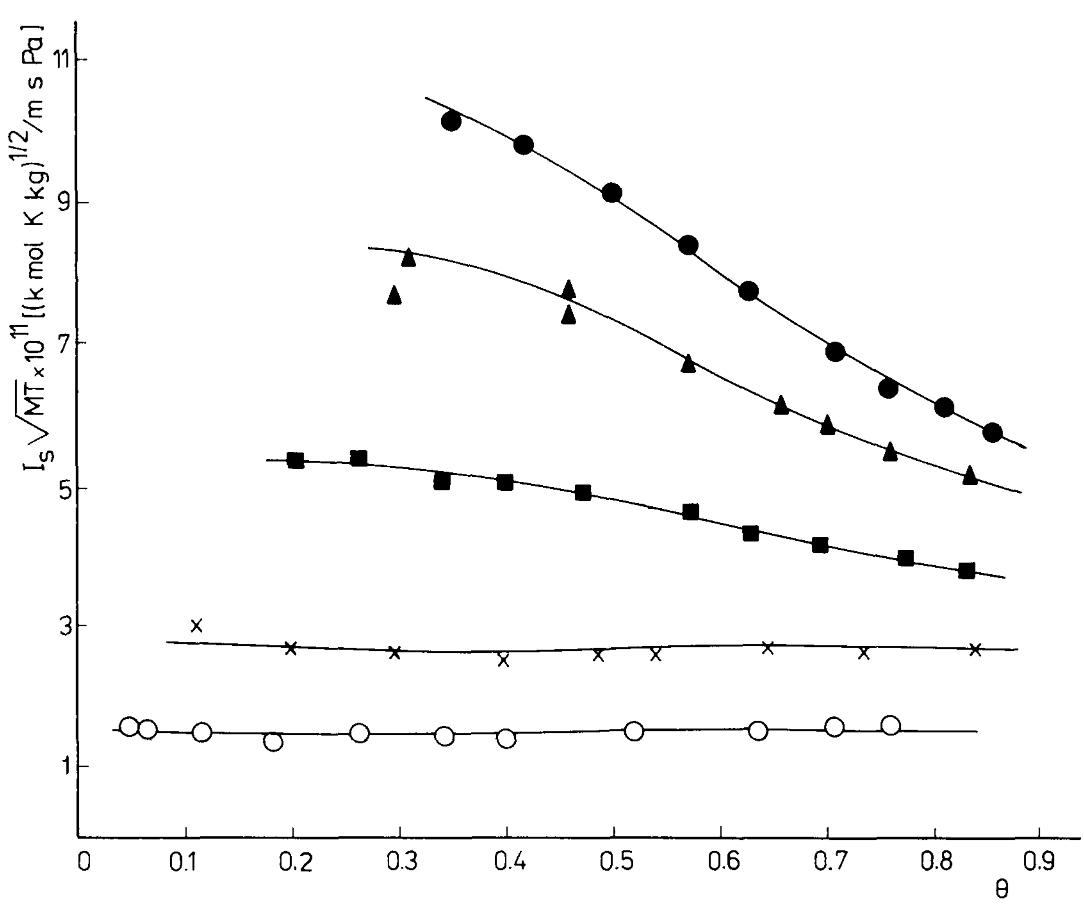

Figure 6. Surface permeabilities for *n*-butane on Carbon Regal 660.
● 283 K; ▲ 298 K; ■ 323 K; X 358 K; O 413 K.

$$D_s = \left[\frac{\tau_g V_{STP}}{\rho_p V_m}\frac{\partial p}{\partial \theta}\right] I_s \tag{34}$$

where τ_g is the gaseous tortuosity, V_{STP} the gas molar volume at standard conditions, V_m the volume for monolayer adsorption, and ρ_p the density of the pellet.

Then we have for the surface permeability the simple expression

$$I_s = I_o \exp\left\{-\left(\frac{T_o}{T}\right)^{1/3}[f(\theta)]^{-2/3}\right\} \tag{35}$$

where

$$I_o = g\frac{\Lambda^3 \phi_o \rho_p V_m}{\tau_g V_{STP} k T}.$$

Finally, we notice that a more general case in which the adsorptive potential probability distribution is not constant but given by some function $P(E)$ can also be treated. In such a case the condition in Eq. 30 becomes

$$\left[\int_E^{E+\Delta E_{max}} P(E)\, dE\right]\cdot(\Delta R_{max})^2 = \delta \tag{36}$$

and the complexity of the result for D_s will depend on the actual form of $P(E)$.

Mean Free Path for Surface Diffusion

All the mean free path calculations for surface diffusion known in the literature are based on the assumption that a molecule contributes to the surface flux from the moment the molecule jumps to the activated state until it is adsorbed back on the surface. However, a molecule that jumps to the activated state can instead jump to the gas phase, thereby desorbing completely. We shall discuss briefly the way we can get the coverage dependence for a generalized concept of λ.

On the basis of a random walk with no return to the origin, λ is found to be (Ponzi et al., 1977).

$$\lambda = \frac{\lambda_o}{P_{ef}(\theta)} \tag{37}$$

where P_{ef} is the effective probability for a molecule to be captured when passing over an unoccupied site.

All we have to do is to interpret P_{ef} as the effective probability for a molecule either to be captured when passing over an unoccupied site or to evaporate to the gas phase in passing over an occupied site.

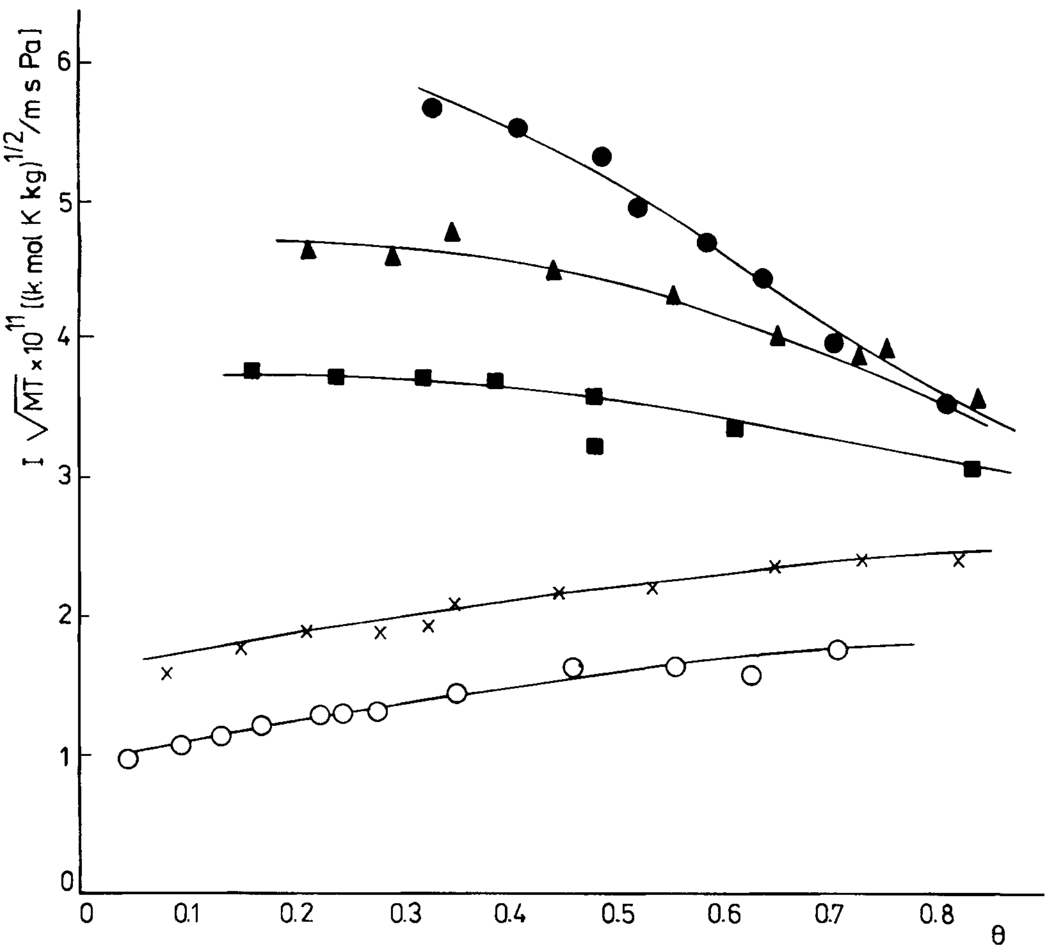

Figure 7. Surface permeabilities for ethylene on Carbon Regal 660.
● 194 K; ▲ 206 K; ■ 225 K; X 248 K; O 278 K.

Then we can write.

$$P_{ef}(\theta) = a_o(1 - \theta) + a_1\theta + a_2\theta^2 + \cdots \tag{38}$$

where a_o is the probability of capture by an unoccupied site, a_1 the probability of evaporation in passing over a singly occupied site, a_2 the probability of evaporation in passing over a doubly occupied site, and so on. In general it will be sufficient to take up to the a_2 term, and in most cases it is enough to take only up to the a_1 term.

With this, and Eqs. 11 and 37, the function $f(\theta)$ in Eq. 33 and 35 is given by.

$$f(\theta) = \frac{1}{a_o(1 - \theta) + a_1\theta + a_2\theta^2} \tag{39}$$

Analysis of Experimental Results

We have used Eq. 35 to fit experimental data for surface permeability of several gases on Carbon Regal 660 (Ponzi et al., 1977; Horas et al., 1980; Marchese et al., 1982); the parameter values obtained are shown in Table 1.

At constant θ the exponential temperature dependence $\exp(T)^{-1/3}$ fits very well all experimental data. However the usual dependence $\exp(T)^{-1}$ fits the data equally well. This is due to the fact that there are not data, for a given gas-solid system, that cover a temperature range long enough to distinguish between the two laws. We realize that to obtain, for a given gas-solid system, surface diffusion data on a temperature range such as 100 to 300 K is a very difficult matter. However our results could encourage such experimental work.

Data-fitting for the θ-dependence at constant temperatures is shown in Figures 4 to 7, with a satisfactory reproduction of experimental data. However, we must analyze the consistency of the values obtained for the characteristic temperature T_o. Un-

Table 2. T_o Values for Experimental Data and Their Relation to Isoteric Heat of Absorption

Gas	$\langle T_o a_o^2 \rangle$ K	$R_g T_o (a_o = 1/2)$ kJ/mol	$q_{st} (\theta = 1/2)$ kJ/mol	Ref.
Freon 12	307	10.174	26.377	Ponzi et al. (1977)
n-butane	243	8.081	19.259	Marchese et al. (1982)
1,3-butadiene	249	8.248	18.213	Marchese et al. (1982)
Ethylene	163	5.401	13.398	Horas et al. (1980)

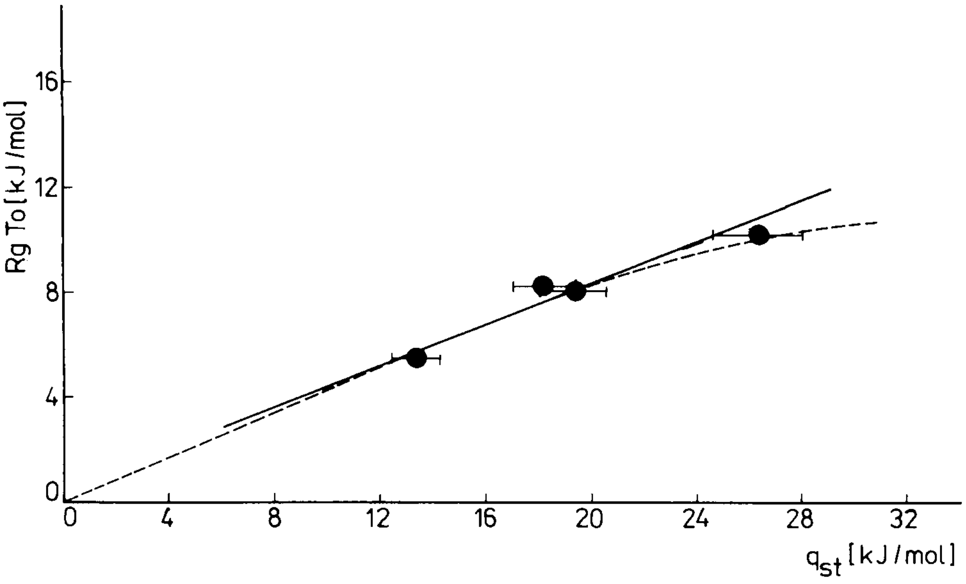

Figure 8. ***RT_o* vs. *q_{st}* correlation.**

Experimental points shown with error bars —— $R_gT_o = (q_{st})^\alpha$ correlation; — lineal correlation.

fortunately T_o interacts with parameter a_o of Eq. 38, and only values for $(T_oa_o^2)$ can be obtained from experimental data. Now, these values should show some correlation with the isosteric heat of adsorption q_{st}, due to the fact that R_gT_o, where R_g is the gas constant, stands for the molar activation energy for diffusion.

If we tentatively use $a_o = 1/2$ for the probability that a molecule is captured in passing on an empty site, then we obtain the values of R_gT_o shown in Table 2, which are compared to the experimental values for q_{st} at $\theta = 1/2$.

As it can be seen from Table 2 and Figure 8, there is a quite strong correlation between R_gT_o and q_{st}, with very plausible values for RT_o as molar activation energies.

Conclusion

A new approach has been given for the discussion of surface transport of adsorbable gases on solids, one that leads to plausible models for the surface diffusion coefficient and surface permeability. This approach is particularly useful to discuss connectivity or nonlocal effects due to heterogeneous adsorption potentials on the solid surface. A more realistic treatment for the surface molecular migration mean free path is also given.

Experimental data are reproduced satisfactorily, but new data are necessary to distinguish the temperature dependence given by exp $(T)^{-1/3}$ from the well known exp $(T)^{-1}$ law.

Acknowledgment

We thank J. B. P. Rivarola for his constant encouragement on the work being done at Instituto de Investigaciones en Tecnología Química.

Notation

a_o, a_1, a_2 = constants, Eq. 38
A_o = characteristic area for the gas-solid system, m^2
D_s = surface diffusion coefficient, m^2/s
ΔE = activation energy, kJ/mol
G_c = critical conductance, 1/s
G_{ij} = conductance between points *i* and *j*, 1/s
g = geometrical factor, m^2
I_s = surface permeability, kmol/m · s · Pa
I_o = constant, Eq. 35, kmol/m · s · Pa
k = Boltzmann's constant, kJ/K
m = molecule's mass, kg
M = molecular weight, kg/mol
N_p = number of phonons
q_{st} = isosteric heat of adsorption, kJ/mol
p = pressure mean value, Pa
P_a = probability for phonon absorption
P_e = probability for phonon emission
P_{ef} = effective probability for a molecule either to be captured or to evaporate from surface
$P(R)$ = probability per unit time for an adsorbed molecule to migrate through a distance R
R_{ij} = distance between sites *i* and *j*, m
R_g = universal gas constant, kJ/mol
S_i = displacement vector for the *i*th migration, m
T = temperature, K
T'_o, T_o = characteristic temperatures of the gas-solid system, K
V_m = volume for monolayer coverage, m^3/kg
V_{STP} = gas molar volume at standard conditions, m^3/kg
$V_{(x,y)}$ = adsorption potential at a point (x, y) on the surface, kJ/mol
W = width of adsorptive potential's distribution, kJ/mol

Greek Letters

β = constant, Eq. 15, 1/kJ
Φ_{ij} = number of molecules migrating from site *i* to site *j* per unit time, 1/s
Φ_o = constant, Eq. 16, 1/s
θ = mean surface coverage
θ_i = mean coverage at site *i*
λ = mean free path for surface migration, m
Λ = constant, Eq. 15
μ = chemical potential, kJ
ν_o = characteristic frequency for the gas-solid system, 1/s
ρ = density of the pellet, kg/m^3
σ = conductivity of the sample, m^2/s
τ = tortuosity factor
Ω = typical volume in the (E, R) space, J/m^2

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