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The Surface Transport of Adsorbed Molecules

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A detailed mechanistic model is developed to describe the process by which adsorbed molecules migrate over the surface of an adsorbent. The migration is assumed to occur as a result of a random hopping of partially desorbed species; explicit expressions are derived for the hopping rate and the distance traversed in a single jump for the case of a gas adsorbed on a homogeneous surface. In the degree of detail developed herein experimental determinations are still required (to evaluate an otherwise unknown ratio of partition functions, and the activation free energy) but the pressure or surface concentration dependency of the transport rate is given explicity.

The predictions are tested by comparison with three sets of experimental data for hydrocarbons adsorbed on porous glass; these systems were chosen as they may be shown to meet the assumption of an adsorbate migrating over an energetically homogeneous surface under the conditions studied. Reasonable values are found for the parameters and excellent agreement between the observed and predicting trends with pressure is noted in all cases.

The transport of an adsorbate along a solid surface or through a porous solid is known to occur by several different mechanisms. In the case of a gas being transported through a porous solid, for example, the ratio of the mean free path in the gas phase to the width of the pores or cavities in the solid determines whether the gas phase transport corresponding to an imposed pressure gradient can be described by the Knudsen mechanism of free molecular flow, by the mechanism of viscous laminar flow, or by a combination of the two (*1, 5, 11, 15*). Furthermore, if the gas is adsorbed appreciably onto the solid, an additional transport due to the migration of the adsorbed gas on the inner surface of the porous solid must be considered (*4, 5*); it has been observed that for many systems the transport rate of the adsorbed phase is comparable to and sometimes greater than that of the gas phase (*1, 2, 7, 9, 16*). Therefore, an understanding of the transport characteristics of adsorptive solids (including porous adsorbents and catalysts, for example) requires consideration of surface transport mechanisms. Recent studies (*1* to *3, 9, 16*), while contributing to our knowledge of the subject, also reveal major limitations, especially in theoretical and predictive abilities. Thus, this work is directed toward an improved understanding of surface transport processes, primarily by means of a theoretical analysis. This analysis is evaluated by employing transport rate data for several adsorbing and nonadsorbing gases in a porous solid of known uniform structure.

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DERIVATION AND USE OF THE BASIC RATE EXPRESSION

The basic rate expression is expected to be applicable equally to porous adsorbents and to planar surfaces. Because the former may be of greater industrial interest they were chosen for use in the evaluation of the rate expressions and the details of the development herein will be directed accordingly.

The total transport rate of a gas through a porous solid is given as the sum of the contributions due to the gaseous and the adsorbed phases:

$$\dot{n}_T = \dot{n}_G + \dot{n}_A \tag{1}$$

The following assumptions have been made in the theoretical analysis of the adsorbate flux $\dot{n}_A$:

1. The gas phase and the adsorbed phase are in equilibrium at all points within the porous medium. This equilibrium is characterizable by means of adsorption isotherms.
2. The adsorbed molecules migrate by means of small hopping movements on the surface. In order for a molecule to hop, it must desorb partially, this process being characterized by an activation energy $\Delta F^{\ddagger}$.
3. All molecules hopping from the surface leave the surface with the initial speed v_o, which is then taken as the arithmetic mean speed based on a Maxwell-Boltzmann energy distribution.
4. The process is isothermal.
5. The gaseous and the adsorbed phases consist of single components.

In principle there is no difficulty in relaxing the fourth and fifth assumptions. In practice the algebraic manipulations are aided by them and it is in any event necessary to establish the theory first for the isothermal, single-component case.

If a single-component gas adsorbs appreciably in a porous solid pellet and a pressure gradient (dP/dz) is imposed across the pellet, a corresponding gradient in the surface concentration (dx/dz) arises, provided the adsorbate is in dynamic equilibrium with the gas. It is due to this surface concentration gradient and to the surface mobility of the adsorbed molecules that a net transport of adsorbate occurs. The rate at which the adsorbed molecules hop in random directions on the surface is designated r in mg.-moles per second per square centimeter of surface. It is a function of the temperature and of the surface concentration x. The distance which a molecule hops is designated λ. It is necessary to derive an equation relating the net flux of adsorbate $\dot{n}_A$ to the hopping rate r and the hopping distance λ:

$$\dot{n}_A = \dot{n}_A\,(r, \lambda) \tag{2}$$

This relationship is obtained by making a material balance on all molecules hopping across a given arbitrary reference surface in the porous medium.

Consider a cylindrical pellet in which the net flux is in the axial direction. Let the reference surface be a plane perpendicular to the axis at an axial reference position z_o. The *net* rate at which molecules cross the plane in the positive z direction may be written as the difference between the rates at which molecules originating from the two sides of this plane move across it:

$$\dot{N}_A = \dot{n}_A A_p = \int_o^{-\infty} r(\zeta) f(\zeta)\, dS - \int_o^{+\infty} r(\zeta) f(\zeta)\, dS \tag{3}$$

The distance ζ is measured from the reference plane along the axis of the pore rather than the axis of the pellet and is related to z as follows:

$$\zeta = j\,(z - z_o)$$

Due to geometrical considerations as indicated in Figure 1 only a fraction $f(\zeta)$ of the molecules hopping from a given ζ position reach or cross the reference plane at z_o (*19*):

$$f(\zeta) = \frac{\arccos\,(|\zeta|/\lambda)}{\pi} \tag{4}$$

The quantities $\bar{\lambda}_+$ and $\bar{\lambda}_-$ are defined as the average values of the hopping distance λ to the right and left of the reference plane, respectively. With these substitutions the material balance takes the form:

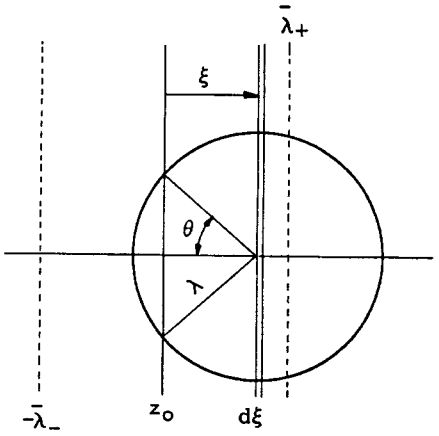

Fig. 1. Analysis of net surface transport rates.

$$\dot{n}_A = \frac{s\rho}{\pi j}\left\{ \int_o^{-\bar{\lambda}_-} r(\zeta) \arccos \frac{|\zeta|}{\bar{\lambda}_-}\, d\zeta - \int_o^{\bar{\lambda}_+} r(\zeta) \arccos \frac{|\zeta|}{\lambda_+}\, d\zeta \right\} \tag{5}$$

By expanding the functions $r(z)$ and $\lambda(z)$ in Taylor series in z about z_o and substituting into the integrals above, the following result is obtained:

$$\dot{n}_A = \frac{s\rho r(z_o)}{\pi j}\,(\bar{\lambda}_- - \bar{\lambda}_+) - \frac{s\rho r'(z_o)}{8j^2}\,(\bar{\lambda}_-^2 + \bar{\lambda}_+^2) + \frac{s\rho r''(z_o)}{9\pi j^3}\,(\bar{\lambda}_-^3 - \bar{\lambda}_+^3) \tag{6}$$

in which

$$\bar{\lambda}_+ = \frac{\lambda(z_o)}{1 - \dfrac{\lambda'(z_o)}{2j}}; \qquad \bar{\lambda}_- = \frac{\lambda(z_o)}{1 + \dfrac{\lambda'(z_o)}{2j}} \tag{7}$$

The Taylor series in $\lambda(z)$ was terminated after the second term; the series in $r(z)$ was terminated arbitrarily after the third term, but even the third term was unnecessary, as is discussed below. After combining these three equations, clearing fractions, and neglecting all terms in $(\lambda')^2$ and $(\lambda')^3$, the adsorbate flux has the form

$$\dot{n}_A = -\frac{s\rho r\lambda\lambda'}{\pi j^2} - \frac{s\rho r'\lambda^2}{4j^2} - \frac{s\rho r''\lambda^3\lambda'}{3\pi j^4} \tag{8}$$

The third term of Equation (8) may be shown to be fifteen orders of magnitude smaller than the first and second terms, which are of comparable magnitude (*19*), and thus may be neglected. The rate of surface migration may be written in the form of the flux $\dot{n}_A$ or in terms of the adsorbate permeability I_A, defined as the molar flux divided by the negative pressure gradient:

$$\dot{n}_A = -\left(\frac{s\rho}{2\pi j^2}\right)\left[\, r(\lambda^2)' + \frac{\pi}{2}\lambda^2 r' \,\right] \tag{8a}$$

$$I_A = \frac{\dot{n}_A}{-\nabla P} = \frac{s\rho}{2\pi j^2}\left[r\left(\frac{\partial \lambda^2}{\partial P}\right)_T + \frac{\pi}{2}\lambda^2\left(\frac{\partial r}{\partial P}\right)_T \right] \tag{9}$$

Equation (9) represents the basic rate expression. The two basic parameters — r, the hopping rate, and λ, the hopping distance, must be evaluated to enable a priori predictions.

Evaluation of the Hopping Rate

The hopping rate will be estimated with the transition state theory of chemical kinetics. The adsorbed molecule undergoes an energy exchange with the surface and with the other adsorbed molecules. If in the process it attains sufficient energy it is capable of leaving its adsorption position and either desorbing into the gas phase or hopping to another position on the surface. The nonactivated molecules, with a surface concentration x, are assumed to be in chemical equilibrium with the activated species, having a surface concentration $x^{\ddagger}$. According to the transition state theory, the rate of hopping r is equal to the rate at which the activated molecules cross the activation energy barrier. By applying the conventional approach of Eyring and others (8) to this particular problem, the following rate expression is obtained:

$$r = k_R x = \left(\frac{x}{s}\right)\left(\frac{Q_o^{\ddagger 1}}{Q_o}\right)\left(\frac{kT}{h}\right)\exp\left(\frac{-\Delta F^{\ddagger}}{RT}\right) \quad (10)$$

The quantities Q_o and $Q_o^{\ddagger 1}$ are partition functions of the nonactivated and activated species, respectively. Substitution of this result into Equation (9) for the adsorbate permeability I_A gives

$$I_A = \frac{k_R \rho s}{2\pi f^2}\left[x\left(\frac{\partial \lambda^2}{\partial P}\right)_T + \frac{\pi}{2}\lambda^2\left(\frac{\partial P}{\partial P}\right)_T\right] \quad (11)$$

Derivation of the Mean Hopping Distance

A molecule, having escaped from the surface as described above with a velocity v_o at an angle ϕ with respect to the surface, is assumed to follow a quasiballistic trajectory as indicated in Figure 2. During its flight the forces of the solid surface act upon the molecule and eventually pull it back to the surface. The trajectory may be described by the following form of Newton's second law of motion:

$$m\ddot{y} = -F(y) \quad (12)$$

Here $F(y)$ denotes the force of the surface acting upon the molecule, being positive in the negative sense of y, the distance above the surface. The boundary conditions on Equation (12) are the following:

1. at $t = 0$: $\dot{y} = v_{y,o} = v_o \sin\phi$; $y = y_o$
2. at $t = \Theta$: $\dot{y} = 0$; $y = y_{\max}$

The initial condition is obvious. The second condition states that the molecule reaches its maximum height above the surface $y_{\max}$ when the y component of its velocity $\dot{y}$ becomes zero.

The force $F(y)$ may be described by the following modified Lennard-Jones relationship for nonpolar gases and nonionic solids (20):

$$F(y) = 5\pi\epsilon N y_o^2\left[\left(\frac{y_o}{y}\right)^4 - \left(\frac{y_o}{y}\right)^{10}\right] \quad (13)$$

This is derived from the usual 6-12 potential by integrating over all of the atoms in the solid matrix. N denotes the atomic density of the solid and y_o the equilibrium adsorption position above the surface. The intermolecular force parameter ϵ between the solid and the sorbable molecule is a function of the surface coverage as will be discussed later.

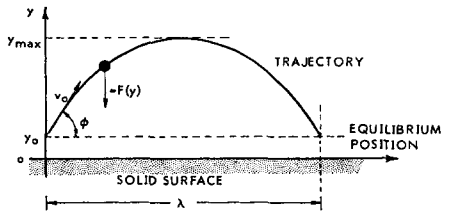

Fig. 2. Trajectory of translating (hopping) molecule.

The differential equation in y, obtained by combination of Equations (12) and (13), may be integrated once analytically, but the second integration must be carried out numerically. The solution for Θ, the time required for the molecule to reach the maximum in its trajectory, $y_{\max}$ is

$$\Theta = \int_{y_o}^{y_{\max}} \frac{dy}{\sqrt{v_o^2\sin^2\phi - \mu\left[2 - 3\left(\frac{y_o}{y}\right)^3 + \left(\frac{y_o}{y}\right)^9\right]}}$$

in which

$$\mu = \frac{10\pi\epsilon N y_o^3}{9m} \quad (15)$$

By assuming that the trajectory is symmetrical about $t = \Theta$ and that there are no forces acting upon the molecule in the direction parallel to the surface, the horizontal range or the hopping distance Λ is

$$\Lambda(\phi) = 2\Theta v_o\cos\phi = 2\cos\phi \int_{y_o}^{y_{\max}} \frac{dy}{\sqrt{\sin^2\phi - \left(\frac{\mu}{v_o^2}\right)\left[2 - 3\left(\frac{y_o}{y}\right)^3 + \left(\frac{y_o}{y}\right)^9\right]}} \quad (16)$$

The upper limit of integration $y_{\max}$ is the first root greater than unity of the following algebraic equation:

$$\dot{y} = 0 = \sqrt{v_o^2\sin^2\phi - \mu\left[2 - 3\left(\frac{y_o}{y_{\max}}\right)^3 + \left(\frac{y_o}{y_{\max}}\right)^9\right]}$$

In order to integrate $\Lambda(\phi)$ over all values of the angle ϕ, it is necessary to determine the proper weighting function in ϕ. The cosine law of emission as postulated by Knudsen (12) states that the directions in which adsorbed molecules are reemited from a surface are distributed according to a cosine distribution over the solid angle ω. That is, the probability dp that a molecule leaves the surface in the solid angle $d\omega$ forming an angle α with the normal to the surface is

$$dp = \frac{d\omega}{\pi}\cos\alpha \quad (17)$$

However, the differential solid angle $d\omega$ is given by

$$d\omega = 2\pi\sin\alpha\, d\alpha \quad (18)$$

Thus

$$dp = 2\cos(\alpha)\sin(\alpha)\, d\alpha \quad (17a)$$

Therefore, the average hopping distance integrated over all values of ϕ is given by

$$\lambda = \int_o^{\pi/2} 2\sin\phi\cos\phi\,\Lambda(\phi)\, d\phi = 4\int_o^{\pi/2}\int_{y_o}^{y_{\max}} \frac{\cos^2\phi\sin\phi\, dy\, d\phi}{\sqrt{\sin^2\phi - \left(\frac{\mu}{v_o^2}\right)\left[2 - 3\left(\frac{y_o}{y}\right)^3 + \left(\frac{y_o}{y}\right)^9\right]}} \quad (19)$$

The hopping distance is defined by Equation (19) except in two special cases:

$$\text{if } \sin^2\phi > 2\frac{\mu}{v_o^2},\ \Lambda = 0$$

$$\text{if } y_{\max} > r_p,\ \Lambda = 0 \quad (20)$$

The first of these describes those molecules which leave the surface (which have sufficient kinetic energy to escape completely from the surface force field), that is, these molecules desorb. The second condition describes molecules which, in the course of their trajectories, are farther removed from the surface than the local pore radius. Such molecules simply return to the surface on the opposite side of the pore. Although they may contribute to the gas phase transport their contribution to a surface migration process is identically zero.

Evaluation of the Intermolecular Force Parameters

The final quantity remaining to be evaluated is the Lennard-Jones parameter ϵ. Since this is the parameter related to the intermolecular force between the adsorbing atom and the adsorbent surface, which is partially covered with adsorbate, it is necessary to devise a suitable combining law to take into account the several force fields involved. First of all, the intermolecular force parameter ϵ_{gg} for the interaction of two gaseous molecules has been combined empirically with the average bond strength in the solid E_{ss} as follows to give the force parameter between the sorbable molecule and the bare solid surface:

$$\epsilon_{gs} = \sqrt{(\epsilon_{gg})\,(E_{ss})} \qquad (21)$$

The bond strength E_{ss} is calculated from heat of formation data and heat of dissociation data according to Pauling's method (*13*). Use of Equation (21) implies the surface to be perfectly uniform with respect to its intermolecular force fields, that is, an absence of active sites.

However, the net force exerted on a molecule by a surface partially covered with adsorbate may differ from the force exerted on the same molecule by the bare surface. The simplest, or first, approximation to this quantity is the linear combination of terms for an energetically homogeneous surface:

$$\epsilon = \epsilon_{gs}\,(1 - \psi \cdot \theta) + \epsilon_{gg}\,(\psi \cdot \theta) \qquad (22)$$

The packing or view factor ψ accounts for the incomplete coverage of the surface due to molecular geometry. That is, even at unimolecular coverage a fraction of the solid surface is not actually covered, and this surface exerts an attractive force on any migrating molecule above it.

PROCEDURE FOR EVALUATING THE ADSORBATE PERMEABILITY, I_A

In order to calculate the surface migration rate in a particular gas-solid system according to the theoretical analysis presented above, the following calculational scheme may be followed:

1. The equilibrium relationship between the surface concentration or amount adsorbed x and the gas phase pressure P must be known. This enables the calculation of θ, the surface coverage, and the derivative $\partial x/\partial P$. Additionally, adsorption isotherms may be used to calculate heats of adsorption as a function of surface coverage, thereby checking the assumed homogeneity of the surface.

2. The intermolecular force parameters ϵ and y_o are determined as follows. The parameter ϵ_{gg} for the gas is obtained from experimental data for viscosity or thermal conductivity (*6, 17*), and the solid interatomic bond energy E_{ss} may be calculated by the Pauling method (*13*) as follows:

$$E_{ss} = \frac{1}{n_{ss}}\,[\Delta H_f - \Sigma \Delta H_{diss,j}] \qquad (23)$$

From these values the parameter ϵ_{gs} is calculated according to Equation (21), and finally $\bullet$ is calculated from the combining law, Equation (22). The separation of an adsorbate molecule from a single atom of the solid r_o is approximated as the arithmetic average of the parameter σ for the gas and the average interatomic spacing r_s in the solid. The parameter y_o is taken as $(0.775\,r_o)$ (*20*) in accordance with the prior observation that the aggregate surface forces bring the adsorbing molecule somewhat closer to the surface than would a single atom of the solid.

3. The hopping distance λ is evaluated by integrating Equation (19) on a digital computer. The hopping distance integral is improper, since the integrand is not bounded above as the upper limit of integration is approached. Nevertheless, it has been proven that the integral itself converges by comparing it with a larger integral which is known to converge (*19*).

4. At this point the quantities x, $(\partial x/\partial P)_T$, λ^2, and $(\partial \lambda^2/\partial P)_T$ have been determined experimentally or calculated. The only remaining unknown quantity in the theoretical rate equations (10) and (11) is the product:

$$\left(\frac{Q_o^{\neq 1}}{Q_o}\right) \exp\left(\frac{-\Delta F^{\neq}}{RT}\right)$$

$(Q_o^{\neq 1}/Q_o)$ denotes the ratio of partition functions of the activated and nonactivated adsorbed molecules and $\Delta F^{\neq}$ the activation energy for surface migration. The activation energy must be considerably less than the heat of adsorption, which is equal to the activation energy for desorption; otherwise the molecules would desorb more readily than they would migrate on the surface. For the systems analyzed $\Delta F^{\neq}$ was roughly one-tenth of the heat of adsorption, and the ratio of partition functions was of the order of magnitude 10. On the other hand, whereas this analysis includes no a priori method of predicting $\Delta F^{\neq}$ and $(Q_o^{\neq 1}/Q_o)$, they may be determined from just two experimental data points. The pressure dependence of I_A is predicted a priori.

EXPERIMENTAL RESULTS

Rate Apparatus

The transport rates were measured in the apparatus shown schematically in Figure 3, employing a quasi steady state procedure similar to that used previously (*16, 18*). The pellet was mounted between two large glass reservoirs maintained at a constant temperature. Gas was fed to the reservoirs at two different pressures and the transport rate was determined by measuring the pressure in each reservoir as a function of time. After an initial transient period the molar rate leaving one reservoir was equal to that entering the other; this rate and the corresponding pressure drop across the pellet were used to calculate the total permeability I_T. All data and results are tabulated in detail elsewhere (*19*).

Gaseous Transport Rates

In order to characterize the Corning porous Vycor glass, which was used as the porous medium in this in-

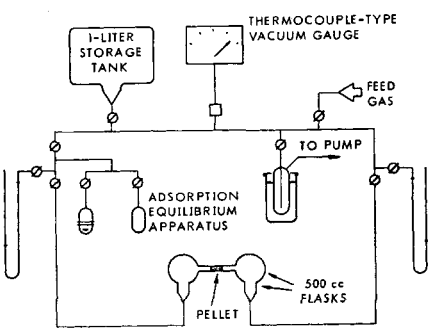

Fig. 3. Schematic diagram of apparatus.

vestigation, and to be able to predict the gas phase transport rates, the rates of diffusion of the nonadsorbing gases argon and helium were measured at 25° and 50°C. As expected, the transport was in the regime of free molecular flow or Knudsen diffusion defined by the relationship (*11, 12*):

$$I_K\sqrt{MT} = \frac{2}{3}\sqrt{\frac{8}{\pi R}}\left(\frac{\epsilon_v r_p}{j^2}\right) \qquad (24)$$

As the expression on the right side of this equation is a function of the properties of the porous medium only (ϵ_v, r_p, and j are the porosity, average pore radius, and tortuosity factor, respectively), the quantity $I\sqrt{MT}$ should be independent of pressure, temperature, and molecular weight. That this is the case for the data with argon and helium is shown in Figure 4; as predicted $I\sqrt{MT}$ is essentially constant over a twentyfold range of pressures. Since $\epsilon_v = 0.28$ and $r_p = 20$ Å. for the porous Vycor glass studied, the tortuosity factor j is found to be equal to 1.77. That is, on the average the effective length of the pores is 1.77 times the length of the pellet. This value of the tortuosity factor is used later in the evaluation of the surface migration rates; its value falls well within the range cited by Satterfield and Sherwood (*14*).

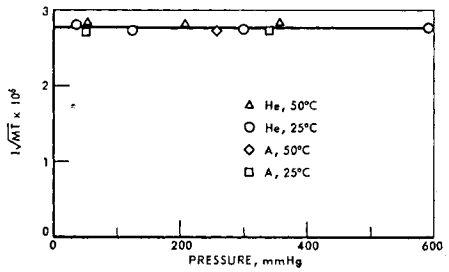

Fig. 4. Test of Knudsen transport mechanism, nonadsorbed gases.

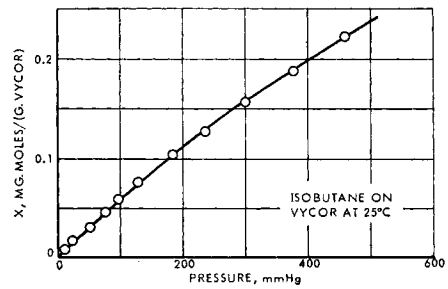

Fig. 5. Adsorption isotherm: isobutane-porous glass.

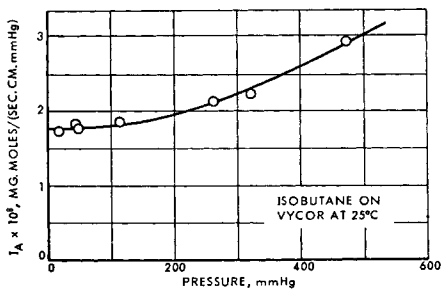

Fig. 6. Permeability (specific transport rate) of adsorbed phase.

TABLE 1. TRANSPORT RATES, ISOBUTANE ON POROUS VYCOR, 25°C.

P, mm. Hg	$I_{Total} \times 10^8$	$I_{Knudsen} \times 10^8$	$I_{Adsorbate} \times 10^8$
18.4	3.837	2.098	1.739
43.6	3.879	2.061	1.818
48.6	3.817	2.056	1.761
114.4	3.846	1.986	1.860
262.7	3.980	1.857	2.123
322.8	4.026	1.809	2.217
472.4	4.611	1.701	2.910

In the case of adsorbed vapors the Knudsen transport rate should decrease with increasing pressure, since the adsorbed molecules decrease the pore radius. The exact magnitude of this decrease depends on the model used to represent the pore geometry and the adsorption process. In the present work it was assumed that the concept of a unimolecular film building up on a cylindrical pore was sufficiently precise to enable useful corrections. This leads to (*19*)

$$I_G = K\left[\frac{(I\sqrt{MT})ave.}{\sqrt{MT}}\right] = 2.780 \times 10^{-6}\left(\frac{K}{\sqrt{MT}}\right) \qquad (24a)$$

with the correction factor K given by

$$K = \left(1 - \frac{x\rho M}{1{,}000\,\epsilon_v \rho_L}\right)^{3/2} \qquad (25)$$

The maximum correction introduced by Equations (24*a*) and (25) was 25% of the Knudsen flux at zero adsorption; this introduces about half as large a correction to the flux of the adsorbed molecules.

Equilibrium Adsorption Data

The volumetric equilibrium apparatus (Figure 3) was designed such that the maximum error in the measurement of the surface concentration should not exceed 1%. The 25°C. results are shown in Figure 5. Similar measurements at several temperatures enabled the calculation of differential isosteric heats of adsorption; these results are of critical importance as they enable an assessment of the assumption of an energetically homogeneous surface. The heat of adsorption was found to 7.05 kcal./mole, ± 7%. As it exhibited no significant functional dependence on surface concentration x, the system chosen for study appears to conform to the energetically homogeneous surface assumed in the analysis.

Adsorbate Transport Rates

The measured total permeability, the Knudsen component of this total flux [calculated by means of Equations (24*a*) and (25)] and, by difference, the flux of the adsorbate, are given in Table 1 for the isobutane-Vycor system. It is seen that the measured adsorbate transport rates varied from about 80 to over 170% of the concomitant gaseous transport. Figure 6 depicts the adsorbate permeabilities as a function of pressure.

INTERPRETATION OF SURFACE MIGRATION DATA

The equations presented earlier may be used to predict the variation of the adsorbate flux with pressure. Values of ϵ_{gg} and σ for isobutane and of E_{ss} and r_s for silica glass are taken from the literature (*6, 10, 17*); this permits calculation of the parameters ϵ and μ [Equations (15) and (22)] and the hopping distance λ as a function of surface coverage θ, provided the packing or view factor ψ in Equation (22) is determined. For spherical adsorbate molecules it would presumably lie between 0.7854

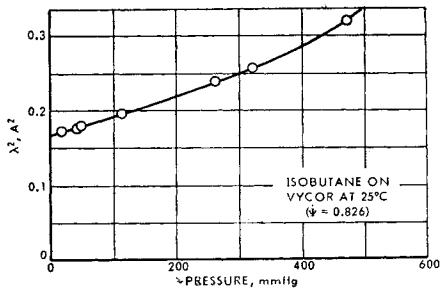

Fig. 7. Relationship between calculated hopping distance and pressure.

and 0.9069, depending on the geometric packing of the molecules on the surface; for nonspherical molecules ψ could range somewhat more widely but presumably would lie between about 0.5 and 1.0. Accordingly, the numerical integration of Equation (19) was carried out for a variety of values of ψ in this general range and the best fit result, $\psi = 0.826$, was chosen. The resulting variation of the surface hopping distance λ (squared) with pressure is shown in Figure 7. The other terms in the square bracket of Equation (11) are evaluated from the isotherm for this system, Figure 5, and the remaining constant term by fitting the equation to the data. The resulting agreement between the trends predicted and the data points may be noted by inspection of Figure 6 or 8; the mean percentage deviation between the predicted and experimental permeabilities, covering as twenty-fivefold range of pressure, is only 2.2% for these data and all scatter is random.

The above results give

$$\frac{k_R \rho s}{2\pi j^2} = 1.013 \times 10^{12} \text{ g. Vycor/(cc.) (sec.)}$$

As ρ and j for the adsorbent are separately known from independent measurements ($\rho = 1.567$ g. Vycor/cc.; $j^2 = 3.13$) this leads [Equations (10) and (11)] to

$$\frac{Q_o^{\neq 1}}{Q_o} \exp \frac{-\Delta F^{\neq}}{RT} = 2.05$$

It should be noted (Figure 6) that the experimental adsorbate permeability I_A does not approach zero in the limit of zero pressure; this is substantiated by the theory as given by Equation (11). As the pressure approaches zero, the quantity $x(\partial\lambda^2/\partial P)_T$ approaches zero as well, but the quantity $\lambda^2(\partial x/\partial P)_T$ approaches a finite nonzero value as neither the hopping distance λ not the derivative $(\partial x/\partial p)_T$ disappear.

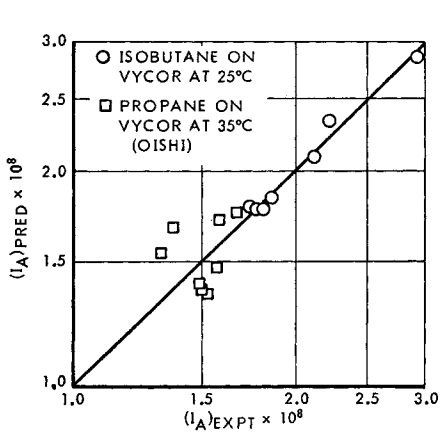

Fig. 8. Comparison of predicted and measured transport rates: isobutane-porous glass and propane-porous glass.

In order to check the theoretical equations further data for the surface migration of propane on Vycor as reported by Higashi, Ito, and Oishi (9) were analyzed also. These were the only other data available for which the heats of adsorption also indicated the surface to be energetically homogeneous. For these results the optimal value of the packing factor was found to be 0.804, in good agreement with the value of 0.826 for isobutane. Average deviations between experimental and predicted permeabilities were 10.8% for the data at 35°C. and 13.0% for those at 22°C.; a comparison between prediction and experiment for the 35°C. results is included in Figure 8.

The fact that two temperatures were studied for the propane-Vycor system enables estimates of the partition function ratio and activation energy separately for this system, yielding

$$\left(\frac{Q_o^{\neq 1}}{Q_o}\right) = 7.74$$

$$\Delta F^{\neq} = 175 \text{ cal./g.-mole}$$

This low value of the activation energy (much below the heat of adsorption, for example) indicates the possibility of a relatively uniform mobility of all adsorbed species, as may be expected on a uniform surface.

Preliminary extensions of the analysis presented here to include effects of surface heterogeneity were carried out (*19*) with the use of data previously published (*16*). While the results of this analysis were inconclusive, they did appear to afford promise of interpreting the data without assuming nearly complete desorption of the molecules during migration, thereby appearing to resolve one of the more controversial assumptions of the earlier analysis.

CONCLUDING REMARKS

The theoretical analysis presented enables the a priori prediction of the pressure dependency of the adsorbate mobility or permeability. Furthermore, the kinetic hopping rate constant k_R is no arbitrary proportionality constant but is related to the kinetics of the molecular hopping process and may be evaluated on the basis of one experimental point. Equation (9) for the permeability $I_A(\lambda, r)$, Equation (10) for the hopping rate r, and Equation (19) for the hopping distance λ are all general in form and should be valid for any type of system in which a physically adsorbed gas migrates along the surface of a porous solid. In order to apply the equations to any particular system, it is necessary to evaluate the intermolecular force parameter ϵ and the intermolecular distance r_0. The evaluation of ϵ according to Equation (22) seems reasonable for homogeneous surfaces, that is, for surfaces on which the adsorption bond energies and the heats of adsorption do not vary greatly with surface coverage. In order to apply the theoretical equations to more complicated heterogeneous solids, it is necessary to develop alternate relationships for ϵ.

The predicted dependence of the surface migration rate on temperature is small but rather complicated. The dependence of the hopping rate on temperature for a fixed value of the surface concentration x is roughly exponential:

$$r \propto T \exp\left(\frac{-\Delta F^{\neq}}{RT}\right) \qquad (26)$$

The dependence of the hopping distance λ on temperature is more complicated and cannot be written in a simple explicit form. However, on the basis of the analysis of the Oishi data for propane at 22° and 35°C., it appears that λ does not vary significantly with temperature. Thus, the temperature dependence of the surface migration rate is given roughly by exp $(-\Delta F^{\neq}/RT)$ for a fixed value of

surface concentration. However, as the activation energies appear to be small, and since the surface concentration decreases, at a given pressure, as the temperature increases, these effects nearly compensate and no large change in surface migration rates appear to occur as temperature is changed. This appears to be true of the surface transport rates on heterogeneous surfaces also, as noted before (*16*).

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NOTATION

A_p = cross-sectional area of pellet, sq. cm.
E_{ss} = interatomic bond strength in solid, cal./mole
$f(\zeta)$ = fraction of all hopping molecules which originate a distance ζ from the control surface and which cross it in a single hop
$F(y)$ = force acting upon a translating molecule, dynes
$\Delta F^{\ddagger}$ = free energy of activation of surface migration, cal./mole
h = Planck's constant
ΔH_f = enthalpy of formation of solid from elements in their standard states
$\Delta H_{diss,j}$ = enthalpy of dissociation of the element j into its atomic form by assuming the standard state to be polyatomic
I_A = permeability of adsorbed molecules; $I_A = \dot{n}_A/(\partial P/\partial z)$
j = tortuousity factor of pores, dimensionless
k = Boltzmann's constant
k_R = grouping of constants defined by Equation (10)
K = correction factor for gas phase flux due to pore blockage
m = mass of the hopping molecule, g.
M = molecular weight, g./g.-mole
n_{ss} = number of solid-solid bonds in one formula weight
$\dot{n}$ = molar flux, mg.-moles/(sq. cm.)(sec.)
N = total (molar) transport rate, mg.-moles/sq. cm.
P = pressure, mm. Hg
Q_o = partition function of the nonactivated species
$Q_o^{\ddagger 1}$ = partition function of the activated adsorbate excluding the contribution due to translation in the direction of the hop
r = hopping rate, mg.-moles/(sq. cm.)(sec.)
r_o = intermolecular separation between an adsorbed molecule and a surface atom, Å. $r_o = \frac{1}{2}(\sigma + r_s)$
r_p = average pore radius, Å.
r_s = interatomic separation in the solid, Å.
R = gas constant
s = specific surface area of the adsorbent, sq. cm./g.
S = inner surface area of adsorbent, sq.cm. $= (s\rho A_p z)$
t = time, sec.
T = temperature, °K.
v_o = initial speed of molecule leaving the surface, cm./sec.
x = surface concentration, mg.-moles/g. solid
y = distance between the solid surface and an adsorbed or hopping molecule, Å.
z = distance in the axial direction of the pellet, cm.

Greek Letters

ϵ_v = porosity of the porous solid
ϵ = intermolecular force parameter in the Lennard-Jones potential, cal./mole
ϵ_{gg} = intermolecular force parameter between two like gaseous molecules, cal./mole
ϵ_{gs} = intermolecular force parameter between an adsorbed molecule and the base solid surface, cal./mole
θ = surface coverage
Θ = time at which the translating molecule reaches the maximum in its trajectory, sec.
Λ = hopping distance for a particular angle of emission, Å.
λ = mean integral hopping distance (independent of ϕ), Å.
μ = grouping of molecular and intermolecular parameters defined by Equation (15), sq. cm./sec.^{2}
ζ = distance along the coordinate of a pore, cm.
ρ = apparent (bulk) or mercury density of adsorbent, g./cc.
σ = molecular diameter of adsorbate molecule, Å.
ϕ = angle of ascent, rad.
ψ = packing or view factor for the adsorbate on the solid surface

Superscript

$'$ = partial derivative with respect to z

Subscripts

A = adsorbate
G = gas phase
K = Knudsen
L = liquid
o = equilibrium
T = total

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