Gas-Adsorbate Collisional Effects and Surface Diffusion in Porous Materials

If gas-adsorbate momentum transfer is ignored, calculated surface fluxes within porous materials often can be grossly incorrect. Methods are introduced for including these interactions when calculating surface fluxes in permeability studies. Developments are carried out for systems with porous materials having both uniform and heterogeneous surfaces. These methods complement one developed earlier for Wicke-Kallenbach experiments, using porous materials with uniform surfaces. Some previous studies are then considered. In one system, including gas-adsorbate momentum transfer changes the proposed surface-diffusion mechanism from a "hopping" phenomenon to the mobility inherent in a two-dimensional gas. Consideration of other systems shows that, while very frequently these collisional interactions are important, experiments can occur where they are not. A criterion is developed for indicating when this momentum transfer is significant and its inclusion in surface-flux determinations is necessary.

SUBHASH C. THAKUR
LEE F. BROWN
and
GARY L. HALLER

Department of Engineering
and Applied Science
Yale University
New Haven, Connecticut 06520

SCOPE

Transport of a substance within an adsorbed phase is known as surface diffusion; it has the possibility of being important in a variety of fields, such as adsorption, catalysis, and membrane-separation processes. In addition, understanding of this type of transport could give significant insight into the molecular structure of adsorbed phases and how this structure varies as circumstances change. Unfortunately, at the present time, in spite of numerous studies over the last several decades, there still exists no model adequate for predicting the surface-diffusion behavior of an adsorbed phase within a porous material. The best correlation thus far developed can predict a surface-diffusion coefficient to within only about 1½ orders of magnitude (Sladek et al. 1974).

One factor which has been ignored in most previous investigations of surface diffusion is the effect of collisions between gas molecules and the mobile molecules in the adsorbed phase. It has been shown recently that momentum transfer during these collisions has two effects which should be important in any study of surface migration in pores. One is concerned with calculating the actual flux of material on the surface. In studies of surface diffusion in porous materials, only the sum of the gas and surface fluxes can be measured, and theoretical considerations are necessary to separate the two components. Taking the momentum transfer between the colliding gas and adsorbate molecules into account in these theoretical considerations can make a significant difference in the calculated surface component of the total flux. The other effect concerns the impact of momentum exchange from these collisions on the migrational behavior of the adsorbed phase.

The present work is concerned with the first of these effects—calculation of the surface flux and how considering the momentum transfer during gas-adsorbate collisions will affect this calculation. Surface diffusion over both energetically uniform and nonuniform surfaces is considered. An example illustrates what can happen to earlier conclusions when the original surface fluxes, calculated without taking these collisional phenomena into account, are revised.

CONCLUSIONS AND SIGNIFICANCE

In previous studies, the existence of gas-adsorbate collisional effects has been demonstrated in surface diffusion systems containing both uniform and heterogeneous adsorbent surfaces. Equations were developed for describing these effects, when studies were carried out using a porous material with a uniform surface in a Wicke-Kallenbach experiment.

In the present work, equations are developed for describing gas-adsorbate interactions in permeability experiments, which make up the majority of previous studies of surface diffusion in porous materials. In addition to developing equations for experiments involving uniform surfaces, a method is proposed for describing these effects on nonuniform surfaces. As a result, surface fluxes can be calculated for permeability experiments, using porous materials with both uniform or heterogeneous surfaces when gas-adsorbate momentum transfer is significant.

If gas-adsorbate collisional effects are used in calculating surface fluxes, values for these fluxes can be markedly different from those obtained when these effects are ignored, and these different values may lead to quite different conclusions about the behavior of the mobile phase. An example is presented of some surface-diffusion measurements in a system where the adsorbed phase should be portrayable as a two-dimensional gas. Nevertheless, it had been concluded that surface transport occurred by molecules "hopping" from one site to another, because the activation energy for the transport was too high to result from the inherent mobility of a two-dimensional gas. When gas-adsorbed molecule momentum transfer is taken into account in determining the surface fluxes, and an activation energy then determined based on the revised values of the fluxes, the new activation energies are much lower than the earlier ones.

The new energies are well within the range that would be observed if the adsorbed phase could be characterized as a two-dimensional gas.

A number of other studies of surface diffusion in porous materials are scanned, and at surface coverages as low as 0.01 mono-layer, gas-adsorbate momentum transfer may begin to affect the value of the calculated surface flux significantly. Yet this is not always so; in other studies, the effect is not noticeable even at moderate coverages.

Present address for Thakur and for Brown: Department of Chemical Engineering, University of Colorado, Boulder, Colo. 80309

0001-1541-80-3248-0355-$01.05.

A criterion is developed for predicting when gas-adsorbate collisional effects will change the calculated value of the surface flux significantly. A modified error is defined as

$$\xi_2 = \tfrac{1}{2}\, \theta_{AA} f \left(\frac{N_A^{g'}}{N_A^{s'}} + \frac{8}{3\pi f \phi} \right)$$

When ξ_2 is below 0.05, gas-adsorbate momentum transfer does not affect the calculated value of the surface flux significantly. When ξ_2 is above 0.10, it does affect the calculated value. When $0.05 < \xi_2 < 0.10$, the situation is uncertain, and further calculations must be made.

Surface diffusion within porous materials often has been investigated using either a zero-pressure-gradient Wicke-Kallenbach apparatus (e.g., Reed and Butt 1971) or a permeability experiment in the Knudsen-flow regime (e.g., Horiguchi et al. 1971). In these experiments it has always been necessary to use a theoretical model for separating the gas and surface components of the total mass transport. In studies of nonadsorbing gas flow using apparatus of either type, the flow rates of the gases are inversely proportional to their molecular weights. When surface diffusion was to be studied, the transport of a nonadsorbing gas was first measured or calculated for the desired temperature, pressure, and pressure drop. Then, when the behavior of an adsorbing gas was being tested, the gaseous portion of the total transport of the adsorbing gas was determined by multiplying the flux of the nonadsorbing gas by the inverse ratio of the two gases' molecular weights, i.e.,

$$N_A^g = \pm\, (M_B/M_A)^{\frac{1}{2}}\, N_B^g \qquad (1)$$

The negative sign would apply to the Wicke-Kallenbach counterdiffusion experiments, and the positive sign to the permeability tests. In Eq. (1), N_B is the flux of the nonadsorbed gas, and takes place only in the gas phase. Having calculated the flux of the adsorbing substance in the gas phase, N_A^g, the surface flux was taken as the difference between the total transport and the calculated gas-phase flux of the adsorbing gas:

$$N_A^s = N_A^T - N_A^g \qquad (2)$$

Horiguchi and his coworkers (1971) point out that this assumes no molecular shear between the gas and the moving adsorbate. This can be examined more closely. When the gases are nonadsorbing, the inverse-square-root-of-molecular-weight relationship results from impinging molecules rebounding diffusely from a surface; this is realistic when the surface has not been rigorously cleaned and/or has not been maintained under ultrahigh vacuum conditions (e.g., de Boer 1968). When this relationship is used to calculate the gaseous portion of total transport in the presence of a surface-diffusing gas, *it also assumes diffuse reflection (relative to the pore wall) of the impinging gas molecules after collisions with the mobile surface molecules.* At first sight, this appears indefensible, especially if a significant portion of the surface is covered with the mobile adsorbate. It is our purpose in the present work to define areas where the errors caused by making this assumption may be negligible, and to define other areas where they may not. To this end, we examine some existing surface-diffusion studies to see in which region their data lie. Only effects associated with surface coverages less than a filled monolayer are treated; gas-adsorbate collisional effects in multilayer systems are not considered here.

PREVIOUS WORK

Thus, calculating the gaseous portion of the total transport in the presence of surface diffusion by combining the inverse-square-root-of-molecular-weight relationship with the flux of a nonadsorbing gas seems obviously questionable. Yet the first to express doubt concerning this method appears to have been Field et al. (1963) in their review of surface diffusion. They caution that surface-diffusion coefficients should be regarded as unreliable until the gas-adsorbed phase interactions could be investigated more fully.

The first to actually observe disparities between results which he obtained and those predicted by the use of the inverse-square-root relationship seems to have been Bell (1971, Bell and Brown 1973; 1974). When he counterdiffused helium through porous Graphon against nitrogen and propane, the flow rates of helium did not show the same pressure or temperature dependence as they did in another system where the counterdiffusing gas possessed no mobile adsorbed component.

Bell concluded that momentum transfer between the gas and the mobile adsorbed phase affected the gaseous flow in his system significantly. Furthermore, a model which assumed elastic collisions between the gas and adsorbate molecules markedly improved the predictability of the helium-transport behavior over that given by the model which assumed diffuse reflection. An additional point concerned a comparison of the surface fluxes, calculated using the elastic-collision model, and those calculated assuming diffuse reflection of the gas molecules which collided with the adsorbed phase. If the surface coverage of the mobile adsorbed phase were at all appreciable, the two calculated surface fluxes could be drastically different.

This means that if the diffuse-reflection model does not describe the momentum-transfer characteristics of the impinging gas molecules where a mobile adsorbed phase is present, then the gas-phase component of the total transport determined using the inverse-square-root-of-molecular-weight relationship may be in serious error. Bell's Graphon possessed a reasonably uniform surface; more recent work using porous materials with heterogeneous surfaces found significant effects of gas-adsorbate collisions on both gaseous and surface diffusion behavior (Spencer and Brown 1975, Wan 1977).

It does not necessarily follow that the presence of a mobile surface phase always affects the gaseous transport. In a study of simultaneous diffusion and reaction (Stoll and Brown 1974), helium was counterdiffused through porous alumina under Knudsen-flow conditions in sequence against non-surface-diffusing nitrogen and then against surface-diffusing butenes. With a freshly activated catalyst, the helium flow rates against the two gases were identical. If momentum-transfer effects resulting from collisions between the helium and the mobile surface butenes had been significant, the two flow rates would not have been equal. In this particular situation, the surface flow rate of the butenes was small, but still noticeable. In later runs, carried out after the catalyst had been used for a period, the helium flow rates were affected by the presence of the mobile butenes.

In spite of the possibility of gas-adsorbate collisions modifying the gaseous transfer within the porous materials when a mobile surface phase exists, present practice still ignores these interactions. Not long ago, a far-ranging study of surface diffusion within porous materials (Gilliland et al. 1974) used the inverse-square-root relationship may sometimes be valid, and on other occasions leads to serious error, it would be desirable if Jackson (1977) still recommended this practice to determine the surface flux when studying surface diffusion within porous materials. Since the experimental evidence indicates that the inverse-square-root relationship may sometimes be valid, and on other occasions leads to serious error, it would be desirable if some means were found for judging this from the experimental data. One of the goals of the present work is to provide this tool.

CALCULATING TRUE SURFACE FLUXES

The Basic Momentum Balance

In this section, we create a method of calculating the surface flux N_A^s without ignoring gas-adsorbed phase collisional effects. The development here refers primarily to permeability measurements, which are the usual experimental means for studying surface diffusion within porous materials. An analogous development has been carried out for Wicke-Kallenbach experiments (Bell and Brown 1974), but although the principles are essentially the same, the resulting equations for the permeability tests are much simpler than these earlier ones.

Since permeability experiments used in studying surface diffusion are carried out in the Knudsen-flow region, an adsorbing gas A flowing down a single capillary in the Knudsen regime will be considered. A momentum balance on the gas phase along the capillary is the starting point. To apply the balance along a single capillary to a porous material, the single-capillary momentum transfer is multipled by the tortuosity factor τ and divided by the porosity ϵ (Satterfield 1970). In Knudsen flow, there are no molecule-molecule collisions in the gas phase, and so the total momentum lost by the gas phase is equal to the sum of momentum losses to the wall and to the adsorbed phase

$$-\,(\vec{d}p/dL) = (\tau/\epsilon)(M_{Aw}^s + M_{AA}^s) \tag{3}$$

To obtain M_{Aw}^s, the momentum transferred from the gas phase directly to the wall, we assume that the molecule reflects diffusely, and on the average all the axial momentum possessed by the molecule is transferred to the wall. Justified earlier, this assumption has been used successfully to derive equations describing gaseous diffusion in porous materials (e.g., Scott and Dullien 1962). To obtain the number of molecules striking the wall, the number of molecules impinging on the surface must be multiplied by the fraction of surface that is not shielded by the adsorbed phase. With these principles, the momentum transferred to the wall is

$$M_{Aw}^s = (n_A^g\bar{v}_A/4)\,(2/r)\,(3\pi m_A u_A^g/8)\,(1 - \theta_{AA}) \tag{4}$$

in which the first term in parentheses is equal to the number of molecular collisions per unit time per unit area, the second term is the surface area per unit volume of a pore, the third is the average momentum lost by a gas molecule under conditions of Knudsen flow if it were nonadsorbing, and the last term in parentheses is the fraction of surface that is not shielded from gas-phase molecules impinging on the surface.

Calculating Surface Fluxes on Uniform Surfaces

The other term in Eq. (3) which must be obtained is the momentum transferred from impinging gas molecules to the adsorbed phase, M_{AA}^s. The first situation which will be considered is the one in which the surface is uniform. The adsorbed phases appear to behave as two-dimensional gases. On uniform surfaces, two-dimensional condensation phenomena have been observed and described (e.g., Hudson and Ross 1964, Broekhoff and van Dongen 1970), two-dimensional equations of state characterize the adsorbate behavior well (e.g., de Boer and Broekhoff 1967) and calculations of entropy change upon uniform-surface adsorption without exception show agreement between that observed experimentally and that predicted for formation of a completely mobile adsorbate (e.g., de Boer and Kruyer 1952, 1953a-c, 1954, 1955, Ross 1955).

When a system involves a uniform surface, therefore, it will be assumed that the adsorbed phase behaves as a two-dimensional gas. We shall also assume that elastic collisions take place between the gas and adsorbed molecules, with the former rebounding freely in three dimensions and the latter in two dimensions. This collisional behavior is the appropriate analog to the simple theory of dilute gases in the three-dimensional case. These ideas have been developed in greater detail in an earlier paper (Bell and Brown 1974), with reasonable experimental confirmation.

When free recoil occurs in three dimensions, a good approximation to the momentum transfer is obtained by multiplying the collision rate by the average momentum transfer per collision (Present 1956). This approximation will be used here, and it will be assumed that there is diffuse rebound from the center-of-mass system, which has been shown to be true for purely three-dimensional collisions. With these assumptions, the momentum-transfer term for gas-mobile adsorbate collisions takes the form

$$M_{AA}^s = (n_A^g\bar{v}_A/4)(2/r)(m_{AA}^*)\,[(3\pi u_A^g/8) - u_A^s](\theta_{AA}) \tag{5}$$

Let

$$N_A^g = n_A^g u_A^g/n_{Av} \tag{6}$$

$$N_A^s = n_A^s u_A^s/n_{Av} \tag{7}$$

$$\phi = n_A^s/n_A^g \tag{8}$$

$$N_A^T = N_A^s + N_A^g \tag{9}$$

and

$$D_{AK} = 2\bar{v}_A r/3 \tag{10}$$

in which

$$\bar{v}_A = (8kT/\pi m_A)^{1/2} \tag{11}$$

Equations (4)-(11) can be substituted into Eq. (3), and some manipulation of the result can yield

$$N_A^g = [-(dp/dL)(D_{AK}\epsilon/RT\tau) + (8\theta_{AA}N_A^T/6\pi\phi)]/\{1 - (\theta_{AA}/2)[1 - (8/3\pi\phi)]\} \tag{12}$$

The only quantity in this equation which is not immediately obtainable from experimental isotherm, pore structure, and permeability flux data is the fraction of surface shielded by the adsorbate from impinging gas molecules, θ_{AA}. It is shown in the Appendix that a reasonable expression for θ_{AA} is

$$\theta_{AA} = 1 - (1 - \theta_A)\{\exp[-5\theta_A/(1 - \theta_A)]\} \tag{13}$$

If the pressure change over the length of the porous pellet is small enough so that no significant change in ϕ or θ_{AA} occurs, then all the parameters in Eq. (12) are invariant and therefore so is the quantity (dp/dL). In this case, the ideal experimental one, numerical values for N_A^g can be obtained very simply from experimental data using Eq. (12). If a large enough change in the pressure of A does occur within the pellet, ϕ and θ_{AA} become functions of p and cannot be assumed invariant. A numerical solution of Eq. (12) is then usually necessary. Once N_A^g is found, the usual means for obtaining N_A^s is followed; it is obtained by subtracting N_A^g from the measured N_A^T [Eq. (2)].

Calculating Surface Fluxes on Heterogeneous Surfaces

When the adsorbent surface is not uniform, the mobility of the adsorbed phase can be restricted in various fashions, and the gas-adsorbate momentum transfer term in Eq. (3), M_{AA}^s, will not be the same as when the surface is uniform. The approach adopted for this situation comes from Lee and O'Connell (1972, 1975), who divided the adsorbate into a portion which was completely localized and the remainder which had unrestricted mobility over the surface. This is also equivalent to regarding the adsorbate molecules as spending a fraction of their residence time on the surface as localized molecules and the remainder of the time in a mobile fashion.

In order to calculate M_{AA}^s, an assumption must be made about the gas-adsorbate momentum transfer to both the localized and mobile portions of the adsorbate. Gas molecules which impinge upon localized adsorbate molecules probably rebound diffusely;

the diffuse reflection of molecules from contaminated surfaces, mentioned earlier, and the behavior of helium when counterdiffusing against nitrogen in porous silica (Bell and Brown 1973) would suggest this. The collisions between gas molecules and adsorbate molecules in the mobile fraction are assumed to be elastic and exhibit free recoil, as in the uniform-surface situation. This conception has not had the experimental corroboration that the model for uniform surfaces has had, but it is a logical extension of the uniform-surface approach.

Let f be the fraction of the adsorbate that is mobile, and $(1 - f)$ the fraction that is localized. The momentum transfer upon diffuse reflection can be obtained from Eq. (4), and that upon the collision of gaseous and mobile-adsorbate molecules from Eq. (5). Combining these expressions with the assumptions in the previous paragraph gives the following equation for the momentum transfer between impinging gas molecules and an adsorbate on a nonuniform surface:

$$M_{AA}^{s} = (n_A^g \bar{v}_A/4)(2/r)(\theta_{AA})\{(3\pi m_A u_A^g/8)(1 - f) + (m_{AA}^{*})[(3\pi u_A^g/8) - u_A^s](f)\} \qquad (14)$$

The first product within the curved brackets on the RHS of this equation is the average momentum lost by a single gas molecule striking a localized molecule multiplied by the probability of its striking a localized molecule. Similarly, the second product within the curved brackets is the average momentum lost by a molecule striking a mobile adsorbed molecule multiplied by the probability of its striking a mobile adsorbed molecule. Combining this equation with Eqs. (3), (4), and (6)-(11) together with some manipulation can yield the following expression for the gas-phase flux within a porous material having a heterogeneous surface

$$N_A^g = [-(dp/dL)(D_{AK}\epsilon/RT\tau) + (8f\theta_{AA}N_A^T/6\pi\phi)]/\{1 - (f\theta_{AA}/2)[1 - (8/3\pi\phi)]\} \qquad (15)$$

This equation converges to Eq. (12) as f approaches one, as it should.

The only term in this equation for which no expression has yet been given is the fraction of the adsorbate which is mobile, f. Lee and O'Connell calculated their mobile fraction from a statistical-mechanical model of the adsorbed phase. Here, the fraction of adsorbate which is mobile will be determined by comparing entropies of adsorption (evaluated from adsorption isotherms) with theoretical values determined for localized and mobile adsorption. The methods used here for entropy-of-adsorption calculations have been detailed by Kemball (1950) and by de Boer (de Boer and Kruyer 1952, Scholten and Kruyer 1970), and these techniques have given significant insight into characteristics of adsorbed phases.

To determine the value of f using entropies of adsorption, three adsorption-entropy changes are needed. One would occur if the adsorbed molecules were all localized and immobile, another would occur if the adsorbed molecules were completely mobile, and the actual entropy change is determined from experimental data. The fraction f of the adsorbed phase which is mobile can then be calculated

$$f = \frac{\Delta S_{\text{exp}} - \Delta S_l}{\Delta S_m - \Delta S_l} \qquad (16)$$

The expressions for determining the various ΔS's where taken from the work of de Boer and Kruyer (1952). It was assumed that the molecules upon adsorption gained no external vibrational degrees of freedom, preserved their rotational and internal vibrational degrees, and lost only translational degrees; localized adsorbate molecules lost all three translational degrees of freedom, and mobile molecules one translational degree. The specific formulas used for calculation are given in the list of notation.

Some selected results from applying Eq. (16) to systems involving heterogeneous adsorbent surfaces are presented in Table 1. There is a significant degree of mobility in the adsorbed phases at all coverages. At even a fractional coverage as low as 0.03, over one-half of the adsorbed phase is envisioned as being mobile. This agrees with the results of Kemball (1950) and Scholten and Kruyer (1970) in similar situations. The latter found that physically adsorbed molecules approached localized behavior only at fractional coverages below 10^{-5}, and that the degree of mobility increased with coverage. This predicts that momentum-transfer results similar to those seen on uniform surfaces would also be seen on those which are nonuniform.

TABLE 1. FRACTIONAL MOBILITY OF PHASES ADSORBED ON NONUNIFORM SURFACES FROM ENTROPY-OF-ADSORPTION CALCULATIONS

System	Fractional Coverage, θ_A	ΔS_{exp} e.u.	ΔS_m, e.u.	ΔS_l, e.u.	f
Physical adsorption of C_2H_6 on Vycor (Horiguchi, 1969)	0.18	−21.7	−15.6	−32.6	0.64
Physical adsorption of C_3H_8 on molybdenum sulfide (Reed and Butt, 1971)	0.027	−19.4	−11.8	−30.1	0.59
Physical adsorption of SO_2 on Vycor (Gilliland et al., 1974)	0.46	−19.6	−18.6	−37.9	0.95

It should be pointed out that there are simplifications involved in calculating the value of f that may affect its value somewhat. For example, there are undoubtedly rotational restrictions and vibrational freedoms that are unaccounted for in calculating the various values of ΔS, and so the results should be viewed with caution. Nevertheless, Eq. (16) is a practical and simple way to calculate the approximate mobile fraction of adsorbate on a heterogeneous surface, which is necessary for taking gas-adsorbate collisional effects into account.

With the ability to calculate the mobile fraction f, it is now possible to use Eq. (15) to calculate the gaseous flux within a porous material having a heterogeneous surface when gas-mobile adsorbate collisions are significant. As in using Eq. (12) for uniform surfaces, Eq. (15) can be solved very simply if the pressure change within the porous material is sufficiently small that the factor ϕ does not change significantly. The surface flux follows immediately by using Eq. (2).

APPLICATIONS TO PREVIOUS STUDIES

n-Butane on Graphitized Carbon

An example of how the inclusion of gas-adsorbate momentum transfer can alter conclusions in an investigation of surface diffusion can be found in a re-analysis of the data of Ross (1955). In a series of careful experiments, he measured the adsorption of n-butane on a graphitized carbon surface and then measured the transport of the butane through a porous plug of the carbon in permeability tests at various pressures. The gaseous component of the total transport was calculated using the inverse-square-root relationship, and the surface component was found by difference. The entropy change upon adsorption was consistent with that which should occur if a two-dimensional gas were on the surface, but the apparent activation energies of the surface diffusion coefficients, based on constant fractional coverage, ranged from 4500 to 10000 cal/gmole. This was too high for a two-dimensional gas to exist on the surface. If a two-dimensional ideal gas were on the surface, and the surface flow were proportional to the drop in two-dimensional pressure, then the effective surface diffusivity should display an apparent activation energy of approximately 600 cal/gmole in the temperature range where Ross' experiments were carried out. Ross and Good (1956) concluded that the principal mechanism for surface transport was probably a "hopping" of the adsorbed molecules, which has been postulated by many investigators in this field (e.g., Weaver and Metzner 1966, de Boer 1968).

TABLE 2. SURFACE DIFFUSION OF n-BUTANE THROUGH GRAPHITIZED CARBON AT 30°C; SOURCE: ROSS, 1955.

Mean Pressure, Torr	Fractional Coverage θ_A	Gas-Phase Flux[a] Prev. Calc.,[b] $N_A^{g\prime} \times 10^9$	Gas-Phase Flux[a] True,[b] $N_A^g \times 10^9$	Surface Flux[a] Prev. Calc.,[b] $N_A^{s\prime} \times 10^9$	Surface Flux[a] True,[b] $N_A^s \times 10^9$	Surface Diffusion Coefficient Prev. Calc.,[b] D_s', cm²/s	Surface Diffusion Coefficient True,[b] D_s, cm²/s
11.2	0.26	2.73	4.85	16.3	14.2	0.524	0.455
26.3	0.54	2.73	5.51	14.8	12.0	0.750	0.606
50.7	0.76	3.65	7.42	15.6	11.8	1.55	1.18
82.4	0.88	4.09	8.27	13.0	8.79	2.33	1.57
104.3	0.93	5.75	11.6	16.8	11.0	2.91	1.89

---

[a] All fluxes are reported in g moles/(cm²)(s).

[b] The "previously calculated" values are from using the inverse-square-root relationship; the "true" values are those resulting from Eq. (12), which takes the gas-adsorbate collisional effects into account.

TABLE 3. SURFACE DIFFUSION OF n-BUTANE THROUGH GRAPHITIZED CARBON AT41.7°C; SOURCE: ROSS, 1955.

Mean Pressure Torr	Fractional Coverage, θ_A	Gas-Phase Flux[a] Prev. Calc.,[b] $N_A^{g\prime} \times 10^9$	Gas-Phase Flux[a] True,[b] $N_A^g \times 10^9$	Surface Flux[a] Prev. Calc.,[b] $N_A^{s\prime} \times 10^9$	Surface Flux[a] True,[b] $N_A^s \times 10^9$	Surface Diffusion Coefficient Prev. Calc.,[b] D_s', cm²/s	Surface Diffusion Coefficient True,[b] D_s, cm²/s
10.7	0.15	2.63	3.93	11.8	10.6	0.623	0.552
20.4	0.28	2.60	4.78	10.7	8.53	0.764	0.482
40.6	0.50	3.93	7.93	13.8	9.84	0.985	0.550
79.8	0.72	5.00	10.1	16.1	9.70	2.16	1.06

---

[a] All fluxes are reported in g moles/(cm²)(s).

[b] The "previous calculated" values are those from using the inverse-square-root relationship; the "true" values are those from Eq. (12), which takes the gas-adsorbate collisional effects into account.

The uniform-surface adsorption studies mentioned earlier, which emphasized that a two-dimensional gas or liquid almost certainly exists on these surfaces, were generally carried out using graphitized carbon. This substance has been shown on many occasions to exhibit a very high degree of surface homogeneity (e.g., Beebe and Young 1954, Cochrane et al. 1967) and is the material commonly used when studying phenomena associated with uniform surfaces. Thus in the work of Ross and Good, there was most probably a two-dimensional gas on their graphitized carbon surface. Yet there remains the problem of the activation energies they calculated, which clearly are not consistent with two-dimensional gas behavior.

The answer can be found in a recalculation of Ross' surface fluxes, taking gas-adsorbed phase interactions into account. If this is done, using Eq. (12), then a surface-diffusion coefficient can be evaluated in the usual manner (see Horiguchi et al. 1971; the formula for obtaining D_s is presented here in the Notation). The results of such calculations are shown in Tables 2 and 3. Ignoring the gas-adsorbate collisional effects caused a consistent error of 33-51% in the calculated gas-phase fluxes, which in turn caused errors of 12-66% in the calculated surface fluxes.

TABLE 4. ACTIVATION ENERGIES FOR SURFACE DIFFUSION ON A UNIFORM SURFACE [TRANSPORT OF n-BUTANE WITHIN PELLETED GRAPHITE, SOURCE: ROSS, 1955].

Fractional Coverage, θ	D_s at 30°C, cm²/s	D_s at 41.7°C, cm²/s	Activation Energy cal/g mole
0.26	0.46	0.49[a]	1400
0.50	0.55[a]	0.55	0
0.72	1.03[a]	1.06	600

---

[a] Interpolated value

TABLE 5. ERRORS RESULTING FROM USE OF INVERSE-SQUARE-ROOT RELATIONSHIP FOR SYSTEMS WITH UNIFORM SURFACES.

System	Fractional Coverage, θ_A	$\left[\frac{\text{Prev. Calc. Sfc. Flux*}}{\text{True Sfc. Flux}}\right]$ $N_A^{s\prime}/N_A^s$
Physical adsorption of n-butane on graphitized Spheron 6 (Ross, 1955)	0.26 0.93	0.87 0.65
Physical adsorption of N_2 on Graphon (Horiguchi, 1969)	0.00055 0.020	0.996 0.88
Physical adsorption of C_2H_6 on Graphon (Horiguchi, 1969)	0.16 0.49	0.75 0.46
Physical adsorption of N_2 on Graphon (Bell, 1971)	0.006 0.10	0.81 0.23
Physical adsorption of $CHCl_3$ on Graphon (Lee and O'Connell, 1975)	0.014 0.092	0.985 0.925

---

* The "previously calculated surface flux" is that determined using the inverse-square-root relationship; the "true surface flux" is that using Eq. (12), which takes the gas-adsorbate collisional effects into account.

TABLE 6. ERRORS RESULTING FROM USE OF INVERSE-SQUARE-ROOT RELATIONSHIP FOR SYSTEMS WITH NONUNIFORM SURFACES.

	Fractional Coverage, θ_A	$\left[\frac{\text{Prev. Calc. Sfc. Flux*}}{\text{True Sfc. Flux}}\right]$ $N_A^{s\prime}/N_A^s$
Physical adsorption of C_2H_6 on Vycor (Horiguchi, 1969)	0.18	0.52
Physical adsorption of C_3H_8 on molybdenum sulfide (Reed and Butt, 1971)	0.027	0.90
Physical adsorption of SO_2 on Vycor (Gilliland et al., 1974)	0.46	0.91

---

* The "previously calculated surface flux" is from using the inverse-square-root relationship; the "true surface flux" is from Eq. (15), which takes the gas-adsorbate collisional effects into account.

The surface-diffusion coefficients obtained from these surface fluxes can be plotted as a function of surface coverage, and activation energies can be derived from the temperature dependence of these coefficients at constant coverage. Values of these calculated activation energies are shown in Table 4. When gas-adsorbate interactions are considered, the energies are found to vary between 0 and 1400 cal/gmole. These are far less than the earlier values and now well within the range that might be expected if a two-dimensional gas were on the surface of Ross' carbon, considering the scatter in the calculated activation energies. It is interesting that errors of 12-66% in the calculated surface fluxes can lead to a change in the mean activation energy by a factor of ten.

Other Surface Diffusion Studies

The examination and recalculation in the previous section shows that ignoring gas-adsorbate collisional effects can lead to false conclusions about molecular behavior in surface diffusion, which in turn can cause errors in modeling. We looked at a number of other previous investigations in this area to see the range of the errors introduced by ignoring these interactions. Surface fluxes for these were recalculated using either Eq. (12) or (15), depending on whether the study was carried out using a uniform or nonuniform surface, respectively.

Results are presented in Tables 5 and 6. The former considers some studies using uniform surfaces, the latter, some using nonuniform surfaces. Data were chosen which seemed typical of very low, low, and moderate surface coverages. Looking at the results for uniform surfaces, the errors in the surface-flux calculations are not significant when the coverage is very small, as might be expected. Nevertheless, when the coverage begins to exceed a mere 1% of the total surface, errors in the calculated surface flux can exceed acceptable limits if gas-adsorbate interactions are ignored, as shown by the results using the data of Horiguchi (1969) and Bell (1971). This is not invariably true, however. The results of Lee and O'Connell are within acceptable error bounds, even at a coverage of almost 10%.

Table 6 shows much the same behavior for some studies involving nonuniform surfaces. If the inverse-square-root-of-molecular-weight relationship is used to calculate the gaseous portion of the total flux, the error can become significant at quite low coverages. On the other hand, at even moderate coverages under different circumstances the effect may not be significant and error in calculating the gas flow will not affect the calculation of the surface flow appreciably.

The extent to which gas-adsorbate momentum transfer affects a calculation of the surface flux is a complicated function of the comparative flow rates, the amount of material on the surface for a given amount in the gas phase, the relative axial velocities of the materials in the two phases, etc. An example of this can be seen in Table 6, where data from the last two studies cited result in almost identical errors, in spite of there being more than an order of magnitude difference in surface coverage. Thus generalizations are difficult. It does appear that when there is a high ratio of N_A^g to N_A^s, as in Bell's and Horiguchi's systems, a small error in the calculation of the gas-phase flux can cause a large error in the surface flux. When the ratio is low, as in the system of Lee and O'Connell, the converse is true. This phenomenon was postulated by Lee and O'Connell in their argument for ignoring these interactions in the calculation of their surface fluxes.

A PROPOSED CRITERION

Since the data indicate that the consideration of gas-adsorbate momentum transfer on occasion may be necessary for the calculation of the true surface flux, and other times may not be, it would be helpful if a simple criterion could be developed to predict the circumstances when such considerations would be necessary. In this section, such a criterion is developed.

An error is defined:

$$\xi_1 = \frac{\begin{pmatrix}\text{actual transfer of}\\ \text{axial momentum from}\\ \text{gas phase}\end{pmatrix} - \begin{pmatrix}\text{momentum transfer calculated if gas-phase flux}\\ \text{were estimated using inverse-square-root-of-}\\ \text{molecular-weight relationship}\end{pmatrix}}{\text{(actual transfer of axial momentum from gas phase)}} \tag{17}$$

This definition is a typical normalized difference between real and calculated values; multiplying it by 100 converts it to a percentage error. It is an error in calculating the momentum transferred from the gas phase, which makes it an error essentially in this phase. To get an indication of the error in the calculated value of the surface flux, it is necessary to multiply the value of ξ_1 by some factor allied to the relative magnitudes of the gas and surface fluxes. If the error defined in Eq. (1) is multiplied by the ratio of the calculated gas-phase axial momentum to the calculated surface-phase axial momentum, a reasonable error criterion for the surface flux may result:

$$\xi_2 = (\xi_1)\left(\frac{\text{gas-phase axial momentum}}{\text{surface-phase axial momentum}}\right) \tag{18}$$

We recognize that more rigorous measures of error may be derived, but it is desirable that one which is simple to apply should be developed. In the following, the point at which the modified error ξ_2 becomes significant will be determined from the treatment of existing data. Before doing this, a method for determining the value of ξ_2 from surface-diffusion data must be developed.

Since the calculated gas-phase axial momentum is $n_A^g m_A u_A^{g\prime}$ and the calculated surface-phase axial momentum is $n_A^s m_A u_A^{s\prime}$, Eq. (18) can be expressed as

$$\xi_2 = \left[\frac{M_A^0 - (M_{Aw}^{s\prime} + M_{AA}^{s\prime})}{M_A^0}\right]\left(\frac{n_A^g m_A u_A^{g\prime}}{n_A^s m_A u_A^{s\prime}}\right) \tag{19}$$

The actual momentum transfer M_A^0 is equal to

$$M_A^0 = (n_A^g \bar{v}_A/4)(2/r)(3\pi m_A u_A^{g\prime}/8) \tag{20}$$

because it is assumed that the entire pressure drop is caused by collision of the gas-phase molecules with the wall, and $u_A^{g\prime}$ is calculated from that assumption.

Expressions for $M_{Aw}^{s\prime}$ and $M_{AA}^{s\prime}$ can be obtained from Eqs. (4) and (14), respectively, using $u_A^{g\prime}$ and $u_A^{s\prime}$ instead of u_A^g and u_A^s. Then, combining these expressions with Eqs. (6)-(9) and (20) and using $u_A^{g\prime}$, $u_A^{s\prime}$, $N_A^{g\prime}$, and $N_A^{s\prime}$ instead of the unprimed quantities, some manipulation can be carried out together with substitution into Eq. (19) to yield

$$\xi_2 = \tfrac{1}{2}\,\theta_{AA} f\left(\frac{N_A^{g\prime}}{N_A^{s\prime}} + \frac{8}{3\pi f\phi}\right) \tag{21}$$

When the system contains a homogeneous surface, and the adsorbate has unrestricted two-dimensional mobility, then $f = 1$ and

$$\xi_2 = \tfrac{1}{2}\,\theta_{AA}\left(\frac{N_A^{g\prime}}{N_A^{s\prime}} + \frac{8}{3\pi\phi}\right) \tag{22}$$

Equations (21) and (22) were applied to the systems discussed earlier, and the results are presented in Table 7. One observation stands out: At errors of about 50% and below, the absolute error in the calculated flux $N_A^{s\prime}$ ranges between roughly equal to and about twice that of the proposed error ξ_2. If a maximum acceptable error in the calculation of the surface flux is 10%, then a criterion can be proposed: When the value of the modified error ξ_2 is well below 0.05, then no compensation need be made for gas-adsorbate collisional effects, and the inverse-square-root relationship may be used in the determination of surface fluxes. When the value of ξ_2 is well above 0.10, then some compensation must be made for gas-adsorbate collisional effects. If $0.05 < \xi_2 < 0.10$, then the error in the calculated

TABLE 7. COMPARISON OF ERROR IN PREVIOUSLY CALCULATED SURFACE FLUX WITH ξ_2.

System	Fractional Coverage, θ_A	Fractional Error in Prev. Calc. Sfc. Flux*	Modified Error ξ_2
Physical adsorption of n-butane on graphitized Spheron 6 (Ross, 1955)	0.26	−0.13	0.075
	0.93	−0.35	0.18
Physical adsorption of N_2 on Graphon (Horiguchi, 1969)	0.00055	−0.004	0.0044
	0.020	−0.12	0.122
Physical adsorption of C_2H_6 on Graphon (Horiguchi, 1969)	0.16	−0.25	0.167
	0.49	−0.54	0.287
Physical adsorption of N_2 on Graphon (Bell, 1971)	0.006	−0.19	0.214
	0.10	−0.77	1.84
Physical adsorption of $CHCl_3$ on Graphon (Lee and O'Connell, 1975)	0.014	−0.015	0.015
	0.092	−0.075	0.058
Physical adsorption of C_2H_6 on Vycor (Horiguchi, 1969)	0.18	−0.48	0.38
Physical adsorption of C_3H_8 on molybdenum sulfide (Reed and Butt, 1971)	0.027	−0.10	0.10
Physical adsorption of SO_2 on Vycor (Gilliland et al., 1974)	0.46	−0.09	0.048

* The fractional error in the previously calculated surface flux is defined as $(N_A^{s\prime} - N_A^s)/N_A^s$.

surface flux is likely to be in the range of 10%, and, depending on the accuracy desired, it may be advisable to make some compensation for gas-adsorbate collisional effects.

DISCUSSION

We pointed out earlier that no model has yet been proposed which is adequate for predicting the behavior of a significant amount of the existing data on surface diffusion within porous materials. We suggest that a cardinal factor in the inability to create a satisfactory model for this phenomenon is the lack of recognition accorded to gas-adsorbed phase collisional effects.

Ignoring the gas-adsorbate interactions has had two results. We have shown that not considering this type of momentum transfer most probably has created significant errors in the calculation of surface fluxes within porous materials in past studies. Since models based on erroneous surface fluxes are themselves likely to be erroneous, as demonstrated earlier, it is not surprising that the models cannot predict the behavior of more than a small amount of data.

Another factor causing the search for a reasonable model to be unsuccessful might well be a second aspect of the gas-adsorbed phase interactions—how the momentum transfer modifies the behavior of the adsorbed phase itself. It has been shown that there can be significant and sometimes even startling ways that gas-adsorbate momentum transfer affects how the adsorbate acts under various conditions (Spencer and Brown 1975). In one set of experiments, it was observed that the adsorbed phase could move *counter* to the gas phase, against the concentration gradient, because of momentum transfer from the gas phase. Therefore, in addition to the inclusion of gas-adsorbate interactions in the calculation of surface fluxes, the momentum transfer resulting from these interactions probably needs to be included in any successful model describing the behavior of a surface-diffusing phase.

Including gas-adsorbate collisional effects is thus necessary in the analysis of many, if not most, studies of surface diffusion within porous materials. Perhaps, considering these effects will provide a beginning understanding of this bewildering, perverse, and fascinating phenomenon.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation, under Grant No. ENG 76-80535.

NOTATION

A = area per molecule, cm^2
C = concentration, gmoles/cm^3 of porous material
D_s = surface diffusion coefficient, cm^2/s $[= -N_A^s\,\tau/(dC^s/dz)]$
f = fraction of adsorbed phase which is mobile; remainder is localized
h = Planck's constant; 6.626×10^{-27} erg-s
ΔH = change of enthalpy upon adsorption, cal/gmole
k = Boltzmann's constant; 1.38×10^{-16} ergs/(molecule) (K)
m = mass of a molecule, g
M = rate of momentum transferred from gas phase per unit volume, (g) (cm)/(s^2) (cm^3)
n = concentration, molecules/cm^3
n_{Av} = Avogadro's number, 6.022×10^{23} molecules/gmole
N = molar flux, gmoles/(cm^2) (s)
p = pressure or partial pressure of adsorbing subtance, *Pa*
r = radius of a capillary, cm
R = gas constant, cal/(gmole) (K)
ΔS = entropy change upon adsorption, e.u. [cal/(gmole) (K)]

$$\begin{aligned} \Delta S_{\exp} &= (\Delta H/T) - R\ln(p/p^0) \\ \Delta S_m &= R\{\ln(2\pi mkT)^{1/2}V^0/hA^0 - 1/2\} + R\ln(A_0/A^0) \\ \Delta S_l &= R\{\ln(2\pi mkT)^{3/2}V^o/h^3 - 5/2\} + R\ln[\theta/(1-\theta)] \end{aligned}$$

T = temperature, K
u = average axial velocity of all molecules, cm/s
$\bar{v}$ = average speed of a molecule, cm/s
V = volume per molecule, cm^3
z = axial distance along porous material, cm
α = area of adsorbent surface, cm^2
ϵ = void fraction or porosity of porous material
η = number of molecules adsorbed on surface
θ = fraction of surface covered by adsorbed substance
ϕ = ratio of surface concentration of a substance to gaseous concentration; obtained from adsorption isotherm
ξ_1 = error in calculation of momentum transferred from gas phase, defined by Eq. (17)
ξ_2 = modified momentum-transfer error, defined by Eq. (18)
τ = tortuosity factor

Subscripts

A = referring to substance A
AA = resulting from impinging A molecule colliding with adsorbed A molecule
Aw = resulting from impinging A molecule colliding with the wall
exp = obtained from experimental data
l = referring to localized adsorbate molecules
m = referring to completely mobile adsorbate molecules
0 = amount available per molecule

Superscripts

g = occurring in gas phase
0 = referring to the standard state or to total momentum transfer
s = occurring in surface or adsorbed phase
T = total; sum of gas and adsorbed-phase contributions
$'$ = primed values refer to those calculated using the inverse-square-root-of-molecular-weight relationship

LITERATURE CITED

Beebe, R. A., and D. M. Young, "Heats of Adsorption of Argon on a Series of Carbon Blacks Graphitized at Successively Higher Temperatures," *J. Phys. Chem.*, **58**, 93 (1954).

Bell, W. K., "Interactions between a Mobile Adsorbed Phase and Diffusing Gases in Porous Media," Ph.D. thesis, University of Colorado, Boulder (1971).

Bell, W. K., and L. F. Brown, "Interactions between a Mobile Adsorbed Phase and Diffusing Gases in Porous Media—an Experimental Study," *J. Chem. Phys.*, **59**, 3566 (1973).

Bell, W. K., and L. F. Brown, "Kinetic Theory Approach to Simultaneous Gas and Surface Diffusion in Capillaries," *J. Chem. Phys.*, **61**, 609 (1974).

de Boer, J. H., *The Dynamical Character of Adsorption*, 2nd ed., pp. 20-24, 95-98, 226-230, Oxford, London (1968).

de Boer, J. H., and J. C. P. Broekhoff, "Two-Dimensional Condensation Phenomena. I. Condensation of Adsorbed Gases on a Homogenous Carbon Surface; III. Evaluation of the Constant k_1 from Experimental Data of Adsorption of Energetically Homogeneous Surfaces," *Proc. Kon. Ned. Akad. Wetensch., Ser. B*, **70**, 317, 333 (1967).

de Boer, J. H., and S. Kruyer, "Entropy and Mobility of Adsorbed Molecules. I. Procedure; Atomic Gases on Charcoal," *Proc. Kon. Ned. Akad. Wetensch., Ser. B*, **55**, 451 (1952); "II. Nitrogen on Charcoal," *ibid.*, **56**, 67 (1953a); "III. Hydrogen and Oxygen on Charcoal," *ibid.*, **56**, 236 (1953b); "IV. Aliphatic Hydrocarbons on Charcoal," *ibid.*, **56**, 415 (1953c); "V. Carbon Monoxide, Carbon Dioxide, and Carbon Disulfide on Charcoal," *ibid.*, **57**, 92, (1954); "VI. Polar Gases on Charcoal," *ibid.*, **58**, 61 (1955).

Broekhoff, J. C. P. and R. H. van Dongen, "Mobility and Adsorption on Homogeneous Surfaces. A Theoretical and Experimental Study," in *Physical and Chemical Aspects of Adsorbents and Catalysts*, B. G. Linsen, ed., pp. 63-146, Academic Press, New York (1970).

Cochrane, H., P. L. Walker, Jr., W. S. Kiethorn, and H. C. Friedman, "Xenon Adsorption on Graphitized Carbon Blacks over a Wide Coverage Range," *J. Colloid Interface Sci.*, **24**, 405 (1967).

Field, G. J., H. Watts, and K. R. Weller, "Diffusion of Gases Physically Adsorbed on Solids," *Rev. Pure Appl. Chem.*, **13**, 2 (1963).

Gilliland, E. R., R. F. Baddour, G. P. Perkinson, and K. J. Sladek, "Diffusion on Surfaces. I. Effect of Concentration on the Diffusivity of Physically Adsorbed Gases," *Ind. Eng. Chem. Fundam.*, **13**, 95 (1974).

Horiguchi, K. Y., "Effect of Surface Heterogeneity on Surface Migration in Microporous Solids," Ph.D. thesis, U. of Waterloo, Ontario (1969).

Horiguchi, Y., R. R. Hudgins, and P. L. Silveston, "Effect of Surface Heterogeneity on Surface Diffusion in Microporous Solids," *Canad. J. Chem. Eng.*, **49**, 76 (1971).

Hudson, J. B., and R. Ross, "Adsorption and Condensation Processes," *Ind. Eng. Chem.*, **56** (11), 30 (1964).

Jackson, R., *Transport in Porous Catalysts*, p. 62, Elsevier, New York (1977).

Kemball, C., "Entropy of Adsorption," in *Advances in Catalysis*, vol. II, W. G. Frankenburg, et al., eds., pp. 233-250, Academic Press, New York (1950).

Lee, C. S., and J. P. O'Connell, "Statistical Mechanics of Partially-Mobile Adsorption of Gases on Homogeneous Solid Surfaces," *J. Colloid Interface Sci.*, **41**, 415 (1972).

Lee, C. S., and J. P. O'Connell, "Measurement of Adsorption and Surface Diffusion on Homogeneous Solid Surfaces," *J. Phys. Chem.*, **79**, 885 (1975).

Present, R. D., *Kinetic Theory of Gases*, pp. 52-55, McGraw-Hill, New York (1958).

Reed, E. M., Jr., and J. B. Butt, "Surface Diffusion of Single Sorbates at Low and Intermediate Surface Coverage," *J. Phys. Chem.*, **75**, 133 (1971).

Ross, J. W., "Flow of Gases and Vapors through Porous Media. Part I. Effect of Non-Uniform Porosity on Knudsen Flow in Porous Media. Part II. Adsorption and Surface Diffusion of n-Butane on Graphon Carbon Black," Ph.D. thesis, U. of Cincinnati (1955).

Ross, J. W., and R. J. Good, "Adsorption and Surface Diffusion of n-Butane on Spheron 6 (2700°) Carbon Black," *J. Phys. Chem.*, **60**, 1167 (1956).

Satterfield, C. N., *Mass Transfer in Heterogeneous Catalysis*, p. 33, MIT Press, Cambridge, (1970).

Scholten, J. J. F., and S. Kruyer, "Some Recent Applications of the Calculation of the Entropy of the Adsorbed Phase According to de Boer," in *Physical and Chemical Aspects of Adsorbents and Catalysts*, B. G. Linsen, ed., pp. 147-169, Academic Press, New York (1970).

Scott, D. S., and F. A. L. Dullien, "Diffusion of Ideal Gases in Capillaries and Porous Solids," *AIChE J.*, **8**, 113 (1962).

Sladek, K. J., E. R. Gilliland, and R. F. Baddour, "Diffusion on Surfaces, II. Correlation of Diffusivities of Physically and Chemically Adsorbed Species," *Ind. Eng. Chem. Fundam.*, **13**, 100 (1974).

Spencer, J. L., and L. F. Brown, "Experimental Observations of Gas Phase-Adsorbed Phase Interactions during Counterdiffusion in Porous Aluminas," *J. Chem. Phys.*, **63**, 2882 (1975).

Stoll, D. R., and L. F. Brown, "Catalytic Reaction and Fouling Effects on Intraparticle Diffusion," *J. Catal.*, **32**, 37 (1974).

Wan, C.-Z., "Counterdiffusion of Gas Mixture in Gamma-Alumina Pellet," *J. Chinese Inst. Chem. Engr.*, **8**, 67 (1977).

Weaver, J. A., and A. B. Metzner, "The Surface Transport of Adsorbed Molecules," *AIChE. J.*, **12**, 655 (1966).

DERIVATION OF THE SURFACE-SHIELDING FUNCTION θ_{AA}

The amount of surface shielded from molecules impinging from the gas phase by those which are adsorbed is greater than the projected area of the adsorbed molecules. This is true because gaseous molecules approaching from any direction other than normal to the surface are prevented from striking a portion of the surface not covered by adsorbed molecules, as illustrated in Fig. A1. When no mutual sharing of the surface shielded by adsorbed molecules is considered, the average area shielded by adsorbate has been shown to be six times the projected area (Bell and Brown 1974). This means that

$$\theta_{AA1} = \frac{\eta\sigma}{\alpha} = \frac{6\eta b}{\alpha} = 6\theta_A \tag{A1}$$

The total area shielded can, however, be shared among the adsorbed molecules (Fig. A2). When only two molecules are allowed to share any shielded area, the surface-shielding function becomes

$$\theta_{AA2} = \frac{1}{\alpha}\left\{\eta\sigma - \eta(\sigma - b)\left[\frac{\eta(\sigma - b)}{\alpha(1 - \theta_A)}\right](½)\right\} \tag{A2}$$

in which $\eta\sigma$ is the total surface area that would be shielded by two adsorbed molecules if there were no mutual sharing of shielded areas, $\eta(\sigma - b)$ is the shielded empty space available for mutual coverage, and $[\eta(\sigma - b)]/[\alpha(1 - \theta_A)]$ is the probability of any portion of empty surface being covered by a shielded empty space. The factory ½ occurs because otherwise each molecule would be counted twice.

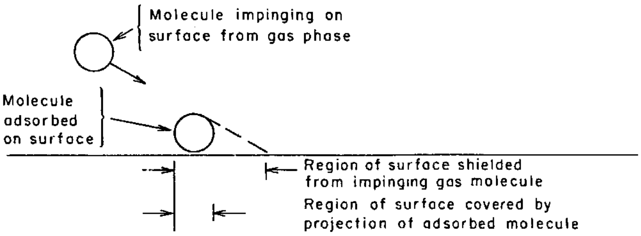

Figure A1. Why surface area shielded from impinging gas molecule is greater than projected area of absorbed molecule.

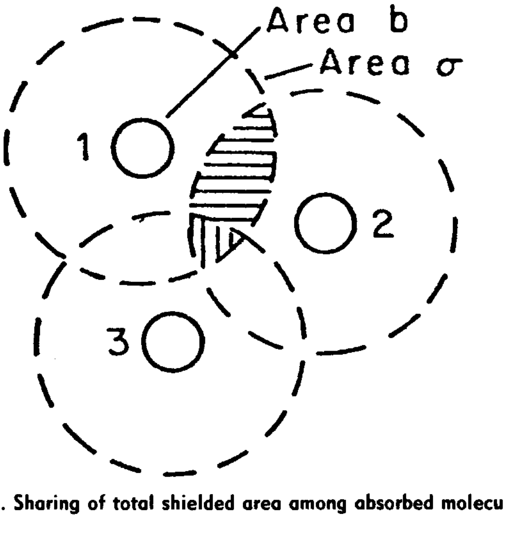

Figure A2. Sharing of total shielded area among absorbed molecules.

With the possibility of three molecules sharing the shielded area, the expression becomes

$$\theta_{AA3} = \frac{1}{\alpha}\left\{\eta\sigma - \left[\tfrac{1}{2}\,\frac{\eta(\sigma - b)(\sigma - b)}{\alpha(1 - \theta_A)}\right]\left[1 - \frac{1}{3}\,\frac{\eta(\sigma - b)}{\alpha(1 - \theta_A)}\right]\right\} \quad (A3)$$

In like fashion, when a simultaneous shielding of a portion of the surface by a very large number of molecules is considered, one obtains

$$\theta_{AA} = \frac{\eta\sigma}{\alpha} - \tfrac{1}{2}\left[\frac{\eta(\alpha - b)}{\alpha}\right]^2 \frac{1}{1 - \theta_A} + \frac{1}{6}\left[\frac{\eta(\sigma - b)}{\alpha}\right]^3 \frac{1}{(1 - \theta_A)^2} - \frac{1}{24}\left[\frac{\eta(\sigma - b)}{\alpha}\right]^4 \frac{1}{(1 - \theta_A)^3} + \dots \quad (A4)$$

Adding and substracting $\eta b/\alpha$, together with some further manipulation, yields

$$\theta_{AA} = \frac{\eta b}{\alpha} + (1 - \theta_A)\left\{\frac{\eta(\sigma - b)}{\alpha(1 - \theta_A)} - \frac{1}{2!}\left[\frac{\eta(\sigma - b)}{\alpha(1 - \theta_A)}\right]^2 + \frac{1}{3!}\left[\frac{\eta(\sigma - b)}{\alpha(1 - \theta_A)}\right]^3 - \frac{1}{4!}\left[\frac{\eta(\sigma - b)}{\alpha(1 - \theta_A)}\right]^4 + \dots\right\} \quad (A5)$$

Since $\eta b/\alpha = \theta_A$ and $\sigma = 6b$, then $\eta(\sigma - b)/\alpha = 5\theta_A$ and we can write

$$\theta_{AA} = \theta_A + (1 - \theta_A)\left[\frac{5\theta_A}{1 - \theta_A} - \frac{1}{2!}\left(\frac{5\theta_A}{1 - \theta_A}\right)^2 + \frac{1}{3!}\left(\frac{5\theta_A}{1 - \theta_A}\right)^3 - \frac{1}{4!}\left(\frac{5\theta_A}{1 - \theta_A}\right)^4 + \dots\right] \quad (A6)$$

or

$$\theta_{AA} = \theta_A + (1 - \theta_A)\{1 - \exp[-5\theta_A/(1 - \theta_A)]\} \quad (A7)$$

A further simplification gives the final result:

$$\theta_{AA} = 1 - (1 - \theta_A)\exp[-5\theta_A/(1 - \theta_A)] \quad (A8)$$

Manuscript received September 1, 1978; revision received August 8, and accepted August 30, 1979.

A Channel Flow Analysis for Porous Beds Moving Under High G Forces

An analysis is made of centrifugal flow of compacted porous beds through channels against high gas backpressure. One-dimensional compressible gas flow solutions are presented for concurrent and countercurrent solids/gas motion through the variable area channels. The physical process analyzed represents the flow through a newly developed centrifugal pump for feeding dry pulverized material against a pressure barrier. The objective of the analysis is to gain a basic theoretical understanding of this type of device. Good agreement is found between analytical predictions and test data obtained with an experimental pump feeding coal.

J. W. MEYER

Applied Mechanics Laboratory
Lockheed Palo Alto Research Laboratory
3251 Hanover Street
Palo Alto, California 94304

SCOPE

A new centrifugal pump has been recently developed for transporting dry pulverized material across a gas pressure barrier (Bonin et al., 1977). The experimental 1 ton/hr scale machine has successfully pumped coal from atmospheric pressure to delivery pressures as high as 2.8 MPa (400 lb/in.^{2} gauge). The heart of the pump is a high speed rotor that contains many converging radial channels or sprues. Pulverized material is transported into the eye of the rotor and centrifuged outward into the sprues. A compacted moving plug of porous material forms in the sprues and creates a seal against the high pressure gases. The sealing action is a combined effect of both the motion of the plug and its relatively low permeability.

The objective in the present paper is to develop a theoretical description of the basic operation of this new device, as well as a capability for predicting its performance. Specifically, the pump channel flow is analyzed, and solutions to the basic porous media flow problem are presented. A one-dimensional gas flow model is developed representing concurrent or countercurrent solids/gas motion through the variable area channels at high pressure ratios. Experimental data obtained in tests of the experimental machine pumping pulverized coal are presented, and comparisons with the theory are made. Attention here is focused exclusively on the rotor channel flow. Other aspects of the design of practical pump hardware are discussed elsewhere (Bonin et al., 1977; Lockheed, 1977*a*, *b*).

CONCLUSIONS AND SIGNIFICANCE

A theoretical approach has been developed to describe the porous media flow situation in the flow channels of a pulverized material pump. Theoretical model predictions based on uniform bed properties are in good agreement with operational experience with an experimental machine. The apparent permeability of the flowing material in the pump channels is found to be somewhat higher than measured in tests on static material plugs.

The theoretical model can be taken to be sufficiently validated to be useful in designing solids pumping machines to particular sets of requirements.

0001-1541-80-3684-0363-$01.25.