

TABLE I Continued

Solvent	1.07	1.10	1.04	1.08	1.18	1.13	1.07	1.09
Ph. Anh., Solvent	1.14	1.13	1.12	1.09	1.18	1.21	1.11	1.12
Mal. Anh., Solvent	1.09	1.06	1.17	1.14	1.16	1.10	1.09	1.13
Ph. Anh., Mal. Anh., Solv.	1.20	1.20	1.18	1.22	1.20	1.20	1.22	1.21
Solvent	Isopropyl Myristate		m-Nitrobenz- Aldehyde		Isobornyl Methyl Ether		m-Nitro Acetophenone	
Solvent	1.06	1.09	1.02	1.06	1.14	1.14	1.17	1.10
Ph. Anh., Solvent	1.11	1.04	1.15	1.18	1.13	1.16	1.10	1.05
Mal. Anh., Solvent	1.17	1.05	1.14	1.11	1.10	1.08	1.20	1.24
Ph. Anh., Mal. Anh., Solv.	1.22	1.23	1.22	1.22	1.22	1.23	1.25	1.20
Solvent	4-Nitro Phenol		2-Phenyl Phenol		2-Undecanone		Benzaldehyde	
Solvent	1.16	1.12	1.05	1.05	1.04	1.06	1.13	1.10
Ph. Anh., Solvent	1.17	1.08	1.09	1.18	1.11	1.15	1.17	1.13
Mal. Anh., Solvent	1.15	1.13	1.11	1.11	1.07	1.12	1.16	1.13
Ph. Anh., Mal. Anh., Solv.	1.23	1.23	1.21	1.21	1.21	1.20	1.20	1.21
Solvent	Diethylphenyl Malonate		p-Ethyl Benzaldehyde		Dimethyl Succinate		9-Fluorenone	
Solvent	1.09	1.08	1.03	1.10	1.07	1.10	1.09	1.17
Ph. Anh., Solvent	1.15	1.05	1.16	1.06	1.16	1.16	1.09	1.05
Mal. Anh., Solvent	1.08	1.14	1.17	1.05	1.16	1.12	1.13	1.17
Ph. Anh., Mal. Anh., Solv.	1.21	1.22	1.20	1.19	1.22	1.20	1.21	1.22

and the relative volatility remains essentially constant at about 1.21. Without extractive distillation agents, it would have been 1.06. A great many compounds and combinations were investigated and failed to enhance the relative volatility. They are listed in Berg, U.S. Patent 4,292,142 (1981).

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Effects of Gas-Adsorbate Momentum Transfer on the Movement of a Mobile Adsorbed Phase over a Uniform Surface

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INTRODUCTION

This paper examined to what degree gas-adsorbate collisions affect the behavior of surface diffusion in a mobile adsorbed phase. In earlier papers from this laboratory (Bell and Brown, 1973; 1974), it was shown that momentum exchange during the collisions be-

tween gas molecules and mobile adsorbed molecules can influence noticeably the gaseous transport within porous materials. Ignoring the effects of such collisions usually results in significant errors in the calculation of gas and surface-phase fluxes within the material (Bell and Brown, 1974; Thakur et al., 1980). The inverse-square-root-of-molecular-weight relationship, which has been employed frequently in separating the gas and adsorbate components of the total flux in the presence of surface diffusion (e.g., Jackson, 1977; Okazaki et al., 1981), is apparently not obeyed except in unusual circumstances (Thakur et al., 1980).

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TABLE 1. MOLECULAR MOBILITY IN SYSTEMS INVESTIGATED

Source of Data	Adsorbate	Temperature, K	Pressure, kPa	Fractional Coverage, θ	Fractional Mobility, f
Ross and Good (1956)	n-Butane	303	3.5	0.54	0.79
Lee and O'Connell (1975)	Chloroform	318	0.72	7.9×10^{-2}	0.90
Ash et al. (1967)	Argon	304	3.33	2.4×10^{-3}	1.03
Ash et al. (1967)	Sulfur Hexafluoride	303	13.32	3.7×10^{-2}	1.05

In the last reference, it was pointed out that gas-adsorbed phase interactions also had the possibility of affecting the transport process in another way—by modifying the migrational behavior of the adsorbed phase. In an experimental study, Spencer and Brown (1975) apparently found that the adsorbed phase can be affected strongly by gas-adsorbate momentum transfer. The possibility of gas-adsorbate interactions affecting the behavior of the adsorbed phase is considered further in this paper. We examine some experimentally-observed mobile adsorbed phases reported in the literature. Of the total momentum changes in these phases, the fractions caused by gas-adsorbate collisions are calculated, and some inferences are drawn from the results of these calculations.

THEORY

We shall examine systems involving porous materials through which permeability was measured in the Knudsen-flow regime. For systems of this type, the momentum transferred to the adsorbed phase during gas-adsorbate collisions can be calculated from the formula (Thakur et al., 1980)

$$M_{AA}^s = (n_A^s \bar{v}_A / 4) (\theta_{AA}) (m_{AA}^s) [3\pi u_A^s / 8 - u_A^s] \quad (1)$$

Using the substitutions

$$N_A^s = n_A^s u_A^s / n_{AV}$$

$$N_A^s = n_A^s u_A^s / n_{AV}$$

$$N_A^T = N_A^s + N_A^s$$

$$\phi = n_A^s / n_A^s$$

$$\bar{v}_A = (8kT / \pi m)$$

we can obtain

$$M_{AA}^s = (m_{AA}^s n_{AV} / 4) (8kT / \pi m)^{1/2} \times (\theta_{AA}) [(3\pi N_A^T / 8) - N_A^s (3\pi / 8 + 1 / \phi)] \quad (2)$$

If the momentum transferred to the adsorbed phase during gas-adsorbate collisions could be compared with the total momentum gain or loss in the adsorbed phase across the porous pellet, then a quantitative indication of the importance of the gas-adsorbate collisions in the behavior of the adsorbed phase might be deduced. The total momentum loss in the adsorbed phase can be

calculated from the drop in two-dimensional pressure ("spreading pressure") across the porous particle. If the pressure within the pellet does not change too much, the drop in two-dimensional pressure can be related to the change in three-dimensional pressure by the expression

$$\Delta\pi = (RT / p A_{mol}) \Delta p \quad (3)$$

This expression, obtained from the Gibbs adsorption isotherm, has been used before in a study of adsorption and surface diffusion (Gilliland et al., 1958). The surface area per mole adsorbed, A_{mol} can be obtained from the BET surface area and the adsorption isotherm.

RESULTS

Four surface-flow studies are considered in this analysis, all of which involved flow over Graphon surfaces. The adsorbates used in the four systems were n-butane (Ross and Good, 1956), chloroform (Lee and O'Connell, 1975), argon, and sulfur hexafluoride (Ash et al., 1967).

Two-dimensional mobility of an adsorbed phase over Graphon has been observed frequently (e.g., Amberg et al., 1955; Horiguchi et al., 1971). Additional evidence of the highly mobile nature of the adsorbate in the four systems may be obtained from entropy-of-adsorption calculations. A method involving entropy of adsorption has been suggested for calculating the fractional mobility of an adsorbed phase (Thakur et al., 1980). The formula proposed is

$$f = (\Delta S_{exp} - \Delta S_I) / (\Delta S_m - \Delta S_I) \quad (4)$$

Using the adsorption isotherms (Ross, 1955; Lee, 1973; Ash et al., 1967), values of the fractional mobility for the four systems were calculated and are presented in Table 1. The values corroborate the highly mobile nature of the adsorbates on Graphon. The mobility is essentially total at low coverages, though it might be slightly restricted at higher coverages.

For each system, Eq. 2 was used to calculate the momentum transferred during gas-adsorbate collisions down the length of the porous pellet in the surface-flow experiments. Equation 3 was used to calculate the total momentum change in the adsorbed phase along the same distance. The value of the surface flux used in Eq. 2 was obtained taking gas-adsorbate interactions into account as specified in an earlier paper (Thakur et al., 1980).

The results of these calculations are presented in Table 2 for the

TABLE 2. GAS-ADSORBATE MOMENTUM TRANSFER AND TWO-DIMENSIONAL PRESSURE

Systems	Mean Pressure, p	Pressure Drop, $\Delta p / \Delta L$	Fractional Coverage, θ	Total Flux, N_A^T	Surface Flux, N_A^s	Two-Dimensional Pressure Drop, $\Delta\pi / \Delta L$	Gas-Adsorbate Momentum Transfer, M_{AA}^s	Ratio $M_{AA}^s / (\Delta\pi / \Delta L)$
	Pa	Pa/cm		mol/(cm ²)(s)	mol/(cm ²)(s)	N/m ²	N/m ²	
n-C ₄ H ₁₀ -Graphon at 30°C	1.49×10^3	0.59×10^3	0.26	1.90×10^{-8}	1.42×10^{-8}	1.03×10^{-1}	1.01×10^{-4}	9.8×10^{-4}
(Ross and Good, 1956)	1.39×10^4	1.24×10^3	0.93	2.26×10^{-8}	1.10×10^{-8}	8.37×10^{-2}	2.79×10^{-4}	3.3×10^{-3}
CHCl ₃ -Graphon at 45°C	4.90×10^2	3.38×10^2	4.84×10^{-2}	5.80×10^{-7}	5.20×10^{-7}	8.60×10^{-2}	5.52×10^{-4}	6.4×10^{-3}
(Lee and O'Connell, 1975)	1.76×10^3	1.21×10^3	2.1×10^{-1}	2.17×10^{-6}	1.86×10^{-6}	3.70×10^{-1}	8.67×10^{-3}	2.3×10^{-2}
Argon-Graphon at 30°C	6.67×10^3	4.14×10^3	4.84×10^{-4}	1.30×10^{-8}	0.51×10^{-8}	6.06×10^{-4}	4.56×10^{-7}	7.5×10^{-4}
(Ash et al., 1967)	3.33×10^4	2.07×10^4	2.42×10^{-3}	6.5×10^{-8}	2.54×10^{-8}	3.03×10^{-3}	1.14×10^{-5}	3.8×10^{-3}
SF ₆ -Graphon at 31°C	6.67×10^3	4.14×10^3	1.85×10^{-2}	1.52×10^{-8}	0.43×10^{-8}	2.06×10^{-2}	4.34×10^{-5}	2.1×10^{-3}
(Ash et al., 1967)	2.66×10^4	1.66×10^4	7.4×10^{-2}	6.09×10^{-8}	2.06×10^{-8}	8.24×10^{-2}	5.7×10^{-4}	6.9×10^{-3}

smallest and largest fractions of a monolayer tested in each system. Two of the columns in this table present the momentum transferred during gas-adsorbate interactions and the total lost over the length of the particle, or the two dimensional pressure drop. A comparison of the two values of the momenta shows that in all cases the momentum transferred as a result of gas-adsorbate collisions was an extremely small fraction of the total momentum loss by the adsorbed phase over the length of the pellet. The portion of the total momentum change in the adsorbed phase represented by gas-adsorbate momentum transfer ranged from a low of 0.08% to a high of 2.3%.

DISCUSSION

The conclusion from these calculations is direct. For the four systems studied, momentum transferred from the gas to the adsorbed phase is an insignificant fraction of the total momentum change in the adsorbed phase. This suggests that collisions between the gas and the adsorbed phases do not influence the movement of the adsorbed phase appreciably, and models of surface diffusion might not have to consider gas-adsorbate interactions, except in the calculation of the surface flux.

However, earlier counterdiffusion experiments in our laboratory (Spencer, 1976; Spencer and Brown, 1975) reported that gas-adsorbate interactions affected the behavior of the adsorbed phase significantly. In these studies, counterdiffusion through porous alumina of helium and argon, helium and 1-butene, and argon and 1-butene was measured. Three differences between these measurements and those of the systems examined in this note are immediately apparent. The pores of Spencer's alumina averaged about 5 nm in radius, whereas the pores in the Graphons averaged about 20 nm. The surface of Graphon is quite uniform (Cochrane et al., 1954; Bell, 1971), and that of the alumina was almost certainly heterogeneous. Spencer carried out her experiments at 250°C, where chemisorption prevails, and the temperatures of the experiments considered in this note were all well below 50°C and physical adsorption was dominant. Thus the conclusion of this note should be restricted to the type of systems studied.

It is therefore concluded that collisions between the gas and adsorbed phase probably do not influence the behavior of the adsorbed phase appreciably if the surface is uniform and the adsorbed phase consists primarily of physically-adsorbed molecules.

As a final comment, it should be pointed out that the calculations of surface fluxes for the four systems incorporated the effects of gas-adsorbate momentum transfer on the gas-phase behavior. Consideration of these is still essential in most situations for calculation of the proper value of the surface flux (Thakur et al., 1980).

NOTATION

A	= surface area, cm^2
f	= mobile fraction of the adsorbed molecules
k	= Boltzmann's constant, $1.38 \times 10^{-16} \text{ erg}/(\text{molecule})(\text{K})$
m	= mass of a molecule, g
m_{AA}'	= reduced "collisional mass" of molecule A; $= 0.5 m_A$, g
M	= rate of momentum transfer to the unit area of the surface phase, $(\text{g})(\text{cm})/(\text{s}^2)(\text{cm}^2)$
n	= concentration, molecules/ cm^3
n_{AV}	= Avogadro's number, 6.002×10^{23} molecules/mol
N	= molar flow, $\text{mol}/(\text{cm}^2)(\text{s})$
p	= mean pressure or partial pressure of adsorbing substance, Pa
R	= gas content; $8.314 \text{ J}/(\text{mol})(\text{K})$
ΔS	= entropy change upon adsorption, J/K
T	= temperature, K
u	= average axial velocity, cm/s
\bar{v}	= average speed of a molecule, cm/s
θ	= fraction of surface covered by the adsorbed substance

π	= two-dimensional pressure in the adsorbed phase, newtons/m
ϕ	= ratio of surface concentration of a substance to its gaseous concentration; obtained from adsorption isotherm

Subscripts

A	= referring to substance A
AA	= resulting from impinging A molecule colliding with adsorbed A molecule
exp	= obtained from experiments
l	= referring to localized adsorbate molecules
m	= referring to mobile adsorbate molecules
mol	= referring to a quantity per mol

Superscripts

g	= occurring in gas phase
s	= occurring in surface or adsorbed phase
T	= total; sum of gas and adsorbed phase contributions

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