A Statistical Mechanical Model for Adsorption and Flow of Pure and Mixed Gases in Porous Media with Homogeneous Surfaces

Part II: Applications

Application of the model of Part I is made to several systems with various graphitized carbon blacks over wide ranges of temperatures and submonolayer coverage. Agreement with all data for equilibrium and transport is probably within experimental error.

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SCOPE

Equilibrium adsorption and the flux of adsorbable gases through porous media with homogeneous surfaces have been of experimental interest for many years. A number of theoretical models have addressed this system as the initial case for more complex situations. However, most of these theories do not attempt to represent all possible cases with a single model based on statistical mechanics and utilizing intermolecular potential parameters. Instead, only one property or type of system is considered.

Part I (Lee and O'Connell, 1985) has developed a fully generalized theory that includes the essential molecular phenomena and formulates expressions for all the measurable properties of pure and mixed systems at submonolayer coverages. The present paper describes application of the model to gases physically adsorbed on graphitized carbon blacks with surfaces that are essentially homogeneous. Difficulties and inconsistencies of data analysis are discussed and a strategy for fitting the several molecular parameters to the data is indicated.

CONCLUSIONS AND SIGNIFICANCE

Equilibrium and transport data for several pure nonpolar and polar gases have been examined and compared with correlations from the model of Part I. The agreement is probably within experimental error in all cases; the best results occur when the values are compared directly with measurements rather than with manipulated information. As expected, surface diffusion results are quite sensitive to the parameters of the structured adsorption potential but equilibrium isotherm data are not. Localized adsorption is always present to some degree, even on graphitized carbon black surfaces.

At low temperatures, the structure of the adsorption potential is the dominant factor for surface diffusion. At higher temperatures, normal vibration and its anharmonicity have an important effect. However, since the model formulation is based on known physical phenomena, it provides a parameterization for these effects that uses temperature-independent quantities having values that are consistent with other information.

Application to mixed gas adsorption is also successful. Further, the case of binary flux of adsorbable and nonadsorbable substances with interactions between the bulk and adsorbed phase is well predicted.

Finally, an initial attempt at estimating the important parameter for surface diffusion indicates that for these surfaces, rough predictions of surface flux might be made using only equilibrium information.

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INTRODUCTION

The theory presented in Part I of this study is a complete theory for submonolayer equilibrium adsorption and porous bed flux of pure components and mixtures when there is homogeneous surface adsorption. Based on a single statistical mechanical model for partially mobile adsorption and on a single set of parameters, the theory provides a realistic description of flow from the localized limit to the mobile limit. It also provides a method for treating the interactions between surface flow and bulk flow quantitatively. Therefore, the theory should be applicable over wide ranges of temperature and of pressures up to those at which the bulk flow changes from the Knudsen regime to the intermediate regime. In this paper, results of the theory of Part I are compared with data for the adsorption and flow on graphitized carbon black surfaces that are essentially homogeneous.

BASIC EQUATIONS AND CONCEPTS

The equations given in Part I that are to be applied to equilibrium data include Eq. 41, which gives the adsorption isotherm for a pure ideal gas phase, and Eqs. 33–40 for mixed adsorption. Equation 42 is used for the pure component isosteric heat of adsorption.

The equations for transport cover several cases. For pure components under a pressure gradient the porous bed permeability uses Eqs. 52 and 54, total flux uses Eqs. 50 and 53, while the total diffusion coefficient uses Eqs. 49 and 55. If only the pure component surface diffusion coefficient is of interest the relevant equations are 81–91. For mixed gases the transport equation for the tracer diffusion coefficient is Eq. 92 while for two-component total flux the equations are 56 and 100–103.

Table 1 gives the types of data and sources we compare with the model. The model is valid for submonolayer adsorption and when the bulk flow is in the Knudsen regime for pure components or the total pressure is constant for mixture. The theory cannot independently define a "monolayer," but it is expected to be applicable close to the BET monolayer which is, in our terms, a fractional coverage, Θ, of about 0.4. (The value of Θ is the fraction of surface covered by admolecules, not the fraction of the monolayer amount.) Knudsen flow occurs when the mean free path is much larger than the pore diameter. If the ratio of the mean free path to the pore diameter is not much greater than unity, the usual method of calculating the gas phase flux of the adsorbable component from the helium flux by the molecular weight correction becomes unreliable. Such problems related with these porous media are discussed by Ash and Barrer (1967), for example.

MODEL PARAMETERS AND DATA ANALYSIS

For a porous plug, the values of the physical quantities of specific surface area A, void fraction ϵ, surface area per unit bed volume σ, and Knudsen diffusion coefficient D_i^{Ke} for helium must be determined experimentally. Although Knudsen diffusion coefficients obviate the need for tortuosity, τ, in pure component systems, mixture flow calculations require its value along with the bulk gas phase mutual diffusion coefficient D_{ij}. This last property may be determined from a known correlation (e.g., Reid et al., 1976). Table 1 gives the values of all but D_{ij} for the systems we studied. The site density, ϱ_s, and the nearest neighbor distance between sites, σ_N, are best determined from the structure of the solid surface. For graphite basal planes, we have set these values as 0.00192 nm^{-2} and 0.0514 nm, respectively.

In addition to the above adsorbate characteristics, the physical model requires a surface effectiveness factor δ that corresponds to the surface tortuosity discussed by Barrer and Gabor (1960) and Lee and O'Connell (1972), among others. Theoretically, its value may range from 1 to 10, the higher values corresponding to ad-

TABLE 1. SUMMARY OF DATA ON GRAPHITIZED CARBON BLACKS

Adsorbate	Adsorbent	Surface Area, A m^2/g^{-1}	Void Fraction ϵ	Average Pore Dia. $2\gamma_{av}$,nm	Tortuosity τ	Knudsen Diff. Coeff. × 10^{-3}	True Density g/cm^{-3}	Type of Data**	Reference
Ar	Graphon	78.9	0.42	—	—	1.74	1.97	AD, PM	Ash et al. (1967)
SF_6	Graphon	78.9	0.42	—	—	1.74	1.97	AD, TD, PM	Ash et al. (1967)
SO_2	Graphon	89	0.50	—	—	(3.28)	1.89†	AD, SD, TRD	Pope (1967)
$CHCl_3$	Graphon	89	0.38	—	—	4.32	1.89†	AD, TF	Lee and O'Connell (1975)
$n-C_4H_{10}$	Graphon	84.1	0.54	—	—	5.08	1.99	AD, SD	Ross and Good (1956)
C_3H_8	Graphon	89.6	0.65	43.0	1.62†	8.34	1.95	AD, CF (He)	Bell (1971)
	FTG-D5	13	—	—	—	—	—	AM(C_2H_6,C_3H_6)	Friederich and Mullins (1972)
C_3H_6	Graphon	97.6‡	0.51	21.2	1.62	3.28	1.89	AD, SD, PM	Horiguchi (1971)
	FTG-D5	13	—	—	—	—	—	AM(C_3H_8)	Friederich and Mullins (1972)
C_2H_6	Graphon	97.6‡	0.51	21.2	1.62	3.28	1.89	AD, SD, PM	Horiguchi (1971)
	FTG-D5	13	—	—	—	—	—	AM(C_3H_8,C_2H_4)	Friederich and Mullins (1972)

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* $D_k \sqrt{mi/T}$ cm^2 s^{-1} (g mol^{-1}K^{-1})$^{1/2}$

** AD, Adsorption isotherm; PM, Permeability; SD, Surface diffusion coefficient; TD, Total diffusion coefficient; TRD, Tracer diffusion coefficient; TF, Total Flux; CF, Counterflow flux (with another component); AM, Binary adsorption (with another component)

† Assumed value for present calculation

‡ Based on N_2 area of 0.2 nm^2 instead of usual 0.162 nm^2

sorbed molecules having great difficulty moving from one carbon particle to another. Barrer and Gabor postulated that this process was actually accomplished by activated desorption in the course of surface diffusion since local equilibrium between bulk and surface phase means that surface flow is likely to utilize the bulk path when it is more favorable. Thus, a low value of 1.3 has been chosen here. We find it is adequate for all homogeneous adsorbents because, unlike the tortuosity factor for Knudsen diffusion, τ, it is insensitive to the overall void fraction of porous plugs (Lee and O'Connell, 1975). This is probably because the overall void fraction varies only with the macropore structure, while the micropore structure, which is important for surface diffusion, is little affected. However, the value of δ could vary in particular situations.

Our theory of adsorption and surface diffusion requires six potential parameters (U_{oi}, ν_i, σ_{Si}, ϵ_i, σ_{Hi}, and ϵ_{Gi}) for each component. Potential parameters used for the present calculations are listed in Table 2 except for σ_{Si}, which is assumed to be 0.03 nm for all substances. None of these parameters can be determined accurately from bulk properties. The values of σ_{Hi} and ϵ_{Gi} can be well defined by fitting the concentration dependence of the equilibrium adsorption isotherms. There appears to be a connection between ϵ_{Gi} and σ_{Hi} and their corresponding bulk parameters, as discussed below. However, since the solid affects the admolecular interaction (Sinanoglu and Pitzer, 1960) and relative orientation on the surface may not be random as in the bulk gas phase, these are best found by fitting pure component adsorption data. The parameters ϵ_i and σ_{Si} characterize the structured surface potential and adsorbate mobility, as discussed below.

Because of correlations between the parameter values ϵ_i, U_{oi} and ν_i, the latter two are determined by simultaneous fitting of the Henry's constants and the zero coverage surface diffusion coefficients, while the first is then found from the coverage dependence of the transport. In this last fitting, it should be noted that local fluxes are readily calculated from Eq. 56 of Part I. However, the partial pressure profile is not generally known experimentally in an integral plug, so the calculation is started with an assumed (e.g., linear) pressure profile. Then, dC_i/dl and the amounts adsorbed are calculated from Eq. 60 of Part I. At steady state, the pressure profile should be such that, at any point in a plug, the sum of bulk flux and surface flux is a constant. Thus, convergence leads to a profile in which the partial pressure at any point changes linearly with the calculated flux of the corresponding component up to that point.

Measurements of surface diffusion coefficients are subject to several errors. The first source is related with the usual assumption of steady state. Even after waiting a sufficiently long time (Horiguchi et al., 1971), since the flow is measured by the pressure change, the situation is at best a pseudosteady flow (Lee and O'Connell, 1972). The next problem is related with differentiation of the experimental adsorption isotherms, which is often done numerically. We have found significant inconsistencies in surface diffusion coefficients from this. As a result, the experimental information may have errors. The following are our best attempts to analyze all the data available and present comparisons with the model of Part I.

TABLE 2. MODEL POTENTIAL PARAMETERS

Adsorbate	U_{oi} kJ/mol^{-1}	ν_i 10^{12} s^{-1}	ϵ_i kJ/mol^{-1}	σ_{Hi} nm	ϵ_{Gi} kJ/ mol^{-1}
Ar	7.61	0.70	2.72	0.295	3.18
SF_6	14.73	0.90*	10.5*	0.42	7.32
SO_2	19.29	0.40	9.0	0.34	9.00
$CHCl_3$	25.65	2.18	13.0	0.46	9.41
C_2H_6	13.18	0.85	6.7	0.42	6.28
C_3H_6	18.74	2.08	8.4	0.455	6.90
C_3H_8	18.03	1.38	8.4	0.46	6.90
nC_4H_{10}	22.17	1.25	10.0	0.50	7.11

* Anharmonicity corrected with $x = 0.025$ in Eq. 106 part I.

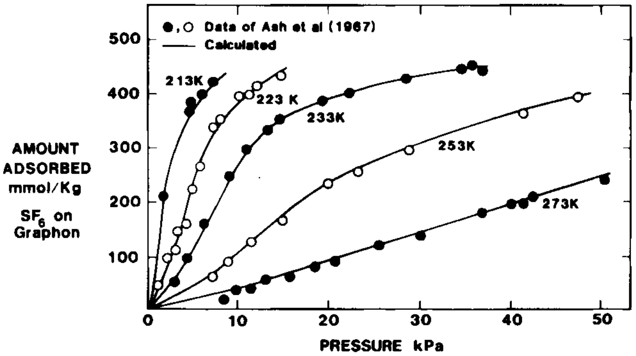

Figure 1. Adsorption isotherms for SF_6 on Graphon.

COMPARISONS WITH DATA

Adsorption isotherms and total diffusion coefficients for SF_6 on Spheron 6 (2700) are shown in Figures 1 and 2 (Ash and Barrer, 1967), while the total permeability ($K_i^T RT$) at high temperature is compared with calculated values for SF_6 and Ar in Table 3. Over a very wide range of temperature, the experimental Henry's constants, adsorption isotherms, and temperature and concentration dependence of total diffusion coefficients agree well with calculated values. The total permeabilities for SF_6 and Ar also probably agree within experimental error, although the calculated values are consistently low, perhaps due to our universal choice of 1.3 for δ. It should be noted that at the low temperatures of Figure 2, the surface diffusion is limited by the structured potential, whereas at the high temperatures of Table 3, the accommodation of normal vibrations is also important.

Adsorption isotherms and surface diffusion coefficients for SO_2 (Pope, 1967) are compared with calculated values in Figures 3 and 4. The composition dependence of both pure component and trace diffusion coefficients agree very well with the data; only the experimental inconsistency at zero coverage causes the apparent discrepancy. We have chosen the pressure flow limit as the correct one. It is higher than the tracer flow limit, so the differences are larger for this property.

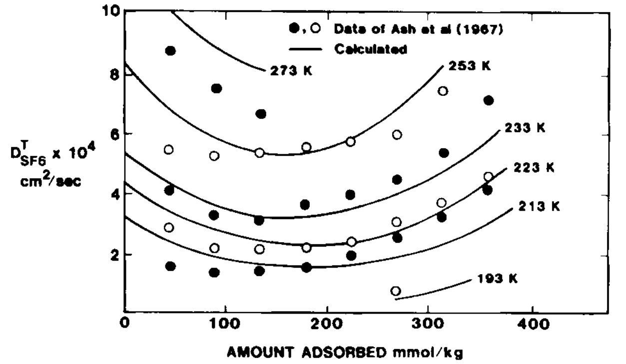

Figure 2. Surface diffusion coefficients for SF_6 on Graphon.

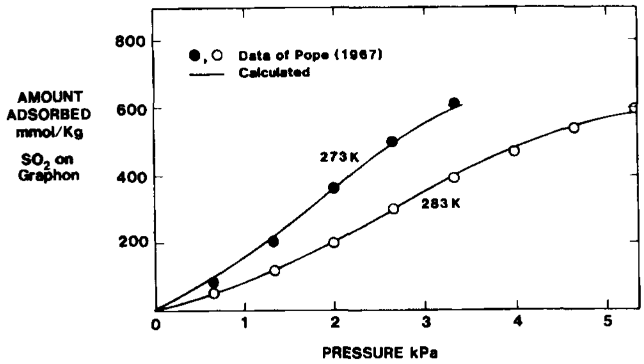

Figure 3. Adsorption isotherms for SO$_2$ on Graphon.

Table 3. Comparison of Total Permeability (K_i^TRT) for Sulfur-Hexafluoride at High Temperatures (10^{-3}cm^2/s)

Component	Temp. K	Calculated	Ash et al. (1967)
SF$_8$	304	9.64	9.3
	333	7.69	7.9
	373	6.44	6.9
	423	5.75	6.3
	473	5.48	6.0
Ar	195	9.17	10.38
	231	7.61	8.92
	273	7.04	8.09
	303	6.93	7.90
	323	6.93	7.71

Experimental adsorption isotherms and total flux data for CHCl$_3$ are compared with calculated values in Figures 5 and 6. The flux does not involve the derivative of the adsorption isotherm and thus can be compared directly with calculated values for testing the theory. The better data consistency and agreement in this comparison may be due to being able to compare directly with measured, rather than manipulated, data.

Surface diffusion coefficients and adsorption isotherms for n-butane are compared with calculated values in Figures 7 and 8. The effects of interactions between the bulk and surface flows are important as can be seen by the Γ parameters from Eqs. 58 and 59 of part I as given in Table 4. For SO$_2$, SF$_6$ and CHCl$_3$ the Γ values are within 10% of unity, while here they are more than 1.4 at the highest coverages. The interaction, as indicated by the values of Γ_i^C and Γ_i^S, increases both the bulk flow and the surface flow as the

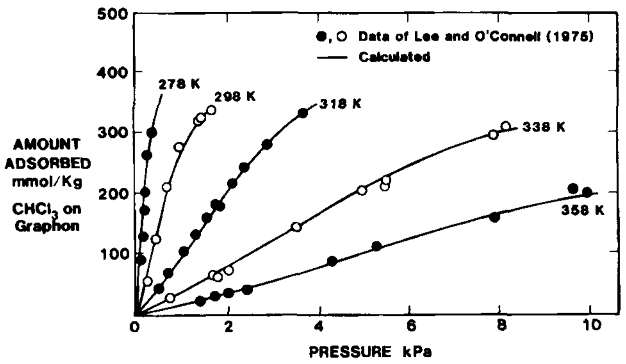

Figure 5. Adsorption isotherms for CHCl$_3$ on Graphon.

amount adsorbed increases. Since the former is larger, the interactions affect the bulk flow the most. Table 5 compares our calculations of the interaction contributions with those from Thakur et al. (1960). Our values are consistently less for two reasons: our fraction of mobile admolecules is not unity as Thakur et al. (1980) assumed, and our admolecular area is normalized differently. However, the trends are consistent.

Figure 9 shows equilibrium data and calculations for ethane and propylene on Graphon. Our analysis of Horiguchi's transport data for propylene and ethane as shown in Figures 10 and 11 encountered two problems in addition to those from measurement and manipulation of flux data mentioned above. First, the reference helium flux deviates from the Knudsen temperature behavior, causing uncertainties in the bulk flux. Second, the pressure range probably puts the bulk into the intermediate region, preventing accurate estimation of the adsorbable substance bulk phase flow. At 273 K and 1 atm (101.3 kPa), the mean free path, λ, for propylene is about 4 nm when calculated from the equation

$$\lambda = 1/\sqrt{2}\pi\sigma_{Hi}^2 n \tag{1}$$

where n is the number density. This corresponds to about 1/5 of the mean pore radius. However, the helium flow may have been in the Knudsen regime because of its smaller size and λ at this pressure. The constancy of permeability over a range of pressure (Horiguchi et al., 1971) is indicative of this. Thus, the 10% discrepancies in the calculated and experimental surface permeabilities may be due to experimental uncertainties for the adsorbed gases. It is interesting to note that the maximum in the propylene permeabilities at low coverages is reproduced by our calculations. For ethane, however, although the magnitudes of the values are similar, the agreement in the pressure dependence of the permeabilities is probably unsatisfactory. We could have reproduced the pressure dependence by changing the values of δ and ϵ_i, but more data would be needed to establish whether this is appropriate.

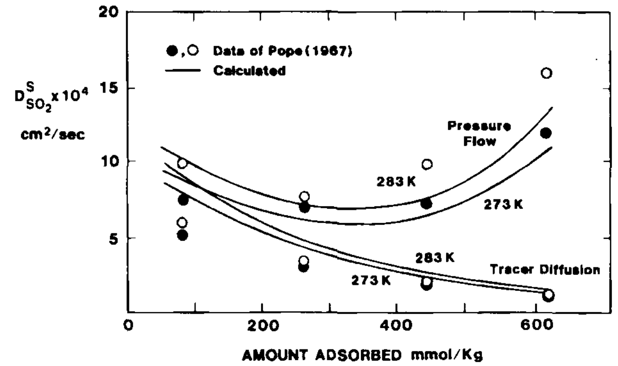

Figure 4. Surface diffusion coefficients for SO$_2$ on Graphon.

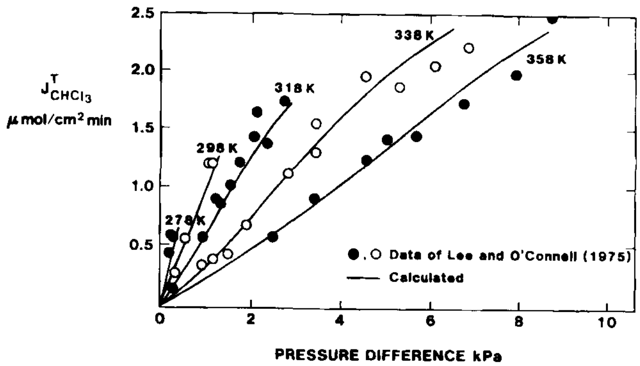

Figure 6. Total flux for CHCl$_3$ through Graphon plug.

Table 4. Bulk and Surface Flow Interaction Parameters for Eqs. 44 and 48 of Part I

Adsorbate	Temp. K	f_{im}	Γ_i^G Low Θ *	Γ_i^G High Θ †	Γ_i^s Low Θ *	Γ_i^s High Θ †	Γ_i^M Low Θ *	Γ_i^M High Θ †
n-Butane	303	0.584	1.26	1.42	1.00	1.01	1.03	1.41
	314.7	0.620	1.28	1.46	1.00	1.02	1.04	1.66
Propane	299.2	0.718	1.29	1.55	1.01	1.05	1.27	2.63
	332	0.781	1.30	1.63	1.03	1.16	1.59	5.03
	367	0.827	1.33	1.71	1.07	1.40	2.13	9.59
	408	0.864	1.35	—	1.15	—	3.09	—
Propylene	273	0.648	1.22	1.47	1.00	1.01	1.04	1.18
	298	0.715	1.25	1.54	1.01	1.03	1.09	1.43
	323	0.766	1.28	1.61	1.01	1.06	1.17	1.87
Ethane	273	0.995	1.26	1.62	1.02	1.05	1.16	1.61
	298	0.833	1.28	1.68	1.03	1.11	1.26	2.08
	323	0.861	1.29	1.73	1.05	1.20	1.40	2.76

* Amount adsorbed is 2.5 cm3(STP)g−1

† Amount adsorbed is 7.5 cm3(STP)g−1

Table 5. Comparison of Interaction Parameter Γ_i^M for *n*-Butane at 314.9 K

Pressure kPa	Present	Thakur et al. (1980)
14.3	1.02	1.13
27.2	1.04	1.58
54.1	1.07	1.79
106.4	1.19	2.04

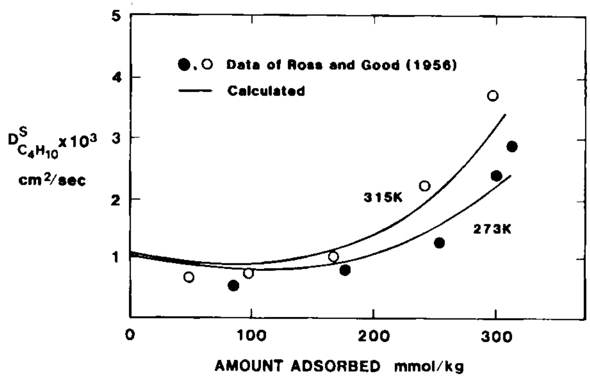

Figure 8. Surface diffusion coefficients for $n-C_4H_{10}$ on Graphon.

As a final note on these hydrocarbon systems, we update our previous (Lee and O'Connell, 1974) comparisons of mixture equilibrium adsorption calculations from the present model to experimental data for binary mixtures of propane, propylene, ethane, and ethylene (Friederich and Mullins, 1972). Since no transport data were available at that time, we estimated values of σ_{si} and ϵ_i for these substances in order to do the analysis. With the somewhat different present values obtained from pure component diffusion data, we still obtain good agreement with the isotherms in the mixed systems, showing the insensitivity of equilibrium properties to details of the model.

The last transport data set to be compared is Bell's (1971) counterdiffusion data of propane and helium. The adsorption isotherms and compared in Figure 12. Total flows of helium and propane are compared in Figures 13 and 14 with calculated values using Eq. 57 of Part I. Several pieces of information had to be established differently here. Bell did not report the helium permeability data, so we had to estimate the Knudsen diffusion coefficients by Eq. 47 of Part I using the measured average pore diameter. These are shown in Figure 13. Also, we used this optimized value of τ. Because of the meager amount of data, we estimated ϵ_i using an idea discussed below. It was taken as 36% of the zero coverage isosteric heat of adsorption. Finally the other parameters were obtained from the adsorption isotherm data. The data and theory show that interactions between bulk and surface flows and between bulk flows are significant. The model appears to satisfactorily describe the data, although, as above, the bulk propane flow may not be strictly in its Knudsen regime. Therefore, it appears that surface diffusion in homogeneous graphite systems

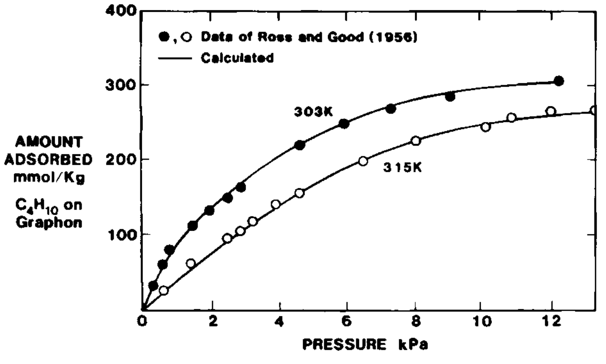

Figure 7. Adsorption isotherms for $n-C_4H_{10}$ on Graphon.

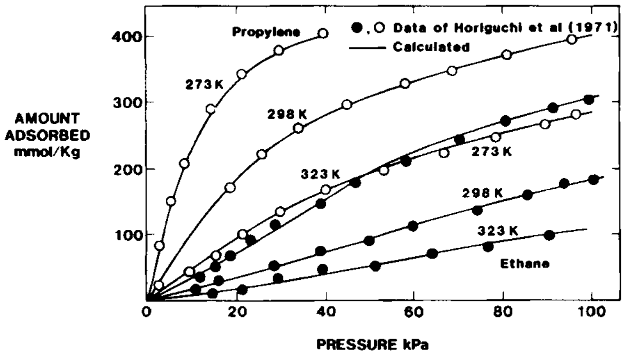

Figure 9. Adsorption isotherms for C_3H_6 and C_2H_6 on Graphon.

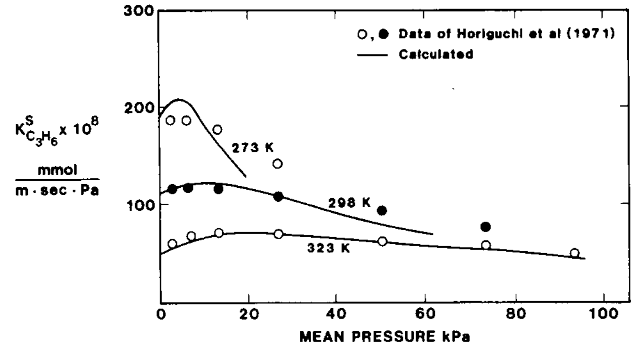

Figure 10. Surface permeabilities for C_3H_6 through Graphon plug.

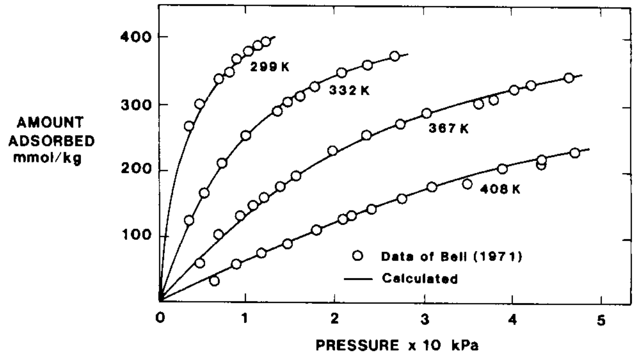

Figure 12. Adsorption isotherms for C_3H_6 on Graphon.

may be predicted using surface structural information, equilibrium adsorption data, and Knudsen flux measurements.

Finally, the zero coverage isosteric heat of adsorption can also be calculated from the parameters listed in Table 2 using Eq. 42 of Part I; the results are shown in Table 6. They agree with other calculated or experimental values to within ± 1 kJ/mol^{-1} except for normal butane, where the data appear almost independent of the amount adsorbed (Ross and Good, 1956). Such a coverage dependence is unusual for homogeneous surfaces. The agreement with calculated values is good at higher coverages but disagrees at lower coverages.

DISCUSSION

The breadth of application of this model can be compared to models limited to equilibrium adsorption only such as that of Ross and Olivier (1964) and those limited to only certain surface flows.

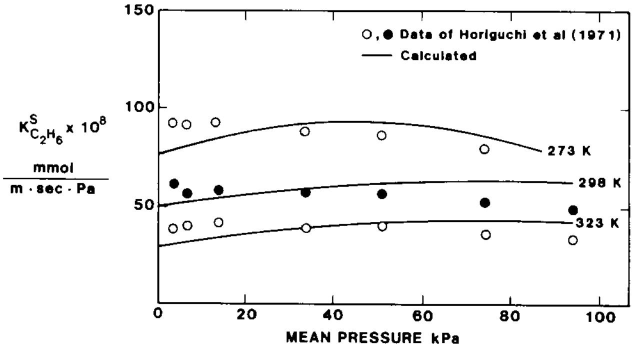

Figure 11. Surface permeabilities for C_2H_6 through Graphon plug.

For example, the hydrodynamic flow model (Gilliland et al., 1958) would be expected to fail for strongly adsorbed substances (Horiguchi et al., 1971). The hopping model (Weaver and Metzner, 1966) would be unsatisfactory if the mobile fraction of admolecules is significant, as in most of the cases here. In addition, its dependence on surface coverage must be found empirically (Okazaki et al., 1981). Finally, these methods are incomplete because they ignore the interaction between bulk and surface flows (Thakur et al., 1980). This interaction is always present, and can be assumed negligible only if the bulk flow is insignificant (Lee and O'Connell, 1975). As can be seen, the present

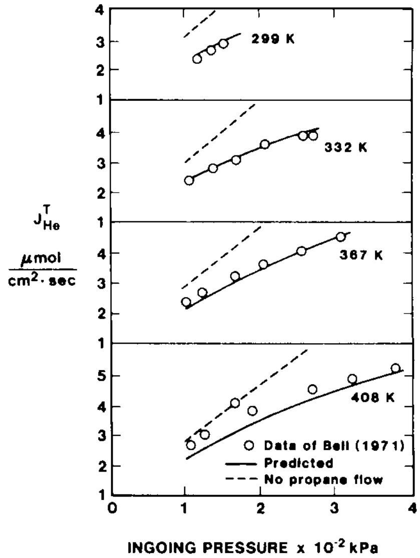

Figure 13. Helium flux counterdiffusing against propane through Graphon plug.

TABLE 6. COMPARISON OF LIMITING ISOSTERIC HEATS OF ADSORPTION, $kJ \cdot mol^{-1}$

Component	Temp., K	Calc.	Exp.	Reference
Ar	(323)	9.7	10.0	Ash et al. (1967)
SF_6	273	26.5	—	—
	473	17.9	18.8	Ash et al. (1967)
SO_2	273	25.1	—	—
$CHCl_3$	278	34.6	33.5*	Ross and Olivier (1964)
C_2H_6	273	17.6	18	Horiguchi, et al. (1971)
C_3H_6	273	24.7	25.5	Horiguchi, et. al. (1971)
C_3H_8	299	23.7	23.0	Taylor and Atkins (1966)
$n - C_4H_{10}$	303	26.9	33.5	Ross and Good (1956)

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* Chromatographically determined value on graphite.

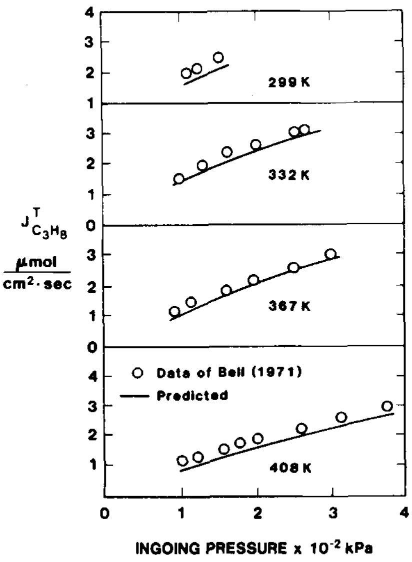

Figure 14. Propane flux counterdiffusing against helium through Graphon plug.

model applies to all cases and yields parameters with physical significance, many of which are applied in all cases.

The potential parameters listed in Table 2 appear constant over a fairly wide temperature range. Although it is difficult to judge from their graphical representation, the present methods seem to describe adsorption equilibrium data better over a wide temperature range than does the completely mobile adsorption theory presented by Ross and Olivier (1961). The data on SF_6, which are from 193 to 473 K, required the use of Eqs. 106 and 107 of part I to make a correction for anharmonicity for both equilibrium and nonequilibrium properties. Using a value of $x = 0.025$ determined from the temperature dependence of Henry's constants, the values of ν_i^s and ϵ_i^s are 0.75×10^{12} s^{-1} and 8.4 kJ/mol^{-1} at 193 K and 0.59×10^{12} s^{-1} and 6.9 kJ/mol^{-1} at 473 K. The importance of this effect is small for temperature variations less than 100 K.

The value of ϵ_i determines the most important characteristic of the structured surface potential. We find that the parameters of Table 2 lead to a fraction of mobile molecules that appears physically reasonable. There is no unique method of obtaining the site size, σ_{si}, and the depth of our cylindrical well, ϵ_i, from the more realistic conical well potential of Steele and Ross (1961). However, to infer whether our values are appropriate, we can take the example of argon, for which the conical well energy variation is about 0.4 kJ/mol^{-1} (Steele, 1973). This would yield $f_{im} = 0.535$ at 80 K assuming a Boltzmann distribution of kinetic energy over the conical potential well. For the cylindrical well model to have the same f_{mi}, our value of ϵ_i must be 2.72 kJ/mol^{-1} with $\sigma_{si} = 0.03$ nm, as we have chosen. (At other temperatures the value of ϵ_i would be different, but the low temperature comparison is most valid.) Regardless of the energy barrier values, it is important to realize that the mobile fraction is never unity, even for argon. While variations from unity may not be readily discernible for any equilibrium property calculation, they cannot be ignored for transport properties.

The differences in intermolecular interactions of gas phase molecules and of admolecules makes it difficult to develop a method for predicting potential parameters needed for the calculation. Nevertheless, for a crude prediction of surface diffusion on graphitized carbon blacks we find the value of ϵ_i can be taken as 36% of the isosteric heat of adsorption at zero coverage. The vibrational frequency may be taken as 1×10^{12} s^{-1}. Then, using only the adsorption isotherm data, σ_{Hi} and ϵ_{Gi} can be determined. With this procedure, the predicted transport properties agree with the above fitted results within 30% except for the SF_6 system at temperatures below 273 K, where the error is up to 100%. Further developments in this estimation method will be communicated later, as will applications to heterogeneous carbon and other surfaces.

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NOTATION

A = surface area of solid per unit mass, m^2/kg^{-1}
C = amount adsorbed per unit bed volume, mol/m^{-3}
D = diffusion coefficients, m^2/s^{-1}
f_{im} = mobile fraction of admolecules of component i
J = flux, $mol/m^{-2} \cdot s^{-1}$
K = permeability, $mol/m^{-1} \cdot Pa^{-1} \cdot s^{-1}$
l = coordinate along the axis of flow, m
n = number density per unit volume, m^{-3}
R = gas law constant, 8.314 $J/mol^{-1} \cdot K^{-1}$
T = temperature, K
U_o = potential of admolecules, J/mol^{-1}

Greek Letters

Γ = gas-adsorbate interaction coefficients
δ = effectiveness factor for surface diffusion
ϵ = void fraction
ϵ_i = admolecule-site interaction energy parameter, J/mol^{-1}
ϵ_{Gi} = admolecule-admolecule interaction energy parameter, J/mol^{-1}
θ = fraction of surface covered by admolecules
λ = mean free path, m
ν = frequency of vertical vibration, s^{-1}
ϱ = number density per unit surface area, m^{-2}
σ = surface area per unit bed volume, m^{-1}
σ_H = hard disk diameter for admolecule-admolecule interaction, m
σ_S = site diameter, m
σ_N = nearest neighbor distance between surface sites, m
τ = tortuosity factor

Superscripts

Ke = effective Knudsen flow
M = superscript for Γ_i^M defined by Eq. 49 of Part I
S = adsorbed phase
T = total flow

Subscripts

i = component i
ij = interaction between component i and j
s = surface sites

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