L = length of the working tube
p = pressure
w = mean velocity of fluid in the tube
w_c = mean velocity in the smallest annular cross-section
γ = specific weight of the fluid
λ = coefficient of longitudinal friction
μ = viscosity
ρ = density

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Adsorption Rates for Sulfur Dioxide and Hydrogen Sulfide in Beds of Activated Carbon

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Beds of activated carbon are useful for separating carbon dioxide, sulfur dioxide, and hydrogen sulfide from air and combustion gases. For *a priori* design of adsorption beds, rate and equilibrium (for reversible adsorption) parameters need to be known. The usual model for the overall process includes four steps. These steps (and their rate constants) are: axial dispersion (E_d), gas-to-particle mass transfer (k_f), intraparticle diffusion (D_a, D_i), and adsorption (k) at a site within the pores of the carbon particle. Since the adsorption step corresponds to physical adsorption, its intrinsic rate is fast enough that this effect on the overall process is negligible. Gas-to-particle mass transport also is a relatively rapid step so that k_f can be estimated accurately enough from available correlations (e.g., Wakao and Funazkri, 1978). In commercial-scale columns, axial dispersion is usually insignificant. However, E_d can be estimated from correlations (for example, Suzuki and Smith, 1972). Hence, intraparticle diffusivities in the macro- and micropore regions and the adsorption equilibrium constant K_A are the parameters that need to be determined from laboratory studies.

Andrieu and Smith (1979) have reported values of these parameters for adsorption of carbon dioxide on a common type (BPL, Calgon Corp.) of activated carbon, prepared by binding microparticles of bituminous coal prior to activation. Pulse-response data were analyzed by the method of moments to obtain K_A, D_a and D_i. The method of analysis, including the accounting for axial dispersion, which is significant in laboratory-scale experiments, is described in the carbon dioxide work.

The purpose of the present paper is to report results for sulfur dioxide and hydrogen sulfide for the same activated carbon. The experimental apparatus, procedure, and method of analysis were the same as employed for the carbon dioxide study. Hence, only the results and comparison for the three adsorbates are given here. More information (Calgon Corp.) is now available for the pore-volume distribution for BPL carbon, and the distribution curve is shown in Figure 1. Pore sizes cover a wide range from an average value of 11Å for micropores (diameter ≤ 50Å) and 3750Å (diameter ≥ 50Å) for macropores. As for carbon dioxide, reasonable values of the diffusivities, and their temperature dependency, could be obtained by dividing the pore volume into micropores and macropores. Mass transfer in the macropores was assumed to occur by bulk and Knudsen diffusion while an activated surface process was assumed for the small micropores, where molecule-wall interaction predominates.

ADSORPTION EQUILIBRIUM RESULTS

Equilibrium constants are obtained from corrected first moments, $(\Delta\mu_1)$, evaluated from the measured response curves. Figure 2 illustrates such data as a function of gas velocity through the bed. The agreement between the data points for different particle sizes is a measure of the reproducibility and accuracy of the measurements.

Equilibrium constants K_A and isoteric heats of adsorption ΔH_A are summarized in Table 1. The temperature range studied for each adsorbate was chosen so as to give rapidly reversible adsorption; the response curves did not have excessively long tails. The K_A values are a measure of the adsorption strength, and the values in the table show that the capacity increases from CO_2 to H_2S to SO_2. The results for the same temperature (343°K) suggest relative capacities of 1.0 (CO_2), 4.8 (H_2S) and 51 (SO_2). The heats of adsorption, which apply at essentially zero surface coverage since the data were obtained chromatographically, increase in the same order. The values for H_2S and SO_2 are about 60% greater than their heats of condensation (at the normal boiling point), while the adsorption and sublimation heats are about the same for carbon dioxide. These results suggest stronger molecule-carbon site interaction for the sulfur gases than for carbon dioxide.

INTRAPARTICLE DIFFUSIVITIES

The results for macropore diffusion, D_a and τ_a, are given in Table 2. The values for the diffusivity for the three absorbates

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J. Andrieu is on leave from National Institute of Applied Science, Lyon, France.

TABLE 1. ADSORPTION EQUILIBRIUM RESULTS

Carbon Dioxide				
Temp., °K	303	313	338	358
K_A, m^3/kg	0.13	0.090	0.048	0.028
Hydrogen Sulfide				
Temp., °K		323	343	363
K_A, m^3/kg		0.37	0.19	0.11
Sulfur Dioxide				
Temp., °K	373	393	408	423
K_A, m^3/kg	0.67	0.34	0.22	0.15

	K_A @343°K m^3/kg	Heat of Adsorption $-\Delta H_A$, kcal/mol	$(\Delta H_A/\Delta H_v)$**
Carbon Dioxide	0.040	6.0	1.0
Hydrogen sulfide	0.19	7.1	1.6
Sulfur dioxide	2.0*	9.5	1.6

* extrapolated value.

** ΔH_v is evaluated at normal boiling point; ΔH_v = heat of sublimation for CO_2.

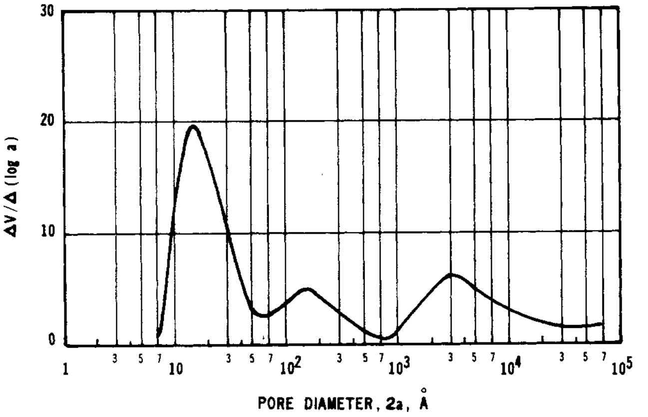

Figure 1. Pore-volume distribution of BPL activated carbon.

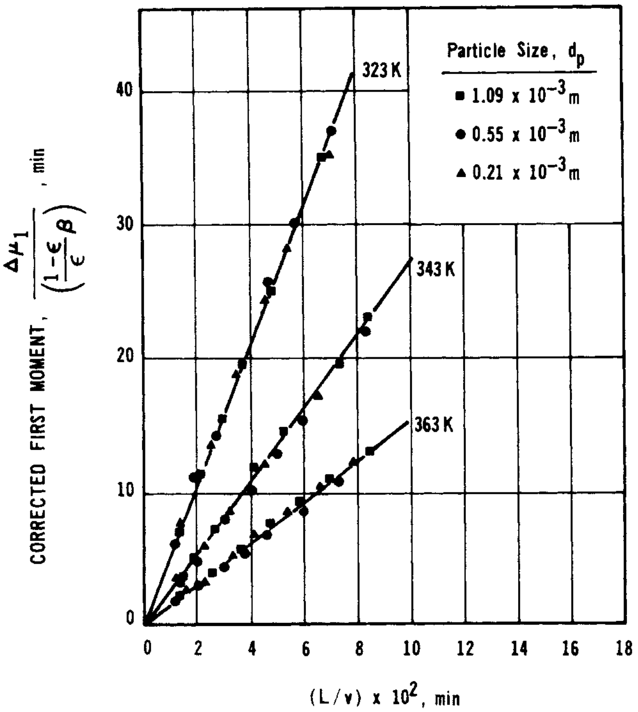

Figure 2. First-moment data for hydrogen sulfide.

are all of the order of 10^{-6}m^2/s. Macropore transport is considered to occur by diffusion in the pore volume. Hence, it is appropriate to interpret D_a values for different gases in terms of a macropore tortuosity factor, τ_a, calculated from the equation

$$\tau_a = \frac{\beta_a D}{D_a} \tag{1}$$

Here, D is a composite molecular diffusivity accounting for both bulk and Knudsen diffusion (Andrieu and Smith, 1979). Such tortuosity factors should be independent of temperature and the nature of the absorbate. They also are a sensitive measure of the validity of the experimental work. The values in Table 2 are about the same for CO_2 and H_2S. The results for SO_2 are somewhat higher, and this probably reflects the somewhat less accurate diffusivities for this component. Kawazoe et al. (1974) reported $\tau_a \sim 4$ from a study of the adsorption of nitrogen on activated carbon.

The lower entries for each gas, in Table 2, give micropore diffusivity results. The radius, r_a, of the microporous particles, from which the carbon particles are made, is unknown. Hence, only the ratio D_i/r_a^2 can be obtained directly from the experimental data. Also, only this ratio is needed to predict the performance of adsorption columns. To present a reasonable value

TABLE 2. MACRO- AND MICROPORE DIFFUSIVITIES

Carbon Dioxide			
Temp., °K	303	313	338
$D_a \times 10^6$, m^2/s	2.2	2.45	3.1
τ_a	5.0	4.7	4.1
D_i/r_a^2, s^{-1}	0.11	0.12	0.13
$D_i \times 10^{11}$, m^2/s	1.1	1.2	1.3
E = 1.4 kcal/mol			
Hydrogen Sulfide			
Temp., °K	323	343	363
$D_a \times 10^6$, m^2/s	3.6	3.7	3.85
τ_a	4.4	4.7	4.8
D_i/r_a^2, s^{-1}	0.077	0.086	0.102
$D_i \times 10^{11}$, m^2/s	0.77	0.86	1.0
E = 1.8 kcal/mol			
Sulfur Dioxide			
Temp., °K	393	408	423
$D_a \times 10^6$, m^2/s	1.95	2.05	2.2
τ_a	6.6	6.5	6.4
D_i/r_a^2, s^{-1}	0.059	0.074	0.093
$D_i \times 10^{11}$, m^2/s	0.59	0.74	0.93
E = 5.0 kcal/mol			

for the micropore diffusivity, the D_i values given in Table 2 correspond to $r_o = 10$ microns. Such diffusivities are of the order of 1×10^{-11} m^2/s and are somewhat lower for the more strongly adsorbed SO_2 and H_2S than for CO_2. Values of the same magnitude were reported by Chihara et al. (1978) for rare-gas adsorbates in molecular-sieving carbon and by Walker et al. (1966) for micropore transport of CO_2 in coal particles. The activation energies obtained from an Arrhenius plot of the D_i/r_o^2 values increase from 1.4 for CO_2 to 1.8 for H_2S and to 5.0 kcal/mol for SO_2. The lower micropore diffusivities for H_2S and SO_2 are expected in view of the stronger attraction between wall atoms and absorbate molecule for the sulfur-containing gases. Further, such results would not be expected if the micropore transport occurred by a pore-volume rather than a surface transport process.

The data for H_2S and SO_2 as well as that for CO_2 indicate that intraparticle transport has a strong effect on the overall adsorption rate. Hence, particle-size and pore-volume distribution information is necessary for a careful design of activated carbon beds for these gases.

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NOTATION

a = pore radius, m
D = composite molecular diffusivity, m^2/s
D_a = effective diffusivity in the macropores, m^2/s
D_i = effective diffusivity in the micropores, m^2/s
d_p = equivalent spherical diameter of carbon particles, m
E = activation energy for micropore diffusion, kcal/mol
E_d = axial dispersion coefficient, based upon cross-sectional area of column, m^2/s
ΔH_A = isoteric heat of adsorption, kcal/mol
ΔH_c = heat of condensation of pure adsorbate at normal boiling point, kcal/mol
K_A = adsorption equilibrium constant, m^3/kg
k = first-order adsorption rate constant, m^3/kg · s
k_f = gas-to-particle mass transfer coefficient, m/s
L = bed length, m
r_o = radius of microparticles in the activated carbon, m
T = absolute temperature, °K
v = gas velocity in interstitial space at temperature of bed, m/s
V = pore volume, m^3/kg

Greek Letters

β_a = macropore porosity
ϵ = bed porosity
τ_a = tortuosity factor for macropores

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Estimation of Solvent Effects on Chemical Reaction Rates Using UNIFAC Group Contribution

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The UNIFAC group contribution method, developed by Fredenslund et al. (1975), provides the chemical engineer with a straightforward, reliable method for predicting activity coefficients in nonelectrolyte solutions when little or no experimental equilibrium data exist. The UNIFAC method has been applied to vapor-liquid, liquid-liquid, and solid-liquid equilibria calculations with good results. In the following, UNIFAC is combined with transition state theory to predict thermodynamic solvent effects on chemical reaction rates in solution.

TRANSITION STATE THEORY

Transition state theory (Evans and Polanyi, 1935; Glasstone et al., 1941) postulates the existence of an intermediate species or transition state, M, for any elementary reaction,

$$A + B \rightleftarrows M \rightarrow \text{Products} \qquad (1)$$

The assumption of thermodynamic equilibrium between this transition state and the reactants, A and B, leads to the following expression for reaction rate in a nonideal system (Brønsted, 1922; Bjerrum, 1924),

$$\text{Rate} = k_o \frac{\gamma_A \gamma_B}{\gamma_M} \cdot (A)(B) \qquad (2)$$

where k_o is the rate constant in an ideal reference system ($\gamma_A = \gamma_B = \gamma_M = 1$), γ_i is the activity coefficient for an individual species i, and (A) and (B) are the reactant concentrations. The Brønsted-Bjerrum relationship for the apparent rate constant in a nonideal solution follows directly from this expression,

$$k = k_o \frac{\gamma_A \gamma_B}{\gamma_M} \qquad (3)$$

Equation 3 is not limited by the assumption of equilibrium between the transition state and reactants (Marcus, 1967) and is

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