Rate Parameters for Adsorption of CO_2 in Beds of Carbon Particles

Adsorption equilibrium constants and intraparticle diffusivities were determined for the adsorption of carbon dioxide on an activated carbon derived from bituminous coal particles. The moment method was used to extract these results from pulse-response measurements for beds of carbon particles. The activated carbon had a very broad pore-size distribution: average radius of micropores was 11Å and macropores 3750Å. Bulk molecular and Knudsen diffusion could not explain mass transfer in the micropores. An activated surface migration concept (Chihara et al., 1978) did give reasonable results. The adsorption rate was also significantly retarded by intraparticle diffusion in the macropores.

J. ANDRIEU and J. M. SMITH

Univ. of California
Davis, CA 95616

SCOPE

The use of activated carbon for separating CO_2 from other gases such as hydrogen sulfide is a potentially promising procedure. For evaluation of a process of this type, rate and equilibrium constants for the various steps in the overall adsorption are necessary. Such information is not available even for pure gases. Our purpose in this paper is to present results for the adsorption equilibrium constant and intraparticle diffusivities for carbon dioxide using a typical activated carbon with a broad pore-size distribution. The data consisted of response measurements to pulses of carbon dioxide introduced into an isothermal bed of carbon particles. Measurements were made in the linear range of the adsorption isotherm so that the moments of the response peaks could be used to interpret the data.

CONCLUSIONS AND SIGNIFICANCE

A major conclusion from analysis of the data was that mass transfer in the small micropores of the carbon particles could not be explained by a pore-volume mechanism. The average diameter in the micropore region was 11Å and the pore walls appeared to retard diffusion. At least reasonable values of the micropore diffusivity, D_i, and its variation with temperature, were obtained when transport was assumed to occur by an activated surface process. The diffusivities were of the order of 10^{-11}m²/s and were of the same magnitude as found by Chihara, et al. (1978) for hydrocarbon gases in molecular-sieve type (pores of 5Å diameter) carbon powders.

For the particle sizes studied (from 14 to 65 mesh), pore volume diffusion in macropores (average diameter = 3750Å) significantly influenced the overall adsorption rate. Macropore diffusivities were 2 to 3 × 10^{-6} m²/s in the temperature range of 303 to 338K and corresponded to a tortuosity factor of about 4.5. The results show that both particle- and pore-size distribution of the activated carbon need to be considered in designing adsorption columns for CO_2 removal.

The adsorption of CO_2 on activated carbon at room temperature, followed by desorption at somewhat higher temperatures, is an attractive process for separating this component from other gases. However, no quantitative information seems to be available for the rate and equilibrium parameters necessary for the design of such adsorption-desorption columns. The only related studies were those reported by Walker, et al. (1966), who report micropore diffusivities for CO_2 in coal particles. Equilibrium isotherms have been determined for paraffin hydrocarbons and sulfur compounds (Grant et al., 1962). Chihara et al. (1978) reported adsorption equilibrium constants, heats of adsorption and micropore diffusivities for rare gases, and hydrocarbons on activated carbon powder; Kawazoe et al. (1974) published data for the adsorption of nitrogen.

Our objective was to determine the relative importance of axial dispersion, gas-to-particle mass transfer, intraparticle diffusion, and adsorption at an interior site for CO_2 on activated carbon. This was done by using the chromatographic technique developed earlier (Schneider and Smith, 1968). This consists of moment analysis of the response curves when a pulse of carbon dioxide in helium carrier is introduced to a packed bed of carbon particles. For the theory to be valid, the experimental conditions must be chosen so that the adsorption process is first order. The axial dispersion coefficients obtained from these laboratory experiments would not be applicable for the design of commercial-scale columns because flow conditions would be different, but the intraparticle diffusivities should be directly applicable.

Data were obtained at atmospheric pressure and constant temperatures from 303 to 338K and for a range of gas flow rates and particle sizes. The activated carbon was type BPL, whose properties are given in Table 1. This carbon is made by binding small (micro-)bituminous particles of coal prior to activation. As noted in Table 1, the macroparticles used for the experiments have a broad pore-size distribution, ranging from 10 to 20 Å pores within the microparticles to 10^2 to 10^5 Å in the macropores surrounding the microparticles. For analyzing the data, the micropores are chosen to be those of 50 Å (diameter) or smaller. There is a minimum in the pore-volume distribution curve at

---

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

0001-1541-80-4212-0944-$00.75.

TABLE 1. PROPERTIES OF TYPE BPL ACTIVATED CARBON[1]

Surface Area (BET)	1050-1150 m^2/g
Solid-Phase Density	2.1×10^3 kg/m^3
Particle Density, ρ_p	0.85×10^3 kg/m^3
Total Particle Porosity, β	0.60
Micropore ($\leq$ 50Å) Porosity	0.30
Macropore ($>$ 50Å) Porosity	0.30
Average Pore Radius[2], $\bar{a}$	
Micropores, $\bar{a}_i$	11Å
Macropores, $\bar{a}_a$	3750Å
Total Pore Volume, V_t	0.77×10^{-3} m^3/kg

---

[1] From Bulletin 23-106a, Pittsburgh Activated Carbon Co.

[2] $\bar{a} = \frac{1}{V}\int a\, dV$

this diameter. The results for different temperatures were sufficient to determine the heat and activation energy for the adsorption process.

The method of analysis consisted of comparing moments calculated from the measured response curves, $C_L(t)$, with theoretical moment expressions based on a model for the carbon particles. A bidisperse model (Hashimoto and Smith, 1974) allowing for bulk molecular and Knudsen diffusion in both micro- and macropores did not give reliable values for the rate parameters. This failure may be due to the presence in the activated carbon of very small pores of the same magnitude as the diameter of the CO_2 molecules. Interaction between pore wall and gas molecule could influence the diffusion process in the micropores. In studies of micropore diffusion in a special molecular-sieve type carbon (pore size 5 Å), Chihara, et al. (1978) were able to interpret their results satisfactorily by proposing an activated, surface diffusion process in the micropores. Combining this concept with pore-volume diffusion in the macropores allowed a satisfactory interpretation of our data for carbon dioxide. In this approach the rate of the adsorption step on the surface of the micropores is assumed to be fast with respect to surface diffusion. Hence, the intraparticle rate parameters are the macro- and micropore effective diffusivities, D_a and D_i.

With this model, solution of the mass conservation equations gives for the first absolute and second central moments:

$$\mu_1 - \frac{t_o}{2} = \frac{L}{v}\left[1 + \frac{1-\epsilon}{\epsilon}\beta_a\left(1 + \frac{K_A\rho_p}{\beta_a}\right)\right] \tag{1}$$

$$\mu_2' - \frac{t_o^2}{12} = 2\frac{L}{v}\left[\frac{E_d}{\epsilon}(1+\delta_o)^2\frac{1}{v^2} + \delta_1\right] \tag{2}$$

where

$$\delta_o = \frac{1-\epsilon}{\epsilon}\beta_a\left[1 + \frac{K_A\rho_p}{\beta_a}\right] \tag{3}$$

$$\delta_1 = \delta_i + \delta_a + \delta_f \tag{4}$$

$$\delta_i = \frac{1-\epsilon}{15\epsilon}\left(\frac{r_o^2}{D_i}K_A\rho_p\right) \tag{5}$$

$$\delta_a = \frac{1-\epsilon}{15\epsilon}\frac{R^2}{D_a}(\beta_a + K_A\rho_p)^2 \tag{6}$$

$$\delta_f = \frac{(1-\epsilon)R}{3\epsilon k_f}(\beta_a + K_A\rho_p)^2 \tag{7}$$

Here, K_A is the absorption equilibrium constant, D_a and D_i macro- and micropore diffusivities, and r_o is the radius of the microparticles from which the macroparticle (radius = R) is made.

The experimental values of the first absolute and second central moments are obtained from the response curves with the equations:

$$\mu_1 = \frac{\int_0^\infty tC_L(t)dt}{\int_0^\infty C_L(t)dt} \tag{8}$$

TABLE 2. CHARACTERISTICS OF PACKED COLUMNS AND OPERATING CONDITIONS

Column No.	1	2	3
Packed Length, m	0.257	0.257	0.257
Column I.D., m $\times 10^2$	0.82	0.82	0.82
Particle Size			
Mesh Range	14-16	28-32	60-65
Ave. Diameter, m	0.109×10^{-2}	0.055×10^{-2}	0.023×10^{-2}
Bed Porosity[1]	0.502	0.446	0.479
Gas Flow Rate,[2] m^3/s		0.5 to 5.8×10^{-6}	
Column Temp., K		303 to 355	

---

[1] Measured from the total volume (determined by filling empty column with mercury) and the mass and density of the dried particles.

[2] Measured at 298 K and 1 atm.

$$\mu_2' = \frac{\int_0^\infty (t-\mu_1)^2 C_L(t)dt}{\int_0^\infty C_L(t)dt} \tag{9}$$

EXPERIMENTAL

The apparatus consisted of a chromatograph in which the column used for analysis was replaced by a 0.82×10^{-2}m (3/8") I.D. copper tube packed to a length of 0.26 m with carbon particles. The apparatus and accessories have been described in detail (Schneider and Smith, 1968). Before use, the carbon particles were boiled for several half-hour periods in demineralized water to remove fines and then dried at 383K. Reproducible, reversible adsorption was achieved after pretreating the packed column before each run with a mixture of 3% CO_2 in He to saturate irreversible sites. To check the first-order requirement, first moments (retention times) were measured for 0.5, 1, and $3 \times 10^{-6}m^3$ injection volumes of 3% CO_2-He mixtures. The three retention times agreed within 1%, which was about the degree of reproducibility of the first moments. Final data were taken using injection volumes of $3 \times 10^{-6}m^3$ and with a constant detector temperature of 373K. The measured moments (from Eqs. 8 and 9) included the retention and dispersion in the dead volumes between pulse injection and column feed and between column exit and detector. The dead volume was found to be $9.8 \times 10^{-6}m^3$ by replacing the column with a short length of 0.16×10^{-2}m (1/16") I.D. tubing and introducing pulses of 3% CO_2 at various flow rates. Second moments for these blank runs were negligible in comparison with the reproducibility (3 to 6%) of the μ_2' values.

Characteristics of the carbon beds and operating conditions are given in Table 2.

RESULTS

Adsorption Equilibrium

By taking $K_A = 0$ in Eq. 1, the following expression for the first moment for a nonadsorbable component is obtained:

$$(\mu_1)_i - \frac{t_o}{2} = \frac{L}{v}\left(1 + \frac{1-\epsilon}{\epsilon}\beta_a\right) \tag{10}$$

This moment can be evaluated from the known characteristics of the bed and the interstitial gas velocity v. In terms of $(\mu_1)_i$, Eq. 1 becomes:

$$\Delta\mu_1 = \mu_1 - (\mu_1)_i = \left(\frac{1-\epsilon}{\epsilon}\right)(K_A\rho_p)\frac{L}{v} \tag{11}$$

The first moment data are shown in Figure 1 where, for convenience, $\Delta\mu_1$ has been divided by the total porosity, β. According to Eq. 11 the results should not be a function of particle size but only of the adsorption equilibrium constant K_A. The points in Figure 1 verify this requirement. The lines shown in the figure were located by least squares analysis. Their slopes are

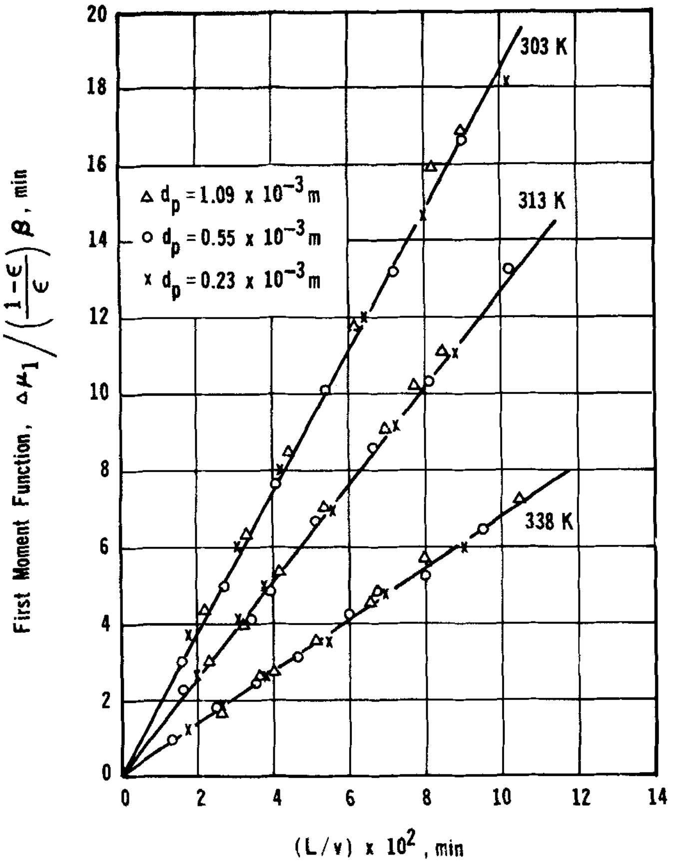

Figure 1. First moment results.

equal to $K_A\rho_p/\beta$. The resulting K_A values, Table 3, are very large indicating that the adsorption capacity of this activated carbon for CO_2 is large. Figure 2 is a plot of the data according to the Van't Hoff equation. From the slope of the straight line the heat of adsorption $\Delta H_A = -6.0$ kcal/mol. This quantity is the isosteric heat of adsorption corresponding to zero coverage, since the adsorbed concentration is extremely low except at the entrance of the bed. For comparison, Gilliland (1975) found ΔH_A for the adsorption of CO_2 on porous glass to be between -4.1 and -6.3 kcal/mol. Kawazoe, et al. (1974) obtained -6.3 kcal/mol for the heat of adsorption of methane on activated carbon powder.

Second Moment Results

Before the intraparticle diffusivities can be evaluated, the axial dispersion and gas-to-particle mass transport contributions to μ_2' must be determined. Axial dispersion was accounted for by a modification of the method used by Hashimoto and Smith (1974). In essence, this is a method of extrapolating the second moment to infinite velocity. Axial dispersion depends on bed geometry, molecular diffusivity of adsorbate, and gas velocity, and can be correlated by:

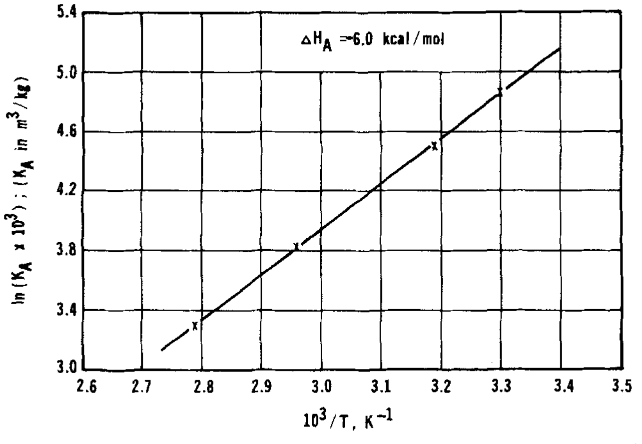

Figure 2. Adsorption equilibrium constant for CO_2 on PAC (type BPL) activated carbon.

TABLE 3. ADSORPTION EQUILIBRIUM CONSTANTS FOR CO_2 ON ACTIVATED CARBON

Temp., K	303	313	338	358
Equil. constant, K_A, m³/kg	0.13	0.090	0.048	0.028

$$\frac{E_d}{D_M} = \eta + l\frac{u}{D_M} \tag{12}$$

The procedure is to insert E_d in Eq. 2 and then evaluate η and l to establish the best fit of the data for μ_2' vs. velocity. Rather than use the least square procedure of Hashimoto and Smith, we employed an optimization subroutine, based on the gradient method, to minimize the sum of the *relative* errors between the data and the predicted values. In this way, separate values of η and l were obtained for each of the three columns and for each temperature. Figure 3 for column 1 ($d_p = 1.09 \times 10^{-3}$m particles) illustrates the fit of the data points and the extrapolated curves for three temperatures. The values of E_d expressed in terms of the Peclet number, ud_p/E_d are 0.40 for column 1, 0.42 for column 2, and 0.14 for column 3. The recent correlation of Langer et al. (1978) gives $Pe = 0.73$, 0.37, and 0.15, respectively, for the three columns.

Gas-to-Particle (External) Mass Transfer

The intercepts at infinite velocity of the second moment data plotted in Figure 3 give values of δ_1. (See Eq. 2.) According to Eq. 4 to 7, when such intercepts are plotted vs. the square of the particle size (R), a straight line should be obtained, provided

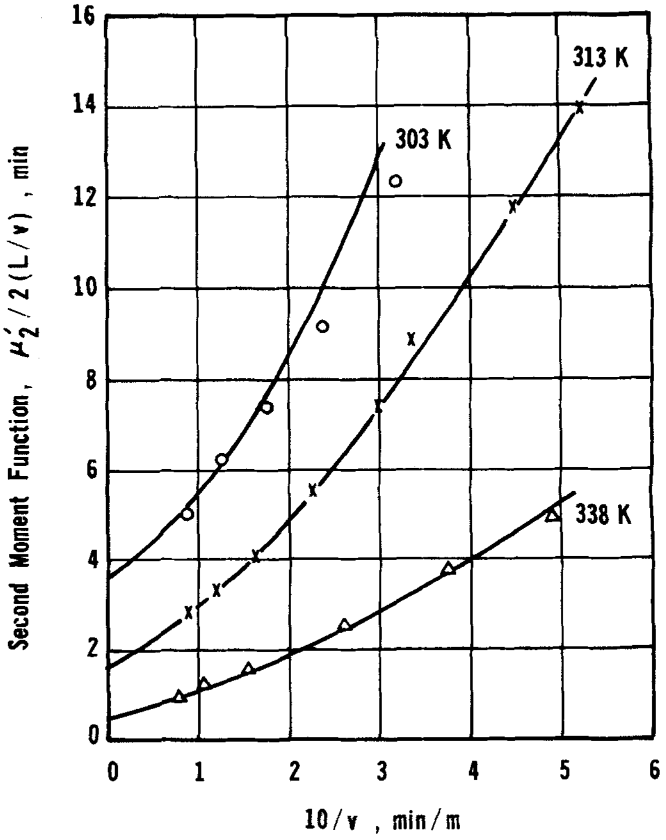

Figure 3. Second central moment for $d_p = 1.09 \times 10^{-3}$m particles (Column 1).

TABLE 4. MACROPORE DIFFUSIVITIES FOR CO_2 IN BPL ACTIVATED CARBON

Temp. K	$(1/D_a + 5/k_fR) \times 10^{-4}$ s/m²	$(5/k_fR) \times 10^{-4}$ s/m²	$D_a \times 10^6$ m²/s	$D_m \times 10^4$ m²/s	$D_{ka} \times 10^4$ m²/s	$D \times 10^4$ m²/s	τ_a
303	51.0	5.4	2.2	0.60	0.95	0.37	5.0
313	46.0	5.1	2.45	0.63	0.97	0.38	4.7
338	37.0	4.5	3.1	0.72	1.0	0.41	4.1

that the contribution due to (k_fR) is independent of particle size. Figure 4 shows that the points for the smallest particles deviate from a straight line relationship. Estimates of k_f from the correlation of Wakao et al. (1958) give values such that the contribution of δ_f to δ_1 is no more than 12%. Hence, the contribution of k_f to the second moment is too small to account for the deviations in Figure 4. It is more likely that these deviations are due to the low values of the second moments (6 to 36 s), when the particle size is so small. The accuracy of the measured μ_2' is relatively poor under these conditions.

Macropore Diffusivity

The slopes of the lines in Figure 4 are equal to:

$$\frac{\beta_a^2}{15}\left(1 + \frac{K_A\rho_p}{\beta_a}\right)^2\left(\frac{5}{k_fR} + \frac{1}{D_a}\right)$$

After accounting for $5/k_fR$ from the Wakao correlation, the effective macropore diffusivities D_a are those shown in Table 4. A macropore tortuosity factor, τ_a, can be estimated by first calculating a composite diffusivity D, applicable in the macropores. If the Knudsen (D_{ka}) and bulk (D_m) molecular diffusivities are combined, D is given by:

$$\frac{1}{D} = \frac{1}{D_{ka}} + \frac{1}{D_m} \tag{13}$$

where D_{ka} is evaluated at $\bar{a}_a = 3750$Å. Then, τ_a is obtained from:

$$\tau_a = \frac{\beta_a D}{D_a} \tag{14}$$

The results in Table 4 give τ_a values varying from 5.0 to 4.1. The tortuosity factor should be independent of temperature so that this variation is a measure of the reproducbility of the data. Kawazoe et al. (1974) reported τ_a of about 4 for his activated carbon.

Diffusion in Micropores

The intercepts in Figure 4, along with Eqs. 4 and 5, can be used to calculate D_i/r_o^2. The results given in Table 5 show that D_i increases with temperature. Treating the micropore diffusion as an activated process, an Arrhenius plot of the D_i/r_o^2 values gives a good straight line corresponding to an activation energy of 1.4 kcal/g·mol.

The radius of the microporous particles in the carbon particles is unknown. However, r_o will be of the order of microns. If r_o = 10 microns, D_i is about 10^{-11} m²/s. This is the same order of magnitude as reported by Chihara et al. (1978) for micropore diffusivities of hydrocarbons and rare gases in a molecular-sieve type carbon and by Walker et al. (1966) for carbon dioxide diffusing in coal particles. For comparison, if pore-volume diffusion were assumed for the micropores, Knudsen diffusion would predominate and $D_{ki} = 3 \times 10^{-7}$ m²/s for $\bar{a}_i$ = 11Å. This diffusivity is four orders of magnitude more than the effective diffusivity evaluated from the experimental data. We conclude that diffusion of CO_2 in the very small pores of BPL activated carbon is hindered by interaction with the pore wall and can be interpreted as an activated surface diffusion process.

From an overall viewpoint, the results of this study also show that intraparticle mass transport, even in the macropores, has a large effect on the global adsorption rate. The macropore diffusivities are low (~10^{-6} m²/s) so that for rapid adsorption rates small particles must be employed.

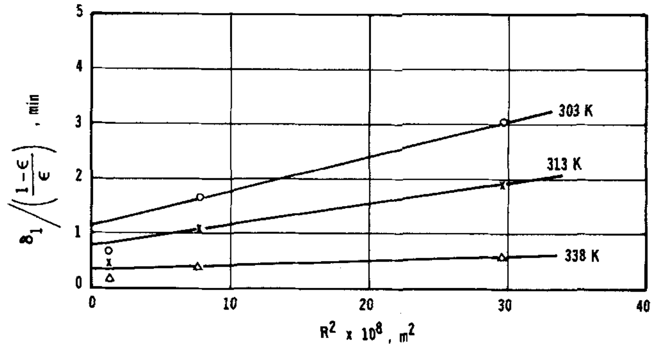

Figure 4. Effect of particle size on second moment.

TABLE 5. MICROPORE DIFFUSIVITIES FOR CO_2 IN BPL ACTIVATED CARBON

Temp., K	303	313	338
$\delta_1/[(1-\epsilon)/\epsilon]$, s	69	43.2	21
D_i/r_o^2, s^{-1}	0.106	0.117	0.131

ACKNOWLEDGEMENT

Activated carbon was provided by the Calgon Corp. The financial assistance of the National Science Foundation, Grant ENG 10166 and a NATO Fellowship is gratefully acknowledged.

NOTATION

a = pore radius, $\bar{a}$ = average value, m
C = concentration of CO_2 in gas; C_L = concentration at bed exit, mol/m³
D = composite molecular diffusivity, defined by Eq. 13, m²/s
D_a = effective macropore diffusivity, m²/s
D_i = effective micropore diffusivity, m²/s
D_m = bulk molecular diffusivity, m²/s
D_k = Knudsen diffusivity, m²/s
d_p = macroparticle diameter, m
E = activation energy, kcal/mol
E_d = axial dispersion coefficient, based on cross-sectional area of column, m²/s
ΔH_A = heat of adsorption, kcal/mol
k = adsorption rate constant, m³/kg·s
k_f = mass transfer coefficient, gas-to-particle surface, m/s
K_A = adsorption equilibrium constant, m³/kg
l = scale of dispersion, m
L = length of packed bed, m
Pe = Peclet number, ud_p/E_d
R = average radius of carbon particles (assumed to be spherical), m
r_o = radius of microparticles, m
t = time, s
t_o = injection time of pulse, s
T = absolute temperature, K

u = superficial gas velocity, m/s
v = interstitial gas velocity in bed, m/s
V = pore volume; V_a and V_i are macro- and micropore values, respectively, m^3/g

Greek Symbols

β = total porosity, sum of macro (β_a)- and micro (β_i)-porosities
δ_o, δ_1, δ_i, δ_a, δ_f = moment contributions defined by Eqs. 3 to 7
ϵ = void fraction in the bed
η = diffusibility, Eq. 12
ρ = gas density, kg/m^3
ρ_p = density of carbon particles, kg/m^3
μ_1 = first absolute moment, s
$(\mu_1)_i$ = first moment for nonadsorbable gas, s
μ_2' = second central moment, s^2
τ_a = macropore tortuosity factor

LITERATURE CITED

Chihara, K., M. Suzuki, and K. Kawazoe, "Adsorption Rate on Molecular Sieving Carbon by Chromatography," *AIChE J.*, 24, 237 (1978).

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).

Grant, R. J., M. Manes, and S. B. Smith, "Adsorption of Normal Paraffins and Sulfur Compounds on Activated Carbon," *AIChE J.*, 8, 403 (1962).

Hashimoto, N., and J. M. Smith, "Diffusion in Bidisperse Porous Catalyst Pellets," *Ind. Eng. Chem. Fundam.*, 13, 115 (1974).

Kawazoe, K., M. Suzuki, and K. Chihara, "Chromatographic Study of Diffusion in Molecular-Sieving Carbon," *J. of Chem. Eng. of Japan*, 7, 151 (1974).

Langer, G., A. Roethe, K. P. Roethe, and D. Gelbin, "Heat and Mass Transfer in Packed Beds. III. Axial Mass Dispersion," *J. Heat Mass Transfer*, 23, 751 (1978).

Schneider, P., and J. M. Smith, "Adsorption Rate Constants From Chromatography," *AIChE J.*, 14, 762 (1968).

Walker, P. L., L. G. Austin, and S. P. Nandi, *Chemistry and Physics of Carbon*, 2, 257-371, ed., Marcel Dekker, New York (1966).

Wakao, N., T. Oshima, and S. Yagi, "Mass Transfer from Packed Beds of Particles to a Fluid," *Chem. Eng. Japan*, 22, 780 (1958).

Manuscript received September 4, 1979; revision received April 11, and accepted May 5, 1980.

Substrate-Inhibited Kinetics With Catalyst Deactivation in an Isothermal CSTR

DUONG D. DO

Dept. of Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

and

RALPH H. WEILAND

Dept. of Chemical Engineering
Clarkson College of Technology
Potsdam, NY 13676

Analytical expressions are developed for the time-dependent reactant concentration and catalyst activity in an isothermal CSTR with Langmuir-Hinshelwood kinetics of deactivation and reaction. Several parallel and series posioning mechanisms are considered for a reactor which, without poisoning, would operate at a unique steady state. The use of matched asymptotic expansions and abandonment of the usual initial-steady-state assumption give results, valid from startup to final loss of activity, whose accuracy can be improved systematically.

I. Unique Pseudosteady State

SCOPE

One of the weaknesses of all catalysts is that they become degraded or deactivated with use. In previous papers (Do and Weiland, 1979a, 1979b), we have presented analyses of the effect of catalyst poisoning by reactants and products of reaction on the performance of a CSTR. Both n-th order and Michaelis-Menten kinetics were examined. This paper presents the same sort of problem, but for a Langmuir-Hinshelwood rate form. Previous work, which specifically tackles catalyst deactivation with substrate inhibition, includes that of Lin (1977) whose analysis was restricted to poisoning at a rate independent from the main reaction; thus, deactivation could be examined quite separately. See also Chu (1968), and Kam and Hughes (1979).

When the reactant or product is responsible for the poisoning, we have shown previously (Do and Weiland, 1980) that the rate forms for the main reaction and for deactivation must bear certain minimum relationships for consistency. Such self-consistent rate expressions are used here to analyze the effect of catalyst poisoning on reactor performance when the Langmuir-Hinshelwood parameters admit of a single steady state in the nonpoisoned case. The method of matched symptotic expansions is used to develop solutions valid over the entire period of reactor operation from initial startup to final loss of activity.

Correspondence concerning this paper should be addressed to R. H. Weiland.

0001-1541-80-4188-0948-$00.95. © The American Institute of Chemical Engineers, 1980.

Part II of this paper appears on page 1020 of this issue.