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Determination of Effective Diffusion Coefficient of Carbon Dioxide in Porous Catalysts by the Isotopic Exchange Reaction

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The effective diffusion coefficient of carbon dioxide in the porous chromia–alumina catalyst was determined from the rate of isotopic exchange reaction over different sizes of the catalyst, and a value of 3.4×10^{-3} cm²/sec was obtained at 450°C.

The value thus obtained coincided with that estimated from the volume average pore radius when a value of 3.4 was taken for the tortuosity factor.

INTRODUCTION

The isotopic exchange reaction between carbon dioxide and monoxide over a chromia–alumina catalyst was studied at 450°C and 1 atm to illustrate the possibility of evaluating effective diffusion coefficients in porous catalysts under reaction conditions.

The advantages of the isotopic exchange reaction are:

1. The heat of reaction is nearly zero, which ensures little temperature gradient within the catalyst particles.
2. The reaction obeys the first order kinetics.
3. The chemical composition remains constant throughout the catalyst particles and the bed during the reaction. Thus, the diffusion process is equimolal and countercurrent.

Wakao, Selwood and Smith (*1*) determined the effective diffusion coefficient of hydrogen in para- to ortho-hydrogen conversion reaction. However, no experimental technique applying such general characteristics of isotopic exchange reaction as illustrated in the "Theory" of this paper has been reported.

EXPERIMENTAL METHODS

Apparatus and Procedure

The apparatus is shown schematically in Fig. 1. It consists of three sections, i.e., the feed preparator, the reactor, and the radiogas chromatograph as the analyzer.

The reactor consists of a vertical 25 mmϕ × 600 mm Pyrex glass tube and is heated by an electric furnace. A weighed amount of catalyst, ranging from 2 to 6 g, was packed onto the porous glass plate mounted in the middle portion of the reactor tube. Upper and lower parts of the catalyst were filled with 4 mm glass beads to serve as preheater and flow stabilizer for the reacting gases. Temperatures of the furnace, the catalyst, and the preheater were measured by the chromel vs alumel thermocouples. The temperature of the catalyst was kept constant within ±1°C by means of transformers and a relay attached to a PID temperature regulator.

Gas flow rates in the feed preparator were controlled by pressure regulators and capillary tube flow regulators, and were measured by capillary flowmeters.

Prior to the isotopic exchange reaction, a mixture of 1:1 of nonradioactive carbon dioxide and monoxide was passed through the reactor at 450°C with a flow rate of 5 ml/sec for 4 hr for preconditioning of the catalyst. Then, the nonradioactive carbon dioxide was switched to the radioactive gas and the run was started.

Product gases were taken into a 10 ml gas sampler and analyzed radio-gas chro-

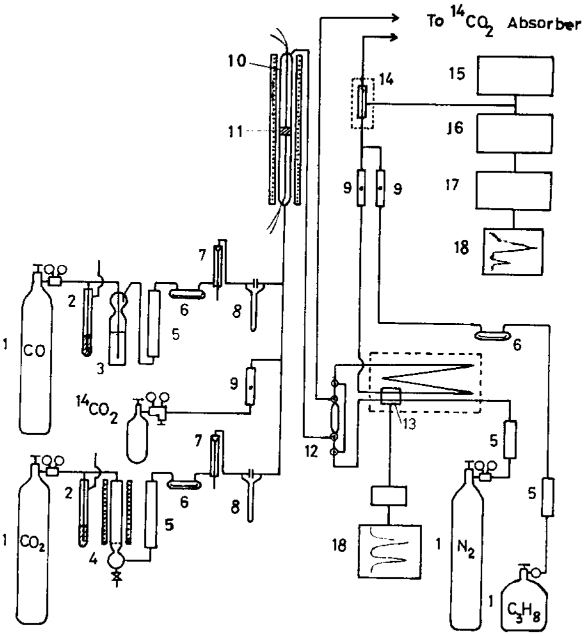

FIG. 1. Radio-gas chromatographic apparatus. (1) Gas cylinders; (2) pressure regulators; (3) sodium hydrosulfite solution; (4) reduced copper; (5) silica gel; (6) phosphorous pentoxide; (7) flow rate regulators; (8) capillary flowmeters; (9) rotameters; (10) reactor; (11) catalyst bed; (12) gas sampler; (13) thermal conductivity cell; (14) proportional flow counter; (15) high voltage supply; (16) linear amplifier; (17) rate meter; (18) recorders.

matographically at room temperature. The column was 0.4 cm i.d. and was packed with 40–60 mesh silica gel over a length of 75 cm. Nitrogen gas was used as the carrier. The separated gases from the column were mixed to a stream of pure propane as the counting gas, which was continuously flowing into the proportional flow counter (*2*) at a rate of 20 ml/sec. Radioactivities of each component were recorded on a radiochromatogram. The counter was operated at the counter voltage of 4.7 kV, the gain of linear amplifier of 4000, and the time constant of rate meter of 0.5 sec.

Catalyst

The catalyst was Harshaw Cr-0105T ⅛ in. chromia–alumina containing 9% chromia promoted with 1.5% K_2O. The sizes of 20 pellets randomly selected from a lot were measured by a micrometer. The mean values were 3.18 mm in diameter and 3.65 mm in height. The effective particle diameter defined by $d_P = 6V_P/S_P$ is 3.32 mm with V_P the particle volume and S_P the external surface area. Granular particles were obtained by crushing and sieving the ⅛ in. pellets. The diameter of the granule is defined by the mean opening of sieves.

The particle density, ρ_P, and the solid density, ρ_C, respectively, were determined by the mercury and water displacement methods. The pore volume and the porosity, respectively, were calculated from $V_g = 1/\rho_P - 1/\rho_C$ and $\epsilon_P = 1 - \rho_P/\rho_C$. The BET surface area, S_g, was determined from the adsorption isotherm of nitrogen at −195°C. The pore size distribution was obtained by mercury porosimetry and nitrogen desorption method. Two methods of evaluating mean pore radius were examined. The one is the equivalent pore radius defined by $r_e = 2V_g/S_g$, and the other is the average pore radius, $\bar{r}$, given by the volume mean.

The pore size distribution and the physical properties of the catalyst pellets, respectively, are shown in Fig. 2 and Table 1.

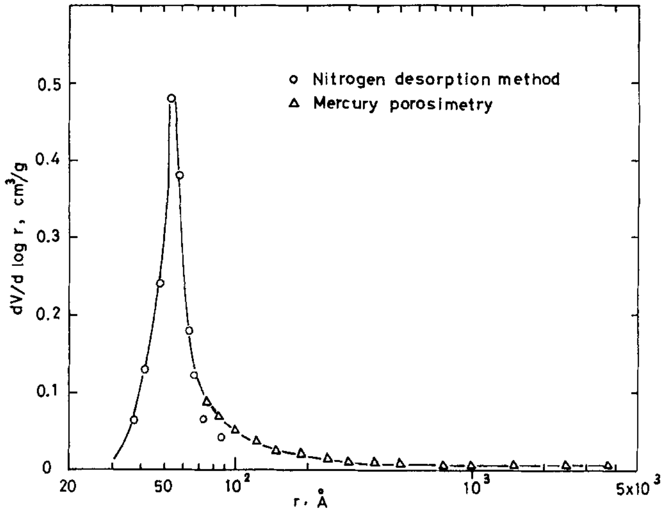

Fig. 2. Pore size distribution of chromia–alumina catalyst.

Reactants

Carbon dioxide of over 99.6% purity was supplied in a commercial gas cylinder. Trace of oxygen was removed by passing over reduced copper heated at 170°C and dried over silica gel and phosphorous pentoxide. Carbon monoxide of over 99.81% purity was supplied in a commercial gas cylinder, too. Trace of oxygen was removed by passing through an alkaline sodium hydrosulfite solution, and dried over silica gel and phosphorous pentoxide.

Radioactive carbon dioxide was generated from the labeled calcium carbonate (New England Nuclear Corp., Boston, MA) by adding ca. 18 *N* sulfuric acid, and was collected in a liquid nitrogen cooled ampule. It was purified twice by sublimation from solid in vacuum, and then was diluted with nonradioactive carbon dioxide so it contained about 1 μCi of ^{14}C in 1 ml. The gas was stored in a 700 ml steel cylinder up to 50 atm.

THEORY

Let us consider a system that a mixture of a molecule, A*, containing a radioactive atom or radical and a nonactive molecule, B, is flowing through an isothermal tubular reactor packed with spherical porous catalysts and the isotopic exchange reaction,

$$A^* + B \rightleftharpoons A + B^*, \qquad (1)$$

is taking place steadily. The concentrations of each chemical species represented by

$$[A] + [A^*] = C_A, \quad [B] + [B^*] = C_B \text{ (mole/cm}^3\text{ gas)}$$

are constant and independent of the location in the packed bed, *l*, and the radial position within the catalyst particles, *r*, in so far as the pressure drop in the bulk fluid is negligible. Therefore, in the absence of an appreciable isotope effect, the adsorption isotherms in the catalyst pellet,

$$q_A = f_A(C_A, C_B), \quad q_B = f_B(C_A, C_B) \quad \text{(mole/cm}^3\text{ cat)}, \qquad (2)$$

TABLE 1
Physical Properties of Catalyst Pellet

ρ_P (g/cm^3)	ρ_C (g/cm^3)	ϵ_P	V_g (cm^3/g)	S_g (m^2/g)	r_ϵ (cm)	$\bar{r}$ (cm)
1.70	3.58	0.529	0.311	67.9	92 × 10^{-8}	59 × 10^{-8}

are independent of the location (l, r), too. Then, the *rate of total exchange reaction*, $R(q_A, q_B)$ in a unit (mole/sec cm^3 cat), which includes, besides the exchange reaction between active and nonactive molecules, those between nonactive and nonactive molecules and between active and active molecules, will remain constant throughout the catalyst pellets (*3*).

Let the local molar fractions of isotopes in the catalyst pore be

$$z_A = [A^*]/C_A, \quad z_B = [B^*]/C_B, \tag{3}$$

then, the local rate of exchange reaction in the unit (mole A*/sec cm^3 cat) is given by

$$\begin{aligned}\mathfrak{R}_{l,r} &= [z_A(1 - z_B) - (1 - z_A)z_B]R \\ &= (z_A - z_B)R,\end{aligned} \tag{4}$$

because the local molar fractions of the adsorbed molecules are identical to those of the molecules in the pore, in so far as the isotope effect is negligible. If we set

$$z_A = z_{A,0}, \quad z_B = 0 \text{ at } l = 0,$$

we get

$$z_{A,0}C_A = z_A C_A + z_B C_B,$$

neglecting the separation of active species which may be produced in catalyst pores by the difference in molecular weights of A and B.

Then, Eq. (4) becomes

$$\frac{\mathfrak{R}_{l,r}}{C_A} = (z_A - z_{A,\infty})\frac{C_A + C_B}{C_A C_B} R \ (\text{sec}^{-1}), \tag{5}$$

where $z_{A,\infty} = z_{A,0}C_A/(C_A + C_B)$.

Using Eq. (5), the steady state material balance for A* in the spherical catalyst pellet gives

$$D_c\left(\frac{\partial^2 y_A}{\partial r^2} + \frac{2}{r}\frac{\partial y_A}{\partial r}\right) = k y_A, \tag{6}$$

where $y_A = z_A - z_{A,\infty}$, $k = (C_A + C_B)R/C_A C_B$ (sec^{-1}), and D_c is the effective diffusion coefficient of A* in catalyst pellet.

Solving Eq. (6) with boundary conditions

$$\begin{aligned} y_A &= y_{A,l} && \text{at } r = d_P/2, \\ dy_A/dr &= 0 && \text{at } r = 0, \end{aligned}$$

we obtain

$$\frac{y_A}{y_{A,l}} = \frac{d_P}{2r}\left(\frac{\sinh 2mr/d_P}{\sinh m}\right), \tag{7}$$

$$m = (d_P/2)(k/D_c)^{1/2}. \tag{8}$$

Here, $y_{A,l} = z_{A,l} - z_{A,\infty}$ and is equal to the local value of y_A in bulk flow so far as the film resistance is negligible.

From Eq. (7) the catalytic effectiveness factor, E_f, is given by

$$\begin{aligned} E_f &= \frac{6}{d_P}\frac{D_c}{k y_{A,l}}\left(\frac{\partial y_A}{\partial r}\right)_{r=d_P/2} \\ &= \frac{3}{m}\left(\frac{1}{\tanh m} - \frac{1}{m}\right). \end{aligned} \tag{9}$$

Equation (9) shows that the effectiveness factor is independent of the location in the packed bed.

With Eq. (9) the steady state material balance for A* in the bulk flow gives, neglecting the effect of axial dispersion,

$$-u(dy_{A,l}/dl) = (1 - \epsilon)E_f k y_{A,l}$$

where u is the superficial gas flow rate in the reactor and ϵ is the voidage. If $y_{A,l} = y_{A,0}$ at the inlet, $l = 0$, and $y_{A,l} = y_{A,L}$ at the outlet, $l = L$, the integration gives

$$-\ln\frac{y_{A,L}}{y_{A,0}} = -\ln(1 - x) = \frac{(1 - \epsilon)E_f kL}{u}, \tag{10}$$

where x is the conversion of the isotopic exchange reaction (1) and is given, by noting that $[A^*]_0 = [A^*]_L + [B^*]_L$, by

$$\begin{aligned} x &= \frac{z_{A,0} - z_{A,L}}{z_{A,0} - z_{A,\infty}} \\ &= \frac{[B^*]_L}{[A^*]_L + [B^*]_L}\Big/\frac{C_B}{C_A + C_B}. \end{aligned} \tag{11}$$

The concentration ratio of isotopes at the outlet of the packed bed, $[B^*]_L/[A^*]_L$, is given by the ratio β/α, i.e., the ratio of the peak areas of B* vs A* on the radiochromatogram, provided that the counting efficiency of the proportional flow counter is same for both components.

From Eqs. (8) and (10)

$$\left.\begin{array}{l} m \propto d_P \\ E_f \propto [u/L(1 - \epsilon)][-\ln(1 - x)] = E_f k \end{array}\right\} \tag{12}$$

and m and E_f are correlated by Eq. (9). Therefore, when the conversions, x, are measured for various sizes of catalyst particles, we can estimate the values of m and k by trial and error. Then, the values of effective diffusion coefficient are obtained from Eq. (8) by

$$D_c = kd_P^2/4m^2. \tag{13}$$

RESULTS

An example of the radiochromatogram is shown in Fig. 3. In this instance, the retention times were 1.9 min for carbon monoxide and 9.5 min for carbon dioxide at the column temperature of 16.5°C and the flow rate of carrier gas of 58 ml/min. Thus the separation was complete. The ratio of the peak areas was determined as $\beta/\alpha = 0.0589$.

The counting efficiency of a proportional counter generally depends on the composition of the gas. But, in the present researches: (a) the quantities of carbon dioxide or carbon monoxide in propane, the counting gas, were less than 2.5% in volume and (b) the addition of 2.5 vol% of carbon dioxide or carbon monoxide to the counting gas had no detectable effect on the counting efficiency for β-ray from uranium oxide-IV,VI. Consequently, it was presumed that the counting efficiencies for both gases were the same. Thus the conversion was determined as

$$x = [(\beta/\alpha)/(1 + \beta/\alpha)]/[C_A/(C_A + C_B)] = 0.117.$$

Results of all the experiments are summarized in Table 2, and the estimated values of Thiele moduli, effectiveness factors, and effective diffusion coefficients are shown in Table 3.

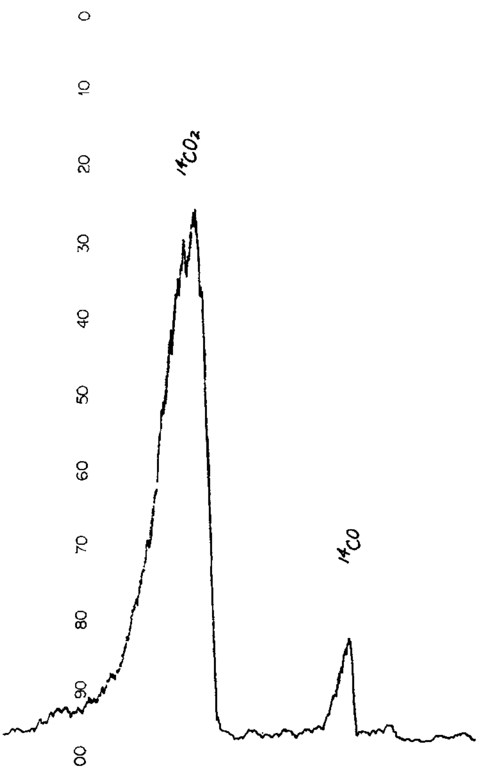

FIG. 3. Radiochromatogram of reaction products. Run No. III-1.

DISCUSSION

Effect of External Diffusion Resistance

When the resistance to film diffusion is taken into consideration, the following relation holds at the steady state of the exchange reaction.

$$E_f k y_{A,l} = k_{c,A} a_P \phi (y_{A,l} - y_{A,s}), \tag{14}$$

with $k_{c,A}$ (cm/sec) the film mass transfer coefficient for A, a_P (cm^{-1}) the external surface area per unit volume of catalyst, ϕ the shape factor, $y_{A,l}$ the local value of y_A in bulk gas, and $y_{A,s}$ the value of y_A on the outer surface of particle.

The film mass transfer coefficient for particles in a fixed bed is correlated with the modified Reynolds number by the correlation (*4*)

$$(k_{c,A} M_m p_{f,A}/R_g TG)(\mathrm{Sc})^{2/3} = 0.84(\mathrm{Re})^{-0.51},$$
$$\text{for } 0.01 < \mathrm{Re} \equiv G/a_P(1 - \epsilon)\phi\mu_f < 50, \tag{15}$$

with M_m (g/mole) the mean molecular weight of fluid, $p_{f,A}$ (atm) the pressure factor for component A, G (g/sec cm^2) the superficial mass velocity, $\mathrm{Sc} = \mu_f/\rho_f D_A$ the Schmidt number, μ_f (g/sec cm) the viscosity of fluid, ρ_f (g/cm^3) the density of fluid, D_A (cm^2/sec) the mean diffusion coefficient of component A in gas mixture, and ϵ the voidage of bed.

TABLE 2
RATE DATA OF ISOTOPIC EXCHANGE REACTION BETWEEN CARBON DIOXIDE AND MONOXIDE OVER DIFFERENT SIZES OF CHROMIA–ALUMINA CATALYST AT 450°C

Run No.	u(450°C, 1 atm) (cm/sec)	$C_A \times 10^5$ (mole/cm^3)	$C_B \times 10^5$ (mole/cm^3)	α (mm^2)	β (mm^2)	x	$-\ln(1-x)$	$\frac{-u\ln(1-x)}{L(1-\epsilon)}$ (sec^{-1})
$d_P = 0.332$ cm, $L = 1.2$ cm, $\epsilon = 0.41$								
I-1	2.03	2.31	2.15	1440	144	0.189	0.210	0.601
2	2.01	2.24	2.23	1330	135	0.185	0.205	0.582
3	4.91	2.28	2.18	1853	77	0.082	0.0856	0.593
4	4.93	2.30	2.17	1555	63	0.080	0.0834	0.590
								0.590
$d_P = 0.103$ cm, $L = 1.0$ cm, $\epsilon = 0.48$								
II-1	2.06	2.35	2.11	2315	170	0.145	0.157	0.622
2	2.01	2.33	2.13	1719	136	0.153	0.166	0.643
3	4.96	2.32	2.14	2325	72	0.063	0.0651	0.622
4	4.93	2.29	2.18	2342	74	0.063	0.0651	0.617
								0.626
$d_P = 0.0251$ cm, $L = 0.65$ cm, $\epsilon = 0.47$								
III-1	2.02	2.34	2.12	2090	123	0.117	0.125	0.728
2	2.03	2.28	2.18	1470	80	0.105	0.111	0.654
3	4.99	2.34	2.12	2151	51	0.048	0.0492	0.712
4	4.91	2.27	2.20	2236	51	0.045	0.0461	0.656
								0.688
$d_P = 0.0127$ cm, $L = 0.39$ cm, $\epsilon = 0.41$								
IV-1	2.02	2.27	2.19	2007	79	0.077	0.0801	0.704
2	3.95	2.30	2.16	1606	34	0.043	0.0440	0.754
								0.729

From Eqs. (14) and (15), the concentration drop across the film is given by

$$\frac{y_{A,l} - y_{A,s}}{y_{A,l}} = \frac{E_f k M_m p_{f,A}}{0.84 R_g T a_P \phi G} (\mathrm{Sc})^{2/3} (\mathrm{Re})^{0.51}. \tag{16}$$

For Run I-1, which may give the largest concentration drop,

$$M_m = 36.1 \text{ g/mole},$$

$$\mu_f = 2.62 \times 10^{-4} \text{ g/sec cm},$$

TABLE 3
EXPERIMENTAL EFFECTIVE DIFFUSION COEFFICIENT AT 450°C

d_P (cm)	d_P (ratio)	$E_f k$ (sec^{-1})	m	E_f	k (sec^{-1})	$D_e \times 10^3$ (cm^2/sec)
0.332	1.000	0.590	2.40	0.7499	0.787	3.7
0.103	0.3092	0.626	0.7421	0.9651	0.649	3.1
0.0251	0.0756	0.688	0.1814	0.9978	0.690	3.3
0.0127	0.0382	0.729	0.0917	0.9994	0.729	3.5
Mean					0.714	3.4

$$\rho_f = 0.61 \times 10^{-3}\ \text{g/cm}^3,\quad D_{\text{A}} = 0.86\ \text{cm}^2/\text{sec},$$

$$G = \rho_f u = 1.24 \times 10^{-3}\ \text{g/sec cm}_2,\quad a_P = 6/d_P = 18.1\ \text{cm}^{-1},$$

$$\phi = 0.91,\ \epsilon = 0.41,\ p_{f,\text{A}} = 1\ \text{atm},\quad \text{Re} = 0.483,\ \text{Sc} = 0.499.$$

These values give

$$(y_{\text{A},l} - y_{\text{A},s})/y_{\text{A},l} = 9.1 \times 10^{-3}.$$

The small value proves a negligible external diffusion resistance.

Effect of Dispersion in Bulk Flow

When the steady state material balance equation for A* in the bulk flow contains the dispersion term, the solution becomes

$$\frac{y_{\text{A},L}}{y_{\text{A},0}} = \frac{4\alpha \exp(uL/2D_L)}{(1+\alpha)^2 \exp(\alpha uL/2D_L) - (1-\alpha)^2 \exp(-\alpha uL/2D_L)}, \tag{17}$$

where $\alpha = [1 + 4(1-\epsilon)E_f k D_L/u^2]^{1/2}$ and D_L is the effective axial dispersion coefficient.

Taking the Peclet number for axial dispersion in packed beds $ud_P/D_L = 2$, the effective axial dispersion coefficient for Run I-4, which may give the largest dispersion effect, $D_L = (4.93)(0.332)/2 = 0.82$ cm²/sec. This value, together with $E_f k = 0.590$ sec^{-1}, $L = 1.2$ cm, $u = 4.93$ cm/sec, and $\epsilon = 0.41$, gives from Eq. (17)

$$(y_{\text{A},L}/y_{\text{A},0})_{\text{dispersed flow}} = 0.920,$$

while Eq. (10) gives

$$(y_{\text{A},L}/y_{\text{A},0})_{\text{plug flow}} = 0.919.$$

The small difference between

$$(y_{\text{A},L}/y_{\text{A},0})_{\text{dispersed flow}}$$

and $(y_{\text{A},L}/y_{\text{A},0})_{\text{plug flow}}$ proves that the effect of dispersion is negligible.

Values of the Effective Diffusion Coefficient

Mass transport in pores is diffusive in nature, when the pressure is uniform, and usually involves Knudsen and ordinary molecular diffusion.

For an equimolal counterdiffusion, the diffusion coefficient in the transition region, $D_{t,\text{A}}$, is given by

$$D_{t,\text{A}} = \frac{1}{1/D_{K,\text{A}} + 1/D_{\text{AB}}} \tag{18}$$

The Knudsen diffusion coefficient, $D_{K,\text{A}}$, and the molecular diffusion coefficient in binary gas mixture, D_{AB}, are given, respectively, by

$$D_{K,\text{A}} = 9.7 \times 10^3 \bar{r}(T/M_{\text{A}})^{1/2},$$

$$D_{\text{AB}} = 0.001858\left[T^3\left(\frac{1}{M_{\text{A}}} + \frac{1}{M_{\text{B}}}\right)\right]^{1/2} \Big/ P\sigma_{\text{AB}}\Omega_{D,\text{AB}}$$

with M_{A}, M_{B} (g/mole) the molecular weights of component A and B, P (atm) the total pressure, σ_{AB} (Å) the collision diameter, and $\Omega_{D,\text{AB}}$ the collision integral.

The effective diffusion coefficient is given by

$$D_{c,\text{A}} = \frac{1}{\tau}\epsilon_P D_{t,\text{A}}, \tag{19}$$

where τ is the tortuosity factor.

For the volume average pore radius, $\bar{r} = 59 \times 10^{-8}$ cm, and for the system conditions under investigation, the values of $D_{K,\text{A}}$ and D_{AB} were found to be 2.32×10^{-2} cm²/sec and 0.74 cm²/sec, respectively, and from Eq. (18), $D_{t,\text{A}} = 2.25 \times 10^{-2}$ cm²/sec. Therefore, the estimated diffusion coefficient coincides with the experimentally evaluated value when a value of 3.4 is assumed for the tortuosity factor, which is an acceptable value for the catalyst.

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