Montogue

QUIZ CE203
Catalytic Reactions
Lucas Montogue and Thierry Deschamps

▶▶ PROBLEMS

▶ Problem 1 (Levenspiel, 1999, w/ permission)

Kinetic experiments on the solid catalyzed reaction $A \rightarrow 3R$ are conducted at 8 atm and 700°C in a basket type mixed reactor 960 cm³ in volume and containing 1 g of catalyst of diameter d_p = 3 mm. Feed consisting of pure A is introduced at various rates into the reactor and the partial pressure of A in the exit stream is measured for each rate. The results are summarized below. Find a rate equation to represent the rate of reaction on catalyst of this size.

Feed rate (L/hr)	100	22	4	1	0.6
$p_{A,\text{out}}/p_{A,\text{in}}$	0.8	0.5	0.2	0.1	0.05

→ Problem 2.1 (Levenspiel, 1999, w/ permission)

The following kinetic data on the reaction $A \rightarrow R$ are obtained in an experimental packed bed reactor using various amounts of catalyst and a fixed feed rate $F_{A,0}$ = 10 kmol/hr. Find the reaction rate at 40% conversion.

W (kg catalyst)	1	2	3	4	5	6	7
X_A	0.12	0.20	0.27	0.33	0.37	0.41	0.44

A) $-r_A$ = 0.11 kmol converted/kg cat·hr
B) $-r_A$ = 0.23 kmol converted/kg cat·hr
C) $-r_A$ = 0.36 kmol converted/kg cat·hr
D) $-r_A$ = 0.45 kmol converted/kg cat·hr

→ Problem 2.2

In designing a large packed bed reactor with a feed rate $F_{A,0}$ = 400 kmol/hr, how much catalyst would be needed for 40% conversion?

A) W = 103 kg catalyst
B) W = 226 kg catalyst
C) W = 310 kg catalyst
**D)** W = 444 kg catalyst

→ Problem 2.3

How much catalyst would be needed in the previous part if the reactor employed a very large recycle of product stream?

A) W = 103 kg catalyst
B) W = 226 kg catalyst
C) W = 310 kg catalyst
D) W = 444 kg catalyst

→ Problem 3.1 (Levenspiel, 1999, w/ permission)

Determine how much catalyst is needed in a packed bed reactor for 80% conversion at 1000 m³/hr of pure gaseous A ($C_{A,0}$ = 100 mol/m³) if the stoichiometry and rate are given by

$$A \rightarrow R \; ; \; -r_A' = \frac{50C_A}{1+0.02C_A} \frac{\text{mol}}{\text{kg} \cdot \text{hr}}$$

1
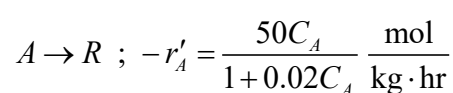
A) W = 64.2 kg catalyst
B) W = 93.1 kg catalyst
C) W = 122 kg catalyst
D) W = 151 kg catalyst

→ Problem 3.2

How much catalyst is needed in a packed bed reactor for 80% conversion of 1000 m³/hr of pure gaseous A ($C_{A,0}$ = 100 mol/m³) if the stoichiometry and rate are given by

$$A \rightarrow R \ ; \ -r'_A = 8C_A^2 \ \frac{\text{mol}}{\text{kg} \cdot \text{hr}}$$
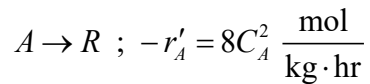
A) W = 5.0 kg catalyst
B) W = 8.61 kg catalyst
C) W = 12.4 kg catalyst
D) W = 16.6 kg catalyst

▶ Problem 4 (Hill & Root, 2014, w/ permission)

The cumene (isopropyl benzene, MW = 120) cracking reaction is often used as a model reaction for determining the relative activities of cracking catalysts.
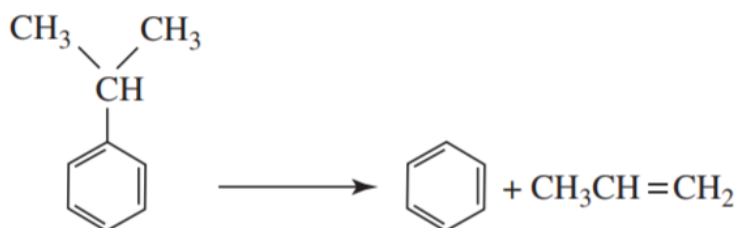
This reaction takes place on silica-alumina catalysts in the temperature range 300 to 600°C. There is negligible production of by-products in the reaction. Suppose we wish to calculate the effective diffusivity of cumene in a mixture of benzene and cumene at 1 atm total pressure and 500°C within the pores of a typical TCC (Thermofor catalytic cracking) catalyst bead. The following properties are associated with the TCC beads.

Surface Area (S_g)	336 m²/g
Porosity (n_p)	0.45
Equivalent Particle Diameter (d_p)	0.39 cm
Density of an individual particle (ρ_p)	1.18 g/cm³

A narrow pore size distribution and a tortuosity factor of 3 may be assumed. The ordinary molecular diffusivity may be taken as $D_{AB} \approx 0.11$ cm²/s. What is the effective diffusivity for this situation?

A) D_{eff} = 2.31×10⁻⁴ cm²/s
B) D_{eff} = 7.98×10⁻⁴ cm²/s
C) D_{eff} = 3.11×10⁻³ cm²/s
D) D_{eff} = 7.71×10⁻³ cm²/s

▶ Problem 5

For a first-order reaction in a porous spherical catalyst pellet, diffusional effects are most likely to lower the observed rate of reaction for

A) a slow reaction and small catalyst pellets.
B) a slow reaction and large catalyst pellets.
C) a fast reaction and small catalyst pellets.
D) a fast reaction and large catalyst pellets.

▶ Problem 6 (Nptel)

Two experiments involving a first-order reaction $A \rightarrow B$ were carried out and the following data were obtained. With the exception of measured rate and catalyst particle radius, all conditions were equal in both experiments. Assuming negligible external mass transfer resistance, estimate the effectiveness factor for each pellet.

	Measured rate (mol/g·cat·s) × 10⁵	Pellet radius (m)
Run 1	4.0	0.02
Run 2	16.0	0.002

2

A) $\eta_1 = 0.229$ and $\eta_2 = 0.636$
B) $\eta_1 = 0.229$ and $\eta_2 = 0.916$
C) $\eta_1 = 0.444$ and $\eta_2 = 0.636$
D) $\eta_1 = 0.444$ and $\eta_2 = 0.916$

▶ Problem 7 (Schmal, 2014, w/ permission)

The reaction

$$\left(CH_3\right)C{=}CH_2 + H_2O \rightarrow \left(CH_3\right)_3 COH$$
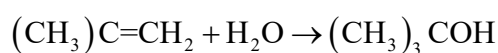
with excess of water is done in a fixed-bed reactor, using a spherical catalyst with radius 0.24 cm and density of 1.82 g/cm³. The reaction is carried out at 100°C and 1 atm, it is reversible and the final conversion is 80% of equilibrium conversion. The equilibrium constant at 100°C corresponds to 16.6. The reaction takes place isothermally, the reaction rate is $1.12{\times}10^{-5}$ mol/s·g cat, and the external concentration of the limiting reactant is equal to $1.54{\times}10^{-5}$ mol/cm³. The mean effective diffusivity is $2.1{\times}10^{-2}$ cm²/s. Determine the effectiveness factor.

A) $\eta = 0.117$
B) $\eta = 0.351$
C) $\eta = 0.675$
D) $\eta = 0.844$

▶ Problem 8 (Schmal, 2014, w/ permission)

A commercial cumene (MW = 120) cracking catalyst is in the form of pellets with a diameter of 0.35 cm which have a surface area A_m of 420 m²/g and a void volume V_m of 0.42 cm³/g. The pellet density is 1.14 g/cm³. The measured 1st-order rate constant for this reaction at 685 K was 1.49 cm³s⁻¹g⁻¹. Assume that Knudsen diffusion dominates and the path length is determined by the pore diameter d_p. An average pore radius can be estimated from the relationship $\bar{r}_p = 2V_m/A_m$. If the pores are modeled as noninterconnected cylinders, determine the effectiveness factor η under these conditions.

A) $\eta = 0.181$
B) $\eta = 0.497$
C) $\eta = 0.736$
D) $\eta = 0.911$

→ Problem 9.1 (Nptel)

A first-order heterogeneous irreversible reaction is taking place within a spherical catalyst pellet plated with platinum. The reactant concentration halfway between the external surface and the center of the pellet (i.e., at $r = R/2$) is equal to one-tenth the concentration of the pellet's external surface. The concentration at the external surface is 0.001 g·mol/dm³, the diameter ($2R_p$) is $2{\times}10^{-3}$ cm, and the diffusion coefficient is 0.1 cm²/s. Find the concentration of reactant at a distance of $3.5{\times}10^{-4}$ cm from the external pellet surface.

A) $C_A = 1.88{\times}10^{-5}$ mol/dm³
B) $C_A = 6.14{\times}10^{-5}$ mol/dm³
C) $C_A = 1.88{\times}10^{-4}$ mol/dm³
D) $C_A = 6.14{\times}10^{-4}$ mol/dm³

→ Problem 9.2

To what diameter should the pellet be reduced if the effectiveness factor is to be 0.75?

A) $d_p = 8.0{\times}10^{-5}$ cm
B) $d_p = 3.2{\times}10^{-4}$ cm
**C)** $d_p = 8.0{\times}10^{-4}$ cm
D) $d_p = 1.4{\times}10^{-3}$ cm

▶ Problem 10 (Vannice, 2005, w/ permission)

A 1.0% Pd/SiO₂ catalyst for SO₂ oxidation is being studied using a stoichiometric O₂/SO₂ feed ratio at a total pressure of 2 atm. At a temperature of 673 K, a rate of 2.0 mole SO₂ s⁻¹ L cat⁻¹ occurs. The average velocity for SO₂ molecules is $3{\times}10^4$ cm/s, and the average pore diameter in the alumina is 120 Å. Assume the Pd is uniformly distributed throughout the catalyst particles. What is the largest particle diameter one can use in the reactor and still be assured that there are no significant diffusional effects?

3

A) $d_p = 4.19 \times 10^{-3}$ cm
B) $d_p = 7.45 \times 10^{-3}$ cm
C) $d_p = 1.32 \times 10^{-2}$ cm
D) $d_p = 6.71 \times 10^{-2}$ cm

▶ Problem 11 (Nptel)

The reaction

$$C + CO_2 \rightarrow 2CO$$
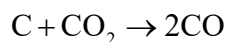
was conducted in a catalytic reactor containing particles of radius $R_p = 0.7$ cm. The bulk concentration was $C_{A,S} = 1.22 \times 10^{-5}$ mol/cm³ and the observed reaction rate was $-r_{obs}\rho_c = 4.67 \times 10^{-9}$ mol/cm³·sec. After the reaction was conducted, the particles were cut open and the reacted carbon profiles were measured. These profiles suggested strong diffusional effects to be present. Verify this observation.

The rate law in concentration units is

$$-r_A = \frac{kC_A}{1 + K_2 C_D + K_3 C_A}$$

where k is the rate constant, $K_2 = 4.15 \times 10^9$ cm³/mol, $K_3 = 3.38 \times 10^5$ cm³/mol, C_A is the concentration of CO_2 (species A), and C_D is the concentration of CO at the surface. The mass diffusivity of species A on the catalyst is 0.1 cm²/sec.

▶ Problem 12 (Vannice, 2005, w/ permission)

Vapor phase benzene (Bz) hydrogenation over carbon-supported Pd catalysts has been studied. A 2.1% Pd/C catalyst prepared with a carbon black cleaned in H_2 at 1223 K had a surface-weighted Pd crystallite size of 21 nm, giving a Pd dispersion of 5% based on transmission electron microscopy (TEM). The carbon itself had an average mesopore diameter of 25 mm, while the average micropore diameter was 0.9 nm; thus the majority of the Pd resided in the mesopores. The highest activity of this catalyst at 413 K and 50 Torr Bz (total P = 1 atm; balance H_2) was 1.99 µmole Bz s^{-1}g^{-1}. The density of the catalyst was 0.60 g/cm³. The catalyst particle radius ranged from 10 to 500 microns. Assuming all the Pd is in the mesopores, are any mass transfer limitations expected based on the Weisz-Prater criterion? If, instead, this catalyst had all the Pd in the micropores and it gave this performance, would mass transfer limitations exist?

	All Pd in mesopores	All Pd in micropores
A)	Pore diffusion limitations are negligible.	Pore diffusion limitations are negligible.
B)	Pore diffusion limitations are **not** negligible.	Pore diffusion limitations are negligible.
C)	Pore diffusion limitations are negligible.	Pore diffusion limitations are **not** negligible.
D)	Pore diffusion limitations are **not** negligible.	Pore diffusion limitations are **not** negligible.

▶ Problem 13 (Vannice, 2005, w/ permission)

Utilizing the data given in the previous problem, assume the benzene hydrogenation reaction is zero order in benzene and first order in H_2, and then calculate the Thiele modulus for the largest and smallest catalyst particles assuming all the Pd is in the mesopores. Also, compute the Thiele modulus for the largest (500 µm) particles if all the Pd were dispersed in only the micropores. Should there be any concern about the pore diffusion limitations for any of the three possibilities? If need be, use $\sigma = 2.4 \times 10^{-8}$ cm as the molecular diameter of hydrogen.

Case 1	Smallest particle, all Pd in mesopores
Case 2	Largest particle, all Pd in mesopores
Case 3	Largest particle, all Pd in micropores

A) Pore diffusion limitations are not a concern in any of the three cases.
B) Pore diffusion limitations are of concern in one of the three cases.
C) Pore diffusion limitations are of concern in two of the three cases.
D) Pore diffusion limitations are of concern in all three cases.

4

▶ SOLUTIONS

P.1 ➡ *Solution*

The initial concentration of A is determined first,

$$C_{A,0} = \frac{p_A}{RT} = \frac{8}{0.0821 \times (700 + 273)} = 0.1 \text{ mol/L}$$

The volume expansion factor is $\varepsilon_A = (3 - 1)/1 = 2$. Accordingly, the ratio $C_A/C_{A,0}$ can be written as

$$\frac{C_A}{C_{A,0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A} = \frac{1 - X_A}{1 + 2X_A}$$

Solving for conversion, we obtain

$$\frac{C_A}{C_{A,0}} = \frac{1 - X_A}{1 + 2X_A} \rightarrow X_A = \frac{1 - C_A/C_{A,0}}{1 + 2C_A/C_{A,0}} \quad \text{(I)}$$

The performance equation to use is

$$\frac{W}{F_{A,0}} = \frac{X_A}{-r'_A}$$

which, solving for r'_A, becomes

$$-r'_A = \frac{X_A F_{A,0}}{W} \quad \text{(II)}$$

This latter expression can be used in conjunction with other results to determine the rate. Thus, the following table is prepared.

C_A	$\frac{C_A}{C_{A,0}} = \frac{P_A}{P_{A,0}}$	X_A (Eq. I)	$F_{A,0} = vC_{A,0}$	$-r'_A$ (Eq. II)
0.08	0.08/0.1 = 0.8	0.2/2.6 = 0.0769	100×0.1 = 10	0.0769×10/1.0 = 0.769
0.05	0.5	0.25	2.2	0.55
0.02	0.2	0.571	0.4	0.228
0.01	0.1	0.75	0.1	0.075
0.005	0.05	0.864	0.05	0.0482

We attempt to fit the data to a first-order reaction, which is the simplest of rate forms. To do so, we plot $-r'_A$, the red column, versus C_A, the blue column, as follows.
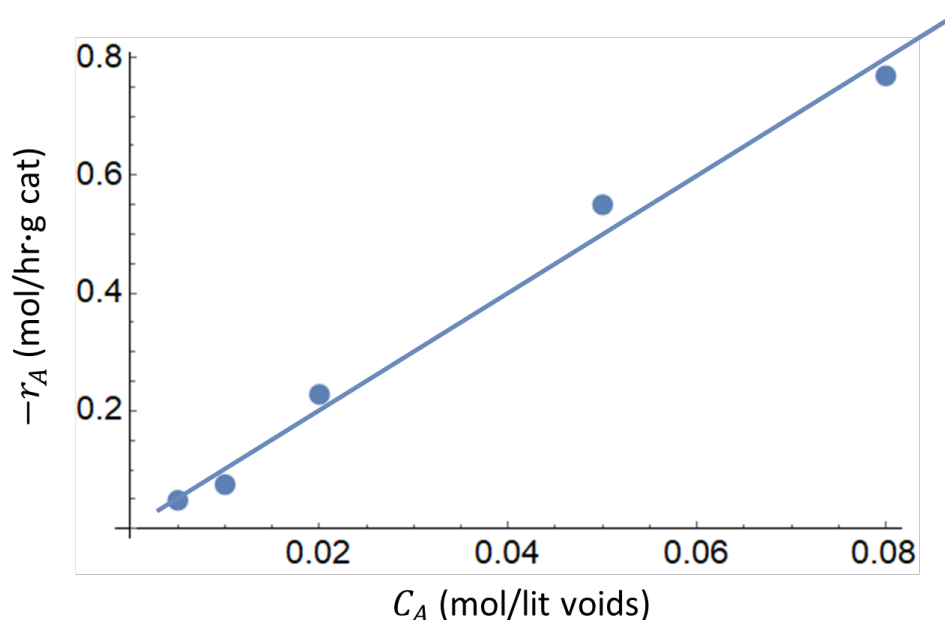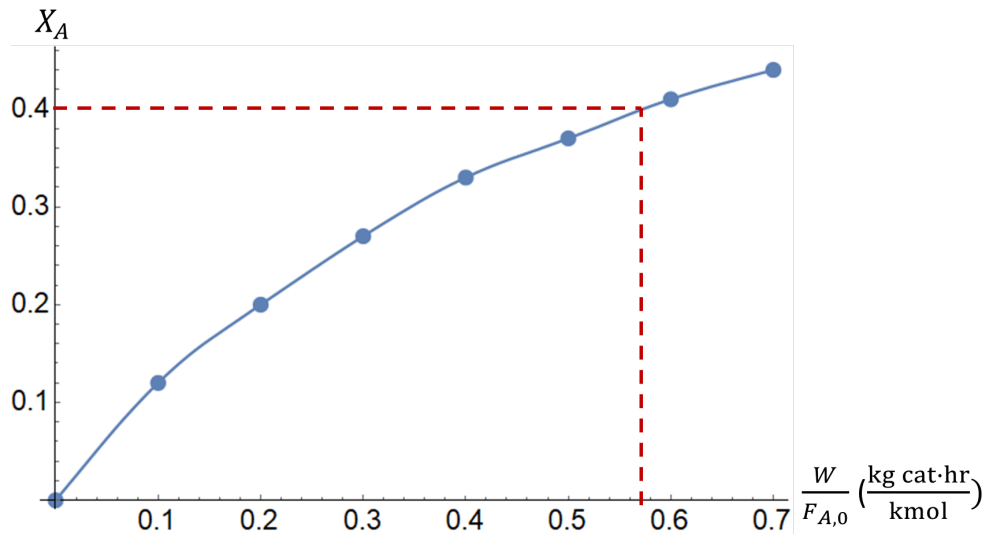

Clearly, we there is a good straight-line fit for the data. The slope of the line is 9.91 ≈ 10. Thus, the rate equation is found to be

$$\boxed{-r'_A = 10C_A \text{ mol/hr} \cdot \text{g cat}}$$

5

P.2 ➡ Solution

Part 1: The data are plotted below.

Since

$$\frac{W}{F_{A,0}} = \int \frac{dX_A}{-r_A}$$

we have, in differential form,

$$\frac{dW}{F_{A,0}} = \frac{dX_A}{-r_A} \rightarrow -r_A = \frac{dX_A}{d\left(W/F_{A,0}\right)}$$

which is the slope of the curve. It follows that, at 40% conversion,

$$-r_A = \frac{0.482 - 0.23}{0.8 - 0.1} = \boxed{0.36 \; \frac{\text{kmol converted}}{\text{kg cat} \cdot \text{hr}}}$$

♦ The correct answer is **C**.

Part 2: Mapping a conversion $X_A = 0.4$ onto the graph, we read $W/F_{A,0} = 0.566$. Thus, the mass of catalyst required is

$$\frac{W}{F_{A,0}} = 0.566 \rightarrow W = 0.566 F_{A,0}$$

$$\therefore W = 0.566 \times 400 = \boxed{226 \; \text{kg cat}}$$

♦ The correct answer is **B**.

Part 3: For completely mixed flow, we can write

$$\frac{W}{F_{A,0}} = \frac{X_A}{-r_{A,40\%}} = \frac{0.4}{0.36}$$

$$\therefore W = \frac{0.4}{0.36} \times 400 = \boxed{444 \; \text{kg}}$$

♦ The correct answer is **D**.

P.3 ➡ Solution

Part 1: For plug flow, we have

$$\frac{W}{v} = C_{A,0} \int_0^{X_{A,F}} \frac{dX_A}{-r_A} = \int_{C_A}^{C_{A,0}} \frac{dC_A}{-r_A} = \frac{1}{k} \int_{20}^{100} \frac{1 + 0.02 C_A}{50 C_A} dC_A$$

Carrying out the integration, we obtain

$$W = \frac{v}{k'}\left[\ln\left(\frac{C_{A,0}}{C_A}\right) + k_2\left(C_{A,0} - C_A\right)\right]$$

where, in the case at hand, $k' = 50$ m³/kg·s and $k_2 = 0.02$ m³/mol. Accordingly,

6

$$W = \frac{1000 \text{ m}^3/\text{hr}}{50 \text{ m}^3/\text{kg} \cdot \text{s}} \left[\ln\left(\frac{100}{20}\right) + 0.02 \frac{\text{m}^3}{\text{mol}} (100 - 20) \right] = \boxed{64.2 \text{ kg cat}}$$

♦ The correct answer is **A**.

Part 2: Since $C_A = C_{A,0}(1 - X_A)$, we can write

$$-r'_A = 8C_A^2 = 8C_{A,0}^2 \left(1 - X_A\right)^2$$

Appealing to the performance equation for plug flow, it follows that

$$\frac{W}{F_{A,0}} = \int_0^{X_{A,f}} \frac{dX_A}{-r_A} = \int_0^{X_{A,f}} \frac{dX_A}{8C_{A,0}^2 \left(1 - X_A\right)^2}$$

The initial molar flow of reactant is $F_{A,0} = vC_{A,0} = 1000 \times 100 = 100{,}000$ mol/hr. Substituting in the equation above, we get

$$W = 100{,}000 \times \int_0^{0.8} \frac{dX_A}{8 \times 100^2 \times \left(1 - X_A\right)^2} = 1.25 \left[\int_0^{0.8} \frac{dX_A}{\left(1 - X_A\right)^2} \right]$$

The integral in brackets can be evaluated to give 4.0. The mass of catalyst required then becomes

$$W = 1.25 \times 4.0 = \boxed{5.0 \text{ kg}}$$

♦ The correct answer is **A**.

P.4 ➡ Solution

The average pore radius $\bar{R}_p$ is given by

$$\bar{R}_p = \frac{2V_g}{S_g}$$

where V_g is the void volume per gram and S_g is the surface area per gram. The former is evaluated as

$$V_g = \frac{n_p}{\rho_p} = \frac{0.45}{1.18} = 0.381 \text{ cm}^3/\text{g}$$

so that

$$\bar{R}_p = \frac{2 \times 0.381}{336 \times 10^4} = 2.27 \times 10^{-7} \text{ cm}$$

or, equivalently, $\bar{R}_p$ = 2.27 nm. The Knudsen diffusivity is given by

$$D_{Kn} = \frac{2}{3} \bar{R}_p \sqrt{\frac{8RT}{\pi M}}$$

When simplified and written in terms of CGS units, this equation becomes

$$D_{Kn} = 9.7 \times 10^3 \bar{R}_p \sqrt{\frac{T}{M}}$$

Noting that the molar mass of cumene is $M \approx 120$ g/mol and substituting the pertinent variables, we obtain

$$D_{Kn} = 9.7 \times 10^3 \times \left(2.27 \times 10^{-7}\right) \times \sqrt{\frac{773}{120}} = 5.59 \times 10^{-3} \text{ cm}^2/\text{s}$$

Equipped with this quantity and the binary diffusivity $D_{AB} = 0.11$ cm²/s, we can determine the combined diffusivity D_c,

$$\frac{1}{D_c} = \frac{1}{D_{Kn}} + \frac{1}{D_{AB}} = \frac{1}{5.59 \times 10^{-3}} + \frac{1}{0.11}$$

$$\therefore D_c = 5.32 \times 10^{-3} \text{ cm}^2/\text{s}$$

Observe that, from the magnitudes of the diffusion coefficients, it is clear that under the conditions cited the majority of the mass transport will occur by

7

Knudsen diffusion. Finally, using the porosity $n_p = 0.45$ and the tortuosity $\tau' = 3$, the effective diffusivity is calculated as

$$D_{\text{eff}} = \frac{D_c n_p}{\tau'} = \frac{\left(5.32 \times 10^{-3}\right) \times 0.45}{3} = \boxed{7.98 \times 10^{-4} \ \text{cm}^2/\text{s}}$$

♦ The correct answer is **B**.

P.5 ➡ *Solution*

Pore diffusion mass transfer limitations are particularly relevant for a fast reaction with large catalyst pellets.

♦ The correct answer is **D**.

P.6 ➡ *Solution*

The Thiele modulus for spherical catalyst particles is of course

$$-\frac{r_{A,\text{obs}} R_p^2 \rho_c}{D_{\text{eff}} C_{A,S}} = \eta \phi_1^2 = 3\left(\phi_1 \coth \phi_1 - 1\right)$$

Let ϕ_{11} and ϕ_{12} denote the Thiele moduli at run 1 and run 2, respectively; in addition, let $-r_{A,1}$ and $-r_{A,2}$ denote the observed reaction rates and R_1 and R_2 the corresponding radii. Substituting the pertinent variables in the equation above and dividing the two ensuing expressions, we get

$$\frac{-r_{A,2} R_2^2}{-r_{A,1} R_1^2} = \frac{\phi_{12} \coth \phi_{12} - 1}{\phi_{11} \coth \phi_{11} - 1} \ \text{(I)}$$

The ratio of Thiele moduli is

$$\frac{\phi_{11}}{\phi_{12}} = \frac{R_1 \sqrt{\dfrac{-r_{A,S} \rho_c}{D_{\text{eff}} C_{A,S}}}}{R_2 \sqrt{\dfrac{-r_{A,S} \rho_c}{D_{\text{eff}} C_{A,S}}}} = \frac{R_1}{R_2} \rightarrow \phi_{12} = \frac{R_2}{R_1} \phi_{11} = \frac{0.002}{0.02} = 0.1 \phi_{11} \ \text{(II)}$$

Substituting in equation (I) gives

$$\frac{16.0 \times 0.002^2}{4.0 \times 0.02^2} = \frac{0.1\phi_{11} \times \coth\left(0.1\phi_{11}\right) - 1}{\phi_{11} \coth\left(\phi_{11}\right) - 1}$$

The equation above can be solved with Mathematica's *FindRoot* command, using an initial guess of, say, 1.0,

$$\text{FindRoot}\left[\frac{16.* 0.002^2}{4.* 0.02^2} - \frac{0.1 * \phi * \text{Coth}[0.1 * \phi] - 1}{\phi * \text{Coth}[\phi] - 1.}, \{\phi, 1\}\right]$$

This returns $\phi_{11} = 12.02$. The corresponding effectiveness factor is then

$$\eta_1 = \frac{3}{\phi_{11}^2}\left[\phi_{11} \coth\left(\phi_{11}\right) - 1\right] = \frac{3}{12.0^2} \times \left[12.0 \times \coth\left(12.0\right) - 1\right] = \boxed{0.229}$$

From equation (II), we have $\phi_{12} = 0.1 \times 12.0 = 1.2$. Lastly, effectiveness factor η_2 is

$$\eta_2 = \frac{3}{\phi_{12}^2}\left[\phi_{11} \coth\left(\phi_{11}\right) - 1\right] = \frac{3}{1.2^2} \times \left[1.2 \times \coth\left(1.2\right) - 1\right] = \boxed{0.916}$$

♦ The correct answer is **B**.

P.7 ➡ *Solution*

We assume a reversible first-order forward and reverse reaction, represented as

$$A \rightleftharpoons R$$
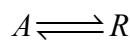
The rate is

$$r'' = kC_A - k'C_R = k\left(C_A - \frac{1}{K}C_R\right)$$

8

At equilibrium, the resulting rate is zero and

$$K = \frac{C_{R,e}}{C_{A,e}} = \frac{X_{A,e}}{1 - X_{A,e}} = 16.6 \rightarrow X_{A,e} = 0.943$$

Since the final conversion is 80% of equilibrium conversion, we write X_A = 0.8×0.943 = 0.754. The observed rate is given by

$$r''_{\text{obs}} = k'' C_{A,0} \frac{K}{K+1}\left(X_{A,e} - X_A\right)\eta = k^* C_{A,0}\left(X_{A,e} - X_A\right)\eta$$

Appealing to the definition of Thiele modulus, we write

$$\phi = \frac{R_p k^{*1/2} \rho_s^{1/2}}{D_{\text{eff}}^{1/2}} = R_p \sqrt{\frac{r''_{\text{obs}} \rho_s}{C_{A,0}\left(X_{A,e} - X_A\right) D_{\text{eff}} \eta}}$$

$$\therefore \phi = 0.24 \times \sqrt{\frac{\left(1.12\times10^{-5}\right)\times1.82}{\left(1.54\times10^{-5}\right)\times\left(0.943 - 0.754\right)\times\left(2.1\times10^{-2}\right)\times\eta}}$$

$$\therefore \phi = 0.24\sqrt{\frac{333}{\eta}}$$

$$\therefore \phi = \frac{4.38}{\sqrt{\eta}} \quad \text{(I)}$$

However, we know that the effectiveness factor and ϕ are related by the equation

$$\eta = \frac{3}{\phi}\left(\frac{1}{\tanh\phi} - \frac{1}{\phi}\right) \quad \text{(II)}$$

Equations (I) and (II) constitute a system of nonlinear equations with two unknowns. We can solve these equations simultaneously with Mathematica's *FindRoot* command,

$$\text{FindRoot}\left[\left\{\phi == 4.38/\sqrt{\eta}, \eta == \frac{3}{\phi}\left(\text{Coth}[\phi] - 1/\phi\right)\right\}, \{\{\phi, 1.\}, \{\eta, 1.\}\}\right]$$

This returns ϕ = 7.39 and η = 0.351.

◆ The correct answer is **B**.

P.8 ➡ *Solution*

The effectiveness factor η is given by

$$\eta = \frac{\mathfrak{R}}{\mathfrak{R}_o} = \frac{k_{\text{meas}}}{k_o} = \frac{3}{\phi}\left(\frac{1}{\tanh\phi} - \frac{1}{\phi}\right)$$

The Thiele modulus is given by

$$\phi = \frac{R_p k_o^{1/2}}{D_{\text{eff}}^{1/2}}$$

so that

$$k_o = \frac{\phi}{3}\frac{k_{\text{meas}}}{\left(\dfrac{1}{\tanh\phi} - \dfrac{1}{\phi}\right)} = \frac{\phi^2 D_{\text{eff}}}{R_p^2}$$

$$\therefore \phi\left(\frac{1}{\tanh\phi} - \frac{1}{\phi}\right) = \frac{k_{\text{meas}}\mathfrak{R}^2}{3D_{\text{eff}}} \quad \text{(I)}$$

The mean pore radius is given by

$$R_p = \bar{r}_p = \frac{2V_m}{S_m} = \frac{2\times0.42\,\text{cm/g}}{420\,\text{m}^2/\text{g}\times\left(100\,\text{cm/m}\right)^2} = 2.0\times10^{-7}\,\text{cm}$$

The average velocity for the cumene catalyst molecules is given by

9

$$\bar{v} = \left(\frac{8k_B T}{\pi m}\right)^{1/2} = \left[\frac{8 \times \left(1.38 \times 10^{-16} \, \text{erg/K}\right) \times 685 \, \text{K}}{\pi \times 120 \, \text{amu} \times \left(1.66 \times 10^{-24} \text{g/amu}\right)}\right]^{1/2} = 3.48 \times 10^4 \, \text{cm/s}$$

The cumene has a typical pore diameter much lower than its mean free path. Accordingly, pore diffusion will be dominated by Knudsen diffusion and the effective diffusivity can be estimated as

$$D_{\text{eff}} \approx D_{\text{Kn}} = \frac{1}{3} d_p \bar{v} = \frac{1}{3} \times \left(4.0 \times 10^{-7}\right) \times \left(3.48 \times 10^4\right) = 4.64 \times 10^{-3} \, \text{cm}^2/\text{s}$$

Substituting the pertinent variables in the right-hand side of equation (I), we obtain

$$\phi\left(\frac{1}{\tanh \phi} - \frac{1}{\phi}\right) = \frac{\left(1.49 \, \text{cm}^3/\text{s} \cdot \text{g}\right) \times \left(1.14 \, \text{g/cm}^3\right) \times \left(0.35 \, \text{cm}/2\right)^2}{3 \times \left(4.6 \times 10^{-3} \, \text{cm}^2/\text{s}\right)} = 3.77$$

To determine the value of ϕ, we apply Mathematica's *FindRoot* function with an initial guess of, say, $\phi = 3.0$. The pertaining code is

$$\text{FindRoot}[\phi(\text{Coth}[\phi] - 1/\phi) - 3.77, \{\phi, 3\}]$$

The command returns $\phi = 4.77$. The final step is to compute the efficiency factor η,

$$\eta = \frac{3}{4.77} \times \left(\coth 4.77 - \frac{1}{4.77}\right) = \boxed{0.497}$$

♦ The correct answer is **B**.

P.9 ➡ *Solution*

Part 1: We have $C_A/C_{A,S} = 0.1$ and $\lambda = 0.5$, so that

$$\psi = \frac{C_A}{C_{A,S}} = \frac{1}{\lambda}\left[\frac{\sinh\left(\phi_1 \lambda\right)}{\sinh \phi}\right] \rightarrow 0.1 = \frac{1}{0.5}\left[\frac{\sinh\left(0.5\phi_1\right)}{\sinh \phi_1}\right]$$

We can solve for the Thiele modulus with Mathematica's *FindRoot* command,

$$\text{FindRoot}[0.1 - 1/0.5 * (\text{Sinh}[0.5 * \phi]/\text{Sinh}[\phi]), \{\phi, 0.5\}]$$

This returns $\phi = 5.9864 \approx 6.0$. The dimensionless length λ for a distance of 3.5×10^{-4} cm from the pellet surface is

$$\lambda = \frac{1 \times 10^{-3} - 3.5 \times 10^{-4}}{1 \times 10^{-3}} = 0.65$$

so that

$$\psi = \frac{C_A}{C_{A,S}} = \frac{1}{\lambda}\left[\frac{\sinh\left(\phi_1 \lambda\right)}{\sinh \phi_1}\right] \rightarrow \frac{C_A}{0.001} = \frac{1}{0.65} \times \left[\frac{\sinh\left(6.0 \times 0.65\right)}{\sinh 6.0}\right]$$

$$\therefore C_A = \boxed{1.88 \times 10^{-4} \, \text{mol/dm}^3}$$

♦ The correct answer is **C**.

Part 2: From the definition of Thiele modulus, we can determine rate constant k_{1r},

$$\phi = R_p \sqrt{\frac{k_{1r}}{D_{\text{AB}}}} \rightarrow 6.0 = 1 \times 10^{-3} \times \sqrt{\frac{k_{1r}}{0.1}}$$

$$\therefore k_{1r} = 3.6 \times 10^6 \, \text{sec}^{-1}$$

For the effectiveness factor to be 0.75, the Thiele modulus must be such that

$$\eta = 0.75 = \frac{3}{\phi_1^2}\left[\phi_1 \coth\left(\phi_1\right) - 1\right]$$

As before, we can apply the *FindRoot* command,

$$\text{FindRoot}[0.75 - 3/\phi^2 * (\phi * \text{Coth}[\phi] - 1), \{\phi, 2\}]$$

10

This returns $\phi = 2.399 \approx 2.4$. From the definition of Thiele modulus, we can establish the catalyst particle radius,
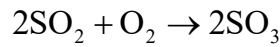
$$\phi = 2.4 = R_p \sqrt{\frac{3.6 \times 10^6}{0.1}} \rightarrow R_p = 4 \times 10^{-4} \text{ cm}$$

$$\therefore \boxed{d_p = 8 \times 10^{-4} \text{ cm}}$$

◆ The correct answer is **C**.

P.10 ➡ Solution

The pertaining reaction is

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Per the Weisz-Prater criterion, diffusional effects are not significant if

$$N_{W-P} = \frac{\Re R_p^2}{C_s D_{\text{eff}}} \leq 0.3$$

Here, C_s is the reactant concentration, which can be estimated from the ideal gas law,

$$C_s = \frac{P}{RT} = \frac{2/3 \times 2 \text{ atm}}{82.06 \dfrac{\text{atm} \cdot \text{cm}^3}{\text{mol} \cdot \text{K}} \times 673 \text{ K}} = 2.42 \times 10^{-5} \text{ mol/cm}^3$$

The mass diffusivity is determined next,

$$D_{\text{eff}} = \frac{1}{3} \overline{v} d_p = \frac{1}{3} \times \left(3.0 \times 10^4 \text{ cm/s}\right) \times \left(120 \times 10^{-8} \text{ cm}\right) = 1.20 \times 10^{-2} \text{ cm}^2/\text{s}$$

In addition, we have the global reaction rate $\Re = 2$ mole SO_2/s· L × 1 L/1000 cm³ = 0.002 mole SO_2/s·cm³. Substituting in the definition of N_{W-P} brings to

$$N_{W-P} = \frac{0.002 \times R_P^2}{\left(2.42 \times 10^{-5}\right) \times \left(1.20 \times 10^{-2}\right)} \leq 0.3$$

$$\therefore R_p \leq \sqrt{\frac{0.3 \times \left(2.42 \times 10^{-5}\right) \times \left(1.20 \times 10^{-2}\right)}{0.002}} = 6.6 \times 10^{-3} \text{ cm}$$

Thus, in order for no relevant diffusional effects to take place, the particle diameter should be no greater than 2×6.6×10⁻³ = 1.32×10⁻² cm.

◆ The correct answer is **C**.

P.11 ➡ Solution

In the situation at hand, the Weisz-Prater parameter is

$$N_{W-P} = \frac{-r_{A,\text{obs}} \rho_c R_P^2}{D_{AB} C_{A,S}} = \frac{\left(4.67 \times 10^{-9}\right) \times 0.7^2}{0.1 \times \left(1.22 \times 10^{-5}\right)} = 1.88 \times 10^{-3} < 0.3$$

Accordingly, the Weisz-Prater criterion does not predict internal diffusion limitations, even though experimental observations suggest otherwise. The main reason why this disparity occurs is the fact that the Thiele modulus used in the WP criterion pertains to a first-order reaction, and the rate law we were given clearly indicates that the reaction in question is not first order. We can still predict diffusional limitation effects with the generalized Thiele modulus. Assuming equimolar counter-diffusion, $D_{\text{eff},A} = D_{\text{eff},D}$, and that the concentration of CO at the surface $C_{D,S} \approx 0$, the rate expression can be rewritten as

$$-r_A' = \frac{kC_A}{\left(1 + 2K_2 C_{A,s}\right) + \left(K_3 - 2K_2\right) C_A}$$

Assuming the pellet was infinitely long with $C_{A,eq} = 0$, we have the modified parameter

11

$$\Phi = \eta\phi^2 = \frac{-r_{A,\text{obs}} R_p^2 \rho_c \left(-r_{A,s}\right)}{2\int_0^{C_{A,s}} D_{\text{eff,A}} \left(-r_A'\right) dC_A}$$

$$\therefore \Phi = \frac{r_{A,\text{obs}} R_p^2 \rho_c}{2 D_{\text{eff,A}}} \left\{ \frac{1 + K_3 C_{A,s}}{K_3 - 2K_2} \left[1 - \frac{1 + 2K_2 C_{A,s}}{C_{A,s}\left(K_3 - 2K_2\right)} \ln\left(\frac{1 + K_3 C_{A,s}}{1 + 2K_2 C_{A,s}}\right) \right] \right\}^{-1}$$

$$\therefore \Phi = \frac{\left(4.67\times10^{-9}\right)\times 0.7^2}{2\times 0.1} \left\{ \begin{array}{c} \dfrac{1 + \left(3.38\times10^5\right)\times\left(1.22\times10^{-5}\right)}{\left(3.38\times10^5\right) - 2\times\left(4.15\times10^9\right)} \times \\[2mm] \left[1 - \dfrac{1 + 2\times\left(4.15\times10^9\right)\times\left(1.22\times10^{-5}\right)}{\left(1.22\times10^{-5}\right)\times\left[\left(3.38\times10^5\right) - 2\times\left(4.15\times10^9\right)\right]} \ln\left(\dfrac{1 + \left(3.38\times10^5\right)\times\left(1.22\times10^{-5}\right)}{1 + 2\times\left(4.15\times10^9\right)\times\left(1.22\times10^{-5}\right)}\right)\right] \end{array} \right\}^{-1} = 2.08$$

This result is substantially greater than the threshold of the WP criterion and indicates that diffusion limitations are in fact appreciable.

P.12 ➡ Solution

To begin, we compute the global reaction rate $\Re$,

$$\Re = 1.99 \frac{\mu\text{mole Bz}}{s\cdot g\ \text{cat}} \times 0.60 \frac{g\ \text{cat}}{\text{cm}^3} = 1.19\,\mu\text{mole Bz/s}\cdot\text{cm}^3$$

The reagent concentration follows from the ideal gas law,

$$C_s = \frac{P}{RT} = \frac{50\ \text{Torr Bz}\times 1\,\text{atm}/760\ \text{Torr}}{82.06\ \dfrac{\text{atm}\cdot\text{cm}^3}{g\cdot\text{mol}\cdot K}\times 413\,K} = 1.94\times10^{-6}\ \text{mol/cm}^3$$

Assuming the mean free path in the gas phase is much greater than the average pore diameter of the catalyst, mass transport is dominated by Knudsen diffusion and we can write $D_{\text{eff}} \approx D_{\text{Kn}}$. The average velocity of benzene molecules is given by

$$\bar{v} = \left(\frac{8k_B T}{\pi m}\right)^{1/2} = \left[\frac{8\times\left(1.38\times10^{-16}\,\text{erg/K}\right)\times 413\ K}{\pi\times 78\,\text{amu}\times\left(1.66\times10^{-24}\text{g/amu}\right)}\right]^{1/2} = 3.35\times10^4\ \text{cm/s}$$

so that

$$D_{\text{Kn}}' = \frac{1}{3}\bar{v} d_p = \frac{1}{3}\times\left(3.35\times10^4\right)\times\left(0.9\times10^{-7}\right) = 1.0\times10^{-3}\ \text{cm}^2/\text{s}$$

where we have used the mesopore diameter $d_p = 25$ nm. Now, the worst case occurs if the catalyst particle radius $R_p = 500$ μm, in which case the Weisz-Prater criterion yields

$$N_{W-P} = \frac{\Re R_p^2}{C_s D_{\text{Kn}}} = \frac{\left(1.19\times10^{-6}\ \text{mol Bz/s}\cdot\text{cm}^3\right)\times\left(500\times10^{-4}\ \text{cm}\right)^2}{\left(1.94\times10^{-6}\ \text{mol/cm}^3\right)\times\left(2.79\times10^{-2}\ \text{cm}^2/\text{s}\right)} = 0.0550$$

In the best case, the catalyst particles have a radius of 10 μm and the W-P criterion becomes

$$N_{W-P} = \frac{\Re R_p^2}{C_s D_{\text{Kn}}} = \frac{\left(1.19\times10^{-6}\ \text{mol Bz/s}\cdot\text{cm}^3\right)\times\left(10\times10^{-4}\ \text{cm}\right)^2}{\left(1.94\times10^{-6}\ \text{mol/cm}^3\right)\times\left(2.79\times10^{-2}\ \text{cm}^2/\text{s}\right)} = 2.20\times10^{-5}$$

Since $N_{W-P} < 0.3$ in both cases, we surmise that diffusional limitations are negligible when all the Pd is in the mesopores. Suppose next that all Pd is contained in the micropores. The Knudsen diffusivity now becomes

$$D_{\text{Kn}}' = \frac{1}{3}\bar{v} d_p = \frac{1}{3}\times\left(3.35\times10^4\right)\times\left(0.9\times10^{-7}\right) = 1.0\times10^{-3}\ \text{cm}^2/\text{s}$$

As before, in the worst case the catalyst particle radius $R_p = 500$ μm. The W-P criterion gives

$$N_{W-P} = \frac{\Re R_p^2}{C_s D_{\text{Kn}}'} = \frac{\left(1.19\times10^{-6}\ \text{mol Bz/s}\cdot\text{cm}^3\right)\times\left(500\times10^{-4}\ \text{cm}\right)^2}{\left(1.94\times10^{-6}\ \text{mol/cm}^3\right)\times\left(1.0\times10^{-3}\ \text{cm}^2/\text{s}\right)} = 1.53$$

12

which of course is greater than 0.3. Now, in the best case the catalyst particles have a diameter of 10 μm, so that

$$N_{W-P} = \frac{\Re R_p^2}{C_s D'_{Kn}} = \frac{\left(1.19\times10^{-6}\ \text{mol Bz/s}\cdot\text{cm}^3\right)\times\left(10\times10^{-4}\ \text{cm}\right)^2}{\left(1.94\times10^{-6}\ \text{mol/cm}^3\right)\times\left(1.0\times10^{-3}\ \text{cm}^2/\text{s}\right)} = 6.13\times10^{-4}$$

We conclude that, if all the Pd is in the mesopores, pore diffusion limitations are negligible. If, however, all the Pd is in the micropores, we cannot conclude that diffusion limitations are negligible.

♦ The correct answer is **C**.

P.13 ➡ *Solution*

The hydrogen concentration is

$$C_{H_2} = \frac{P}{RT} = \frac{710/760\ \text{atm}}{82.06\ \dfrac{\text{cm}^3\cdot\text{atm}}{\text{g mole}\cdot\text{K}}\times413\ \text{K}} = 2.76\times10^{-5}\ \text{mol/cm}^3$$

Since the reaction is zero order in benzene and first order in H_2, we can write

$$\Re = k'P_{H_2} = kC_{H_2} \rightarrow k = \frac{\Re}{C_{H_2}}$$

$$\therefore k = \frac{1.19\times10^{-6}\ \text{mol/s}\cdot\text{cm}^3}{2.76\times10^{-5}\ \text{mol/cm}^3} = 0.0431\ \text{s}^{-1}$$

where we have used $\Re$ obtained in the beginning of the previous problem. Now, the mean velocity of hydrogen molecules is given by

$$\overline{v}_{H_2} = \left(\frac{8k_B T}{\pi m}\right)^{1/2} = \left[\frac{8\times\left(1.38\times10^{-16}\ \text{erg/K}\right)\times413\ \text{K}}{\pi\times2\ \text{amu}\times\left(1.66\times10^{-24}\text{g/amu}\right)}\right]^{1/2} = 2.09\times10^5\ \text{cm/s}$$

The mean free path is, in turn,

$$\lambda = \frac{RT}{\sqrt{2}\pi\sigma^2 P_{H_2}} = \frac{82.06\ \dfrac{\text{cm}^3\cdot\text{atm}}{\text{g}\cdot\text{mol}\cdot\text{K}}\times413\ \text{K}\times\dfrac{1\ \text{mol}}{6.02\times10^{23}\ \text{molec}}}{\sqrt{2}\pi\times\left(2.4\times10^{-8}\ \text{cm}\right)^2\times1\ \text{atm total P}} = 2.20\times10^{-5}\ \text{cm}$$

where, in addition to other familiar variables, we have the molecular diameter of hydrogen σ = 2.4×10⁻⁸ cm. Since $\lambda \gg d_p$, Knudsen diffusion predominates and $D_{\text{eff}} \approx D_{Kn}$, where

$$D_{Kn} = \frac{1}{3}\overline{v}d_p$$

Now, in case 1 we consider the Thiele modulus for the smallest particle with all Pd in the mesopores. The diffusion coefficient is calculated as

$$D_{Kn} = \frac{1}{3}\times\left(2.09\times10^5\ \text{cm/s}\right)\times\left[\left(25\times10^{-9}\ \text{m}\right)\times10^2\ \text{cm/m}\right] = 0.174\ \text{cm}^2/\text{s}$$

so that

$$\phi = \frac{R_p k^{1/2} C_s^{(n-1)/2}}{D_{\text{eff}}^{1/2}} = \frac{\left[\left(10\times10^{-6}\ \text{m}\right)\times10^2\ \text{cm/m}\right]\times\left(0.0431\ \text{s}^{-1}\right)^{0.5}\times\left(2.76\times10^{-5}\ \text{mol/cm}^3\right)^0}{\left(0.174\ \text{cm/s}\right)^{1/2}}$$

$$\therefore \phi = 4.98\times10^{-4}$$

The corresponding efficiency factor is

$$\eta = \frac{3}{\phi}\left(\coth\phi - \frac{1}{\phi}\right) = \frac{3}{4.98\times10^{-4}}\left[\coth\left(4.98\times10^{-4}\right) - \frac{1}{4.98\times10^{-4}}\right] \approx 1.0$$

In case 2, we consider the Thiele modulus for the largest particle with all Pd in the mesopores. The diffusion coefficient remains D_{Kn} = 0.174 cm²/s, with the result that

13

$$\phi = \frac{R_p k^{1/2} C_s^{(n-1)/2}}{D_{\text{eff}}^{1/2}} = \frac{\left[\left(500 \times 10^{-6}\ \text{m}\right) \times 10^2\ \text{cm/m}\right] \times \left(0.0431\ \text{s}^{-1}\right)^{0.5} \times \left(2.76 \times 10^{-5}\ \text{mol/cm}^3\right)^0}{\left(0.174\ \text{cm/s}\right)^{1/2}}$$

$$\therefore \phi = 0.0249$$

The corresponding efficiency factor is

$$\eta = \frac{3}{0.0249}\left(\coth 0.0249 - \frac{1}{0.0249}\right) \approx 1.0$$

In case 3, we consider the Thiele modulus for the largest particle with all Pd in the micropores. The Knudsen diffusivity is updated as

$$D_{\text{Kn}} = \frac{1}{3} \times \left(2.09 \times 10^5\ \text{cm/s}\right) \times \left[\left(0.9 \times 10^{-9}\ \text{m}\right) \times 10^2\ \text{cm/m}\right] = 6.27 \times 10^{-3}\ \text{cm}^2/\text{s}$$

so that

$$\phi = \frac{R_p k^{1/2} C_s^{(n-1)/2}}{D_{\text{eff}}^{1/2}} = \frac{\left[\left(500 \times 10^{-6}\ \text{m}\right) \times 10^2\ \text{cm/m}\right] \times \left(0.0431\ \text{s}^{-1}\right)^{0.5} \times \left(2.76 \times 10^{-5}\ \text{mol/cm}^3\right)^0}{\left(6.27 \times 10^{-3}\ \text{cm/s}\right)^{1/2}}$$

$$\therefore \phi = 0.131$$

The corresponding efficiency factor is

$$\eta = \frac{3}{0.131}\left(\coth 0.131 - \frac{1}{0.131}\right) = 0.999$$

The values of η for all three cases are very close to unity. Thus, pore diffusion limitations are not a concern in any of the three cases.

◆ The correct answer is **A**.

▶ ANSWER SUMMARY

Problem 1		Open-ended pb.
Problem 2	2.1	C
	2.2	B
	2.3	D
Problem 3	3.1	A
	3.2	A
Problem 4		B
Problem 5		D
Problem 6		B
Problem 7		B
Problem 8		B
Problem 9	9.1	C
	9.2	C
Problem 10		C
Problem 11		Open-ended pb.
Problem 12		C
Problem 13		A

▶ REFERENCES

- HILL, C. and ROOT, T. (2014). *Introduction to Chemical Engineering Kinetics and Reactor Design.* 2nd edition. Hoboken: John Wiley and Sons.
- LEVENSPIEL, O. (1999). *Chemical Reaction Engineering*. 3rd edition. Hoboken: John Wiley and Sons.
- SCHMAL, M. (2014). *Chemical Reaction Engineering*. Boca Raton: CRC Press.
- VANNICE, M. (2005). *Kinetics of Catalytic Reactions*. Heidelberg: Springer.

? Got any questions related to this quiz? We can help!
Send a message to contact@montogue.com and we'll answer your question as soon as possible.

14