

## Assignment 6 solutions

1. A first order irreversible reaction  $A \rightarrow B$  is carried out in a packed-bed reactor containing spherical catalyst particles of diameter 3.6 mm. The gas-phase velocity is 150 m/s, entering at a temperature of 300 K. The reaction is considered to be externally mass transfer limited under the operating conditions. If the packed-bed is 0.05 m length, what conversion (percentage) can be expected under isothermal conditions.

Data:

Bed porosity,  $\phi = 40\%$

Kinematic viscosity at 300 K,  $\nu = 4.94 \times 10^{-5} \text{ m}^2/\text{s}$

Diffusivity,  $D_{AB} = 1.42 \times 10^{-4} \text{ m}^2/\text{s}$

Solution:

Design equation for PBR with external mass transfer for a first order reaction:

$$\ln\left(\frac{1}{1-X}\right) = \frac{k_c a_c}{U} Z$$

$$U = 150 \text{ m/s}$$

$$Z = 0.05 \text{ m}$$

$$a_c = 6 \times (1-\phi)/d_p = 6 \times (1-0.4)/(0.0036) = 1000 \text{ m}^2/\text{m}^3$$

Use Frossling correlation for mass transfer coefficient:  $Sh = 2 + 0.6Re^{1/2}Sc^{1/3}$

$$Sc = \frac{\nu}{D_{AB}} = \frac{4.94 \times 10^{-5}}{1.42 \times 10^{-4}} = 0.35$$

$$Re = \frac{d_p U}{\nu} = \frac{0.0036 \times 150}{4.94 \times 10^{-5}} = 10930$$

$$Sh = \frac{k_c d_p}{D_{AB}} = 46.2$$

$$k_c = 1.82 \text{ m/s}$$

Solving for X:  $X = 0.45$

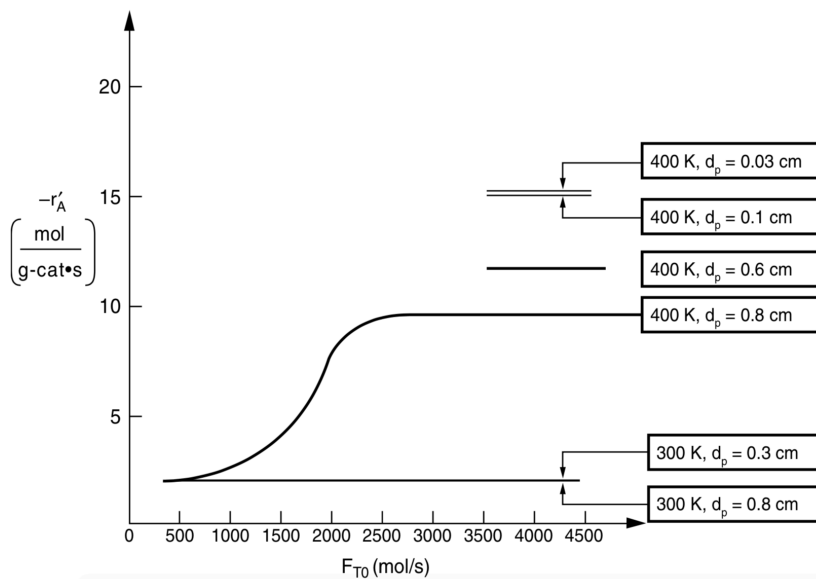
2. Oxygen (pure) is absorbed by xylene in a catalyzed reaction in a mixed-flow reactor. Under constant temperature the following data were obtained.

Stirrer speed (rpm)	Rate of uptake of $O_2$ (mL/hr) for system pressure (abs)			
	1.2 atm	1.6 atm	2.0 atm	3.0 atm
400	15	31	75	152
800	20	59	102	205
1200	21	62	105	208
1600	21	61	106	207

- What would you conclude about the relative importance of liquid-phase diffusion?
- What is the order of the kinetics of this reaction?

**Solution:**

- For all the system pressures, mass transfer is rate limiting at low rpms (upto 800 rpm) and reaction rate limiting at higher rpms. Plot rate of uptake of O<sub>2</sub> vs rpm for all pressures and verify.
  - The rate of uptake of O<sub>2</sub> increases linearly with system pressure. So the order must be 1. Plot rate of uptake of O<sub>2</sub> vs system pressure at 1600 rpm and verify.
3. The reaction  $A \rightarrow B$  is carried out in a differential packed-bed reactor at different temperatures, flow rates and particle sizes. The results are shown in the figure below.

**Solutions:**

- What regions (i.e conditions,  $d_p$ ,  $T$ ,  $F_{T0}$ ) are external mass transfer-limited?  
 $d_p = 0.8 \text{ cm}$ ,  $T = 400 \text{ K}$ ,  $F_{T0} < 2500 \text{ mol/s}$
  - What regions are reaction rate-limited?  
 $T = 300 \text{ K}$ ,  $d_p = 0.3, 0.8 \text{ cm}$ , all  $F_{T0}$ .  
 $T = 400 \text{ K}$ ,  $d_p = 0.03 \text{ cm}$ , all  $F_{T0}$ .
  - What region is internal-diffusion-controlled?  
 $T = 400 \text{ K}$ ,  $d_p > 0.1 \text{ cm}$ ,  $F_{T0} > 2500 \text{ mol/s}$
  - What is the internal effectiveness factor at  $T = 400 \text{ K}$  and  $d_p = 0.8 \text{ cm}$ ?  
Rate in the absence of internal diffusion  $\sim 16 \text{ mol/g.s}$   
Rate at  $T = 400 \text{ K}$  and  $d_p = 0.8 \text{ cm} \sim 10 \text{ mol/g.s}$   
Internal effectiveness factor  $\eta = 10/16 \approx 62\%$ .
4. The second-order gas phase decomposition reaction  $A \rightarrow B + 2C$  is carried out in a tubular reactor packed with catalyst pellets 0.4 cm in diameter. The reaction is internal diffusion limited. Pure A enters the reactor at a superficial velocity of 3 m/s, a temperature of 250 °C, and a pressure of 500 kPa. Experiments carried out on a smaller

pellets where surface reaction is limiting yielded a specific reaction rate of 0.05  $\text{m}^6/(\text{mol} \cdot \text{m}^2 \cdot \text{s})$ . Calculate the length of bed necessary to achieve 80% conversion.

Additional information:

Effective diffusivity ( $D_e$ ):  $2.66 \times 10^{-8} \text{ m}^2/\text{s}$

Bed porosity ( $\phi$ ): 0.4

Pellet density ( $\rho_c$ ):  $2 \times 10^6 \text{ g/m}^3$

Internal surface area (S):  $400 \text{ m}^2/\text{g}$ .

*Some hints:*

- (i) Use mole balance for PBR for a 2<sup>nd</sup> order reaction
- (ii) Calculate Thiele modulus for 2<sup>nd</sup> order reaction
- (iii) Note that  $k_2''$  is given for 2<sup>nd</sup> order. Use the relationship  $k_{2e} = S\rho_b k_2'$ . Note that  $\rho_b$  is the bulk density, calculated as:  $\rho_b = (1 - \phi)\rho_c$
- (iv) First ignore the volume change effect on effectiveness factor in your calculations. If you like to include and see the effect, then refer to the paper “Influence of volume change on gas-phase reactions in porous catalysts”, Journal of Catalysis 4(2), 260 (1965). In this paper an equation is available for effectiveness factor for a 2<sup>nd</sup> order reaction for very large Thiele modulus:

$$\frac{\eta}{\eta'} = \sqrt{3} \left[ \frac{1}{2\epsilon} - \frac{1}{\epsilon^2} + \frac{1}{\epsilon^3} \ln(1 + \epsilon) \right]^{1/2}$$

$\eta$  and  $\eta'$  are effectiveness factor for ‘no volume change’ and for ‘finite volume change’ cases, respectively.

**Solutions:**

Mole balance:

$$F_A|_z - F_A|_{z+\Delta z} + r_A A_c \Delta z = 0$$

$$-r_A = \eta k_e C_A^2$$

$$\frac{1}{A_c} \frac{dF_A}{dz} = r_A = -\eta k_e C_A^2$$

Noting that  $F_A = v_0 C_A = U A_c C_A$

$$-U \frac{dC_A}{dz} = r_A = \eta k_e C_A^2$$

$$-\frac{dC_A}{C_A^2} = \frac{\eta k_e}{U} dz$$

On integration:  $\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{\eta k_e}{U} Z$

From stoichiometry:  $C_A = C_{A0} \left( \frac{1-X}{1+2X} \right)$

Solving for reactor length,  $Z = \frac{U}{C_{A0} \eta k_e} \frac{3X}{1-X}$

$$k_e = S\rho_b k_2'' = S\rho_c(1 - \phi)k_2'' = 400 \times 2 \times 10^6 \times 0.6 \times 0.05 = 2.4 \times 10^7 \text{ m}^3/(\text{mol.s})$$

Suppose, if internal diffusion is not limiting, then  $\eta = 1$ . Then for  $X = 0.8$ ,

$$Z = \frac{3}{115 \times 2.4 \times 10^7} \frac{3 \times 0.8}{(1 - 0.8)} = 1.3 \times 10^{-8} \text{ m}$$

That is  $Z = 13 \text{ nm}!$

*Calculation of internal effectiveness factor:  $\eta$*

Thiele modulus for 2<sup>nd</sup> order reaction:

$$\phi_2 = R\sqrt{k_e C_{A0}/D_e} = 0.002\sqrt{2.4 \times 10^7 \times 115/2.66 \times 10^{-8}} = 6.44 \times 10^5.$$

Effectiveness factor for  $n^{\text{th}}$  order reaction  $\eta \cong \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{\phi_n}$

$$\eta \cong \left(\frac{2}{3}\right)^{1/2} \frac{3}{\phi_n}$$

$$\eta = 3.8 \times 10^{-6}$$

$$Z = \frac{1.3 \times 10^{-8} \text{ m}}{3.8 \times 10^{-6}} = \mathbf{3.4 \text{ mm}!}$$