#1

10. Reaction rate expressions of the form:

$$r = \frac{kC_A}{1 + KC_A}$$

reveal zero-order kinetics when $KC_A \gg 1$. Solve the material balance (isothermal) equation for a slab catalyst particle using zero-order kinetics. Plot $C_A(x)/C_{AS}$ for a Thiele modulus of 0.1, 1.0, and 10.0. If the zero-order kinetics were to be used as an approximation for the rate form shown above when $KC_{AS} \gg 1$, would this approximation hold with the slab catalyst particle for the Thiele moduli investigated?

For zero order kinetics,

$$r = k' \tag{1}$$

The material balance for differential element of a slab catalyst particle at steady state is

$$0 = (\text{rate of A in}) - (\text{rate of A out}) + (\text{rate of generation of A}) \tag{2}$$

$$0 = \left(N_A\big|_x \cdot \pi R_{pore}^2\right) - \left(N_A\big|_{x+\Delta x} \cdot \pi R_{pore}^2\right) + (k' \cdot 2\pi R_{pore}\,\Delta x) \tag{3}$$

where x is the length dimension down the catalyst pore,

πR_{pore}^2 is the area of diffusion and $2\pi R_{pore}$ is the surface area of reaction.

Therefore, the differential equation representing the slab catalyst particle is the following:

$$-\frac{dN_A}{dx} = k' \frac{2\pi R_{pore}}{\pi R_{pore}^2} = \frac{2k'}{R_{pore}} \tag{4}$$

However, Fick's law is

$$N_A = -D\frac{dC_A}{dx} \tag{5}$$

where D is the diffusivity.

After substituting equation (5) into equation (4),

$$D\frac{d^2C_A}{dx^2} = \frac{2k'}{R_{pore}}$$

(6)

In order to non-dimensionalize equation (6),

let $\psi = \dfrac{C_A}{C_{AS}}$ and $\omega = x/\overline{L}$ where C_{AS} is the concentration of A at the surface and $\overline{L}$ is the length of the pore.

Therefore,

$$\frac{d^2\psi}{d\omega^2} = \frac{2k'\overline{L}^2}{R_{pore}DC_{AS}}$$

(7)

let $\quad \phi^2 = \dfrac{2k'\overline{L}^2}{R_{pore}DC_{AS}}$

(8)

The boundary conditions must be determined prior to solving equation (7). The system is split into two different regions within the pore, one where A is present (Region I) and one where A is not present (Region II).

let ω_{ex} be the point where A is not present (extinguished) in the pore.

For Region I,

$\dfrac{d^2\psi}{d\omega^2} = \phi^2$ and the boundary conditions are the following for $0 \leq \omega \leq \omega_{ex}$:

$\psi = 1$ at $\omega = 0$

$\psi = 0$ at $\omega = \omega_{ex}$

$\dfrac{d\psi}{d\omega} = 0$ at $\omega = \omega_{ex}$

Solving the differential equation and using the boundary conditions result in the following relationship;

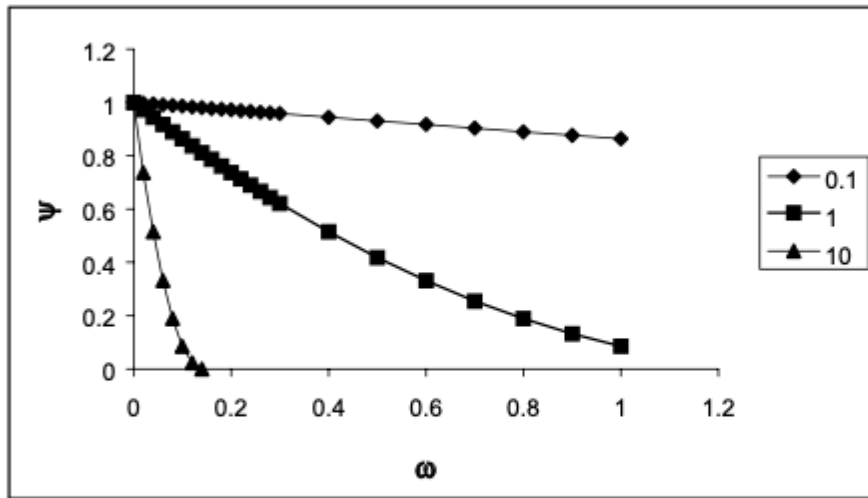$$\psi = \frac{\phi^2\omega^2}{2} - \phi^2\omega_{ex}\omega + \frac{\phi^2\omega_{ex}^2}{2}$$

(9)

At $\psi = 1$,

$$\omega_{ex} = \frac{\sqrt{2}}{\phi}$$

ψ

Plotting ψ vs. ω for $\phi = 0.1$, 1, and 10:

As ϕ increases, A is depleted in a shorter distance in the pellet. Therefore, zero order kinetics is a bad approximation because it assumes $KC_A \gg 1$ which is not true as C_A goes to zero.

12. A first-order irreversible reaction is carried out on a catalyst of characteristic dimension 0.2 cm and effective diffusivity of 0.015 cm²/s. At 100°C the intrinsic rate constant has been measured to be 0.93 s⁻¹ with an activation energy of 20 kcal/mol.

(a) For a surface concentration of 3.25 × 10⁻² mol/L, what is the observed rate of reaction at 100°C?

(b) For the same reactant concentration, what is the observed rate of reaction at 150°C? Assume that D_{TA}^e is independent of temperature.

(c) What value of the activation energy would be observed?

(d) Compare values of the Thiele modulus at 100°C and 150°C.

part a)

The observed rate of reaction is a function of the effectiveness factor.

$$r_{obs} = \eta r \qquad (1)$$

where r is the rate in the absence of diffusion effects.

In order to find the observed rate of reaction, both the effectiveness factor and the rate in the absence of diffusion effects must be determined.

$$r = kC_{AS} = (0.93s^{-1})(3.25\times10^{-2}\ \tfrac{mol}{L}) = 3.02\times10^{-2}\ \tfrac{mol}{L\text{-sec}}$$

The effectiveness factor can be determined by the following equation:

$$\eta = \frac{3}{\phi}\left[\frac{1}{\tanh(\phi)} - \frac{1}{\phi}\right] \qquad (2)$$

where the Thiele modulus is given by:

$$\phi = L_p\sqrt{\frac{k}{D_{TA}^e}} \qquad (3)$$

here L_p is 0.2 cm, $k = 0.93$ s^{-1}, and $D_{TA}^e = 0.015$ cm^2 s^{-1}.

Therefore,

$$\phi = 1.57 \text{ and } \eta = 0.867$$

Substituting the effectiveness factor into equation (1) gives

$$r_{obs} = 2.62 \times 10^{-2} \tfrac{mol}{L \cdot sec}$$

part b)

The rate constant at a different temperature can be determined by the Arrhenius form of k:

$$k_2 = k_1 \exp\left[\frac{-E}{R_g}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \tag{1}$$

Therefore, the rate constant is

$$k_2 = 0.93s^{-1} \exp\left[\frac{-20\tfrac{kcal}{mol}\tfrac{1000cal}{kcal}}{1.98\tfrac{cal}{mol \cdot K}}\left(\frac{1}{423} - \frac{1}{373}\right)\right] = 22.8s^{-1}$$

Therefore, the rate without diffusion effects at 423 K is

$$r = kC_{AS} = (22.8s^{-1})(3.25 \times 10^{-2} \tfrac{mol}{L}) = 0.74 \tfrac{mol}{L \cdot sec}$$

From equations (3) and (2), the effectiveness factor can be determined.

$$\phi = 7.8$$

$$\eta = 0.335$$

Therefore, the observed rate is

$$r_{obs} = \eta r = (0.335)(0.74\tfrac{mol}{L \cdot s}) = 2.48 \times 10^{-1} \tfrac{mol}{L \cdot sec}$$

part c)

The observed activation energy can be determined from the following equation:

$$k_2 = k_1 \exp\left[\frac{-E}{R_g}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

where k_1 and k_2 are the observed rate constants.

$E = 14000 \text{ cal mol}^{-1}$

part d)

$$\frac{\phi_{150}}{\phi_{100}} = \frac{7.8}{1.57} = 4.97$$

Therefore, the diffusion limitation goes up a lot with the temperature increase.