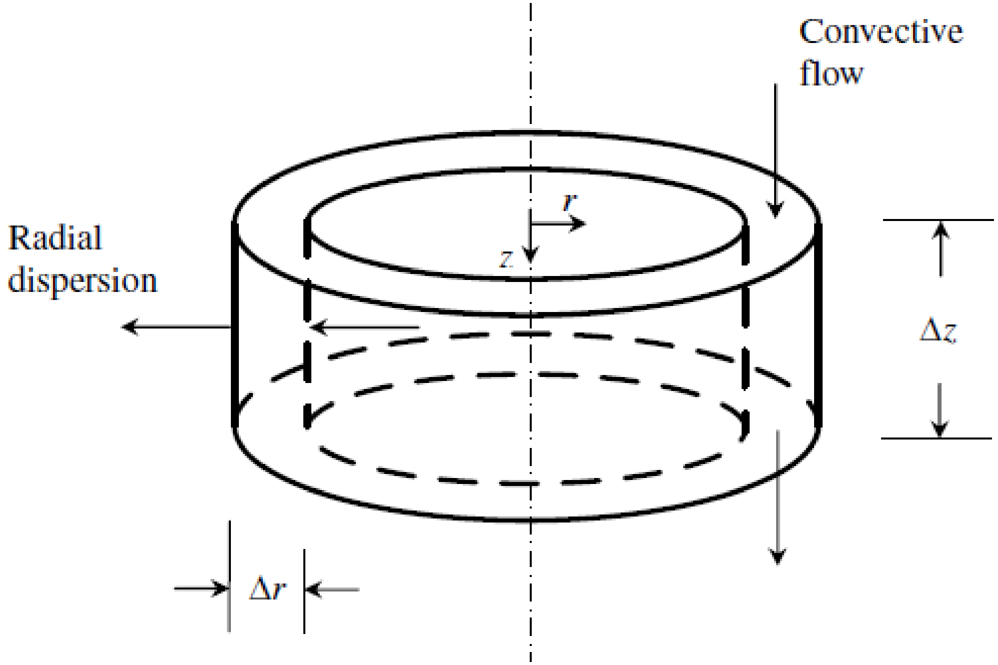
CHE 611
Advanced Chemical Reaction Engineering



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Development of kinetic rate equation based on LHHW dual-site surface reaction for the dehydrogenation of methylcyclohexane

Dehydrogenation of Methylcyclohexane

$$Methylcyclohexane \rightarrow Toluene + 3Hydrogen$$

or

$$C_7H_{14} \rightarrow C_7H_8 + 3H_2$$

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Step two (II) is the rate controlling in dual-site surface reaction

$$\mathrm{MCH} + \mathrm{s} \rightleftharpoons \mathrm{MCH{\cdot}s} \qquad \text{(I)}$$

$$\mathrm{MCH{\cdot}s} + \mathrm{s} \rightleftharpoons \mathrm{MCHe{\cdot}s} + \mathrm{H_2{\cdot}s} \qquad \text{(II)}$$

$$\mathrm{MCHe{\cdot}s} + \mathrm{s} \rightleftharpoons \mathrm{MCHde{\cdot}s} + \mathrm{H_2{\cdot}s} \qquad \text{(III)}$$

$$\mathrm{MCHde{\cdot}s} + \mathrm{s} \rightleftharpoons \mathrm{TOL{\cdot}s} + \mathrm{H_2{\cdot}s} \qquad \text{(IV)}$$

$$\mathrm{TOL{\cdot}s} \rightleftharpoons \mathrm{TOL} + \mathrm{s} \qquad \text{(V)}$$

$$\mathrm{H_2{\cdot}s} \rightleftharpoons \mathrm{H_2} + \mathrm{s} \qquad \text{(VI)}$$

A = MCH, B = TOL, C = H_2, D = MCHe, and E = MCHde

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For Step-I, it may shown that

$$(-r_A) = k_1 \cdot p_A \cdot C_s - k_{-1} \cdot C_{A\cdot s} \tag{1}$$

At equilibrium net rate is zero, so

$$C_{A\cdot s} = K_A \cdot p_A \cdot C_s \tag{2}$$

For Step-II which is the rate controlling step:

$$(-r_A) = k_2 \cdot C_{A\cdot s} \cdot C_s - k_{-2} \cdot C_{D\cdot s} \cdot C_{C\cdot s} \qquad \text{(rate determining step)} \tag{3}$$

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For Step-III at equilibrium

$$C_{D\cdot s} = \frac{C_{E\cdot s} \cdot C_{C\cdot s}}{K_3 \cdot C_s} \tag{4}$$

For Step-IV at equilibrium

$$C_{E\cdot s} = \frac{C_{B\cdot s} \cdot C_{C\cdot s}}{K_4 \cdot C_s} \tag{5}$$

For Step-V at equilibrium

$$C_{B\cdot s} = K_B \cdot p_B \cdot C_s \tag{6}$$

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For Step-VI at equilibrium

$$C_{C\cdot s} = K_C \cdot p_C \cdot C_s \tag{7}$$

For Eq. 3, we need the values of $C_{D.s}$ and indirectly $C_{E\cdot s}$ in the known concentration values, i.e. we need to eliminate these two concentrations from Eq. 3.

Inserting Eq. 5 into Eq. 4, it may shown that

$$C_{D\cdot s} = \frac{\dfrac{C_{B\cdot s} \cdot C_{C\cdot s}}{K_4 \cdot C_s} \cdot C_{C\cdot s}}{K_3 \cdot C_s} \tag{8}$$

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Inserting Eq. 6 and Eq. 7 in Eq. 8, it may be written that

$$C_{D\cdot s} = \frac{\dfrac{K_B \cdot p_B \cdot C_s \cdot (K_C \cdot p_C \cdot C_s)}{K_4 \cdot C_s} \cdot (K_C \cdot p_C \cdot C_s)}{K_3 \cdot C_s}$$

$$C_{D\cdot s} = \frac{K_B \cdot K_C^2 \cdot C_s \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} \tag{9}$$

From Eq. 5 upon inserting Eq. 6 and Eq. 7, it may shown that

$$C_{E\cdot s} = \frac{K_5 \cdot p_B \cdot C_s \cdot K_6 \cdot p_C}{K_4}$$

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Inserting Eq. 2 and Eq. 9 in Eq. 3, it may shown that

$$(-r_A) = k_2 \cdot (K_A \cdot p_A \cdot C_s) \cdot C_s - k_{-2} \cdot \left(\frac{K_B \cdot K_C^2 \cdot C_s \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} \right) \cdot (K_C \cdot p_C \cdot C_s)$$

$$(-r_A) = k_2 \cdot K_A \cdot p_A \cdot C_s^2 \cdot \left(1 - \frac{k_{-2} \cdot K_B \cdot K_C^3 \cdot p_B \cdot p_C^3}{k_2 \cdot K_1 \cdot K_3 \cdot K_4 \cdot p_A} \right)$$

$$(-r_A) = k_2 \cdot K_A \cdot p_A \cdot C_s^2 \cdot \left(1 - \frac{p_B \cdot p_C^3}{K \cdot p_A} \right) \qquad (10)$$

Where,

$$K = \frac{k_2 \cdot K_1 \cdot K_3 \cdot K_4}{k_{-2} \cdot K_5 \cdot K_6^3}$$

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Total concentration of the sites is the sum of all the covered sites and the empty sites

$$C_T = C_s + C_{A\cdot s} + C_{B\cdot S} + C_{C\cdot s} + C_{D\cdot s} + C_{E\cdot s} \tag{11}$$

Inserting the corresponding expression in Eq. 11, it may be shown that

$$C_T = C_s + K_A \cdot p_A \cdot C_s + K_B \cdot p_B \cdot C_s + K_C \cdot p_C \cdot C_s + \frac{K_B \cdot K_C^2 \cdot C_s \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} + \frac{K_B \cdot p_B \cdot C_s \cdot K_C \cdot p_C}{K_4}$$

$$C_T = C_s \cdot \left(1 + K_A \cdot p_A + K_C \cdot p_C + K_B \cdot p_B + \frac{K_B \cdot K_C^2 \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} + \frac{K_B \cdot p_B \cdot K_C \cdot p_C}{K_4} \right)$$

$$C_s = C_T \cdot \left(1 + K_A \cdot p_A + K_C \cdot p_C + K_B \cdot p_B + \frac{K_B \cdot K_C^2 \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} + \frac{K_B \cdot p_B \cdot K_C \cdot p_C}{K_4} \right)^{-1} \tag{12}$$

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Using Eq. 12 with Eq. 10, it may shown that

$$(-r_A) = \frac{k \cdot K_A \cdot p_A \cdot \left(1 - \dfrac{p_B \cdot p_C^3}{K \cdot p_A}\right)}{\left(1 + K_A \cdot p_A + K_C \cdot p_C + K_B \cdot p_B + \dfrac{K_B \cdot K_C^2 \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} + \dfrac{K_B \cdot p_B \cdot K_C \cdot p_C}{K_4}\right)^2}$$

Where, $k = k_2 \cdot C_T^2$

$$\boxed{(-r_A) = \frac{k \cdot K_A \cdot p_A \cdot \left(1 - \dfrac{p_B \cdot p_C^3}{K \cdot p_A}\right)}{\left(1 + K_A \cdot p_A + K_C \cdot p_C + K_B \cdot p_B + K'' \cdot p_B \cdot p_C^2 + K' \cdot p_B \cdot p_C\right)^2}} \qquad (13)$$

Eq. 13 is the final and the required equation.

Note that the denominator is squared in dual-site mechanism which is not the case for single-site mechanism.

Homework problems

- For the simple mechanisms given previously in Part 7 (slide 16), work out the rate equations by considering adsorption, surface reaction, and desorption as the rate controlling step.
- For the Eley-Rideal mechanism,

$$A + s \Leftrightarrow A \cdot s$$

$$A \cdot s + B \Leftrightarrow C \cdot s$$

$$C \cdot s \Leftrightarrow B + s$$

workout the rate equation for the surface reaction.

Homework problems

Modify the mechanism given in slide 2, develop a kinetic rate equation based on LHHW kinetics when the rate controlling step is:

- Adsorption of methylcyclohexane
- Single-site surface reaction for the loss of first hydrogen
- Single-site surface reaction for the loss of second hydrogen
- Single-site surface reaction for the loss of third hydrogen
- Desorption of toluene

Consult Chapter 10 of Fogler [2]. See also Chapter 2 of Froment et al. [1].

Homework problems

Modify the mechanism given in slide 2 for single-site surface reaction while neglecting hydrogen adsorption-desorption step. Develop kinetic rate equation based on LHHW kinetics when the rate controlling step is:

- Adsorption of methylcyclohexane
- Single-site surface reaction for the loss of first hydrogen
- Single-site surface reaction for the loss of second hydrogen
- Single-site surface reaction for the loss of third hydrogen
- Desorption of toluene

Consult Chapter 10 of Fogler [2]. See also Chapter 2 of Froment et al. [1].

Problem: Finding weight of catalyst

A gas phase fixed bed reactor is to be designed for the isothermal dehydrogenation of methylcyclohexane (MCH) to toluene and hydrogen. The feed to the reactor is pure methylcyclohexane flowing at the rate of 100 mol/s. The temperature and pressure conditions are 360°C and 2.0 bar. Assuming the principal reaction is clean and no byproducts are formed, find out the:

a) weight of the catalyst required for a total of 90% conversion of methylcyclohexane

b) the final conversion if the catalyst weight is 100 kg.

The rate equation for the problem is given below:

Problem: Finding weight of catalyst

$$(-r_A) = k \cdot \left(p_A - \frac{p_B \cdot p_C^3}{K} \right)$$

$$K = 3600 \cdot \exp\left(\frac{-217650}{8.3143} \left(\frac{1}{T} - \frac{1}{650} \right) \right), \text{ bar}^3$$

$$k = 1.65 \times 10^{-5} \exp\left(B \cdot \left(1 - \frac{661.8}{T} \right) \right), \text{ mol·s}^{-1}\text{·g-cat}^{-1}\text{·Pa}^{-1}$$

$$B = 18.1$$

Homework problem

Using POLYMATH software find out the weight of the catalyst for the problem described above, however, use the rate equation as described in Usman et al. 2011 [6]. Solve the problem and see the difference for using two different rate equations. What are your comments?

Instead of using POLYMATH software, you can prepare an excel spreadsheet using Euler’s method or Runge-Kutta method for finding the weight of the catalyst, etc.

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