

# Kinetics and Reactor Design HW1

Daniel Naumov

Assigned: January 26, 2022

Due: February 7, 2022

## 1 Problem Statement

### 1.1 P3-11<sub>B</sub>

Determine the rate law for the reaction described in each of the cases below involving species A, B, and C. The rate laws should be elementary as written for reactions that are either of the form  $A \rightarrow B$  or  $A + B \rightarrow C$ .

### 1.2 P3-12<sub>A</sub>

Write the rate law for the following reactions assuming each reaction follows an elementary rate law. Give the units of  $k_A$  for each, keeping in mind some are homogeneous and some reactants are heterogeneous.

- (a) 
$$\text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_4 + \text{H}_2$$
- (b) 
$$\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_2 - \overset{\text{O}}{\text{CH}_2}$$
- (c) 
$$(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3 \rightleftharpoons \text{C}_2\text{H}_6 + 2\text{CH}_3\text{COCH}_3$$
- (d) 
$$n\text{C}_4\text{H}_{10} \rightleftharpoons i\text{C}_4\text{H}_{10}$$
- (e) 
$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{C}_4\text{H}_9\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_4\text{H}_9 + \text{C}_2\text{H}_5\text{OH}$$
- (f) 
$$2\text{CH}_3\text{NH}_2 \xrightleftharpoons{\text{cat}} (\text{CH}_3)_2\text{NH} + \text{NH}_3$$
- (g) 
$$(\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{CH}_3\text{COOH}$$

Figure 1

### 1.3 P4-5<sub>A</sub> (a)

Set up a stoichiometric table for each of the following reactions and express the concentration of each species in the reaction as a function of conversion, evaluating all constants (e.g.,  $\epsilon$ ,  $\Phi$ ). Next, assume the reaction follows an elementary rate law, and write the reaction rate solely as a function of conversion, i.e.,  $-r_A = f(X)$ .

For the liquid-phase reaction

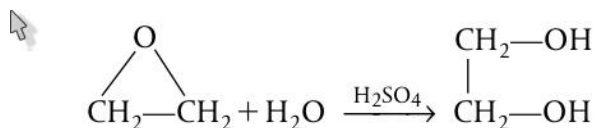


Figure 2

the entering concentrations of ethylene oxide and water, after mixing the inlet streams, are 16.13 mol/dm<sup>3</sup> and 55.5 mol/dm<sup>3</sup>, respectively. The specific reaction rate is  $k = 0.1$  dm<sup>3</sup>/mol s at 300 K with  $E = 12,500$  cal/mol.

(1) After finding  $-r_A = f(X)$ , calculate the CSTR space-time,  $\tau$ , for 90 percent conversion at 300 K and also at 350 K.

(2) If the volumetric flow rate is 200 liters per second, what are the corresponding reactor volumes?

### 1.4 P4-6<sub>A</sub>

Orthonitroaniline (an important intermediate in dyes—called fast orange) is formed from the reaction of orthonitrochlorobenzene (ONCB) and aqueous ammonia (see explosion in Figure E13-2.1 in Example 13-2).

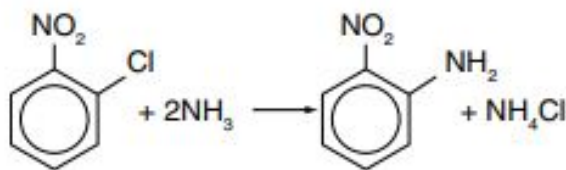


Figure 3

The liquid-phase reaction is first order in both ONCB and ammonia with  $k = 0.0017$  m<sup>3</sup>/kmol min at 188°C with  $E = 11,273$  cal/mol. The initial entering concentrations of ONCB and ammonia are 1.8 kmol/m<sup>3</sup> and 6.6 kmol/m<sup>3</sup>, respectively (more on this reaction in Chapter 13).

(a) Set up a stoichiometric table for this reaction for a flow system.

(b) Write the rate law for the rate of disappearance of ONCB in terms of concentration.

(c) Explain how parts (a) and (b) would be different for a batch system.

- (d) Write  $-r_A$  solely as a function of conversion.  
(e) What is the initial rate of reaction ( $X = 0$ ) [At 25, 188, 288C]  
(f) What is the rate of reaction when  $X = 0.90$  [At 25, 188, 288C]  
(g) What would be the corresponding CSTR reactor volume at 25C to achieve 90 percent conversion and at 288C for a feed rate of 2 dm<sup>3</sup>/min

## 2 Problem Solution

### 2.1 P3-11<sub>B</sub>

$$k = \left[ \frac{dm^3}{mol \times h} \right] \quad (1)$$

Second order reaction.  $-r_A = kC_A C_B$ .

$$k = \left[ \frac{mol}{kg - cat \times h(atm)^2} \right] \quad (2)$$

$$-r'_A = kP_A P_B.$$

$$k = \left[ \frac{1}{h} \right] \quad (3)$$

This is a first order reaction.  $-r_A = kC_A$ .

$$k = \left[ \frac{mol}{dm^3 \times h} \right] \quad (4)$$

$-r_A = k$ , 0th order reaction.

### 2.2 P3-12<sub>A</sub>

- (a) Elementary first order reaction.  $-r_A = kC_A$ ,  $k [=] \frac{1}{s}$   
(b)  $-r_A = kC_A C_B^{1/2}$ ,  $k [=] \frac{dm^{3/2}}{s \times mol^{1/2}}$   
(c)  $-r_A = k[C_A - C_B C_C^2 / K_C]$ ,  $k [=] \frac{1}{s}$   
(c)  $-r_A = k[C_A - C_B / K_C]$ ,  $k [=] \frac{1}{s}$   
(e)  $-r_A = k[C_A C_B - C_C C_D / K_C]$ ,  $k [=] \frac{dm^3}{s \times mol}$   
(f)  $-r_A = kP_A^2$ ,  $k [=] \frac{mol}{kg-cat \times h(atm)^2}$   
(g)  $-r_A = k[C_A C_B - C_C^2 / K_C]$ ,  $k [=] \frac{dm^3}{s \times mol}$

### 2.3 P4-5<sub>A</sub> (a)

Species	Symbol	Initial	Change	Remaining
Ethylene Oxide	A	$C_{A0}$	$-C_{A0}X$	$C_{A0}(1-X)$
Water	B	$C_{A0}\theta_B$	$-C_{A0}X$	$C_{A0}(\theta_B - X)$
Ethylene Glycol	C	$C_{A0}\theta_C$	$C_{A0}X$	$C_{A0}X$

$-r_A = kC_A C_B = kC_{A0}(1-X)C_{A0}(\theta_B - X)$ . We are given the initial concentrations of A and B, and can compute  $\theta_B$  to be 3.441 (initial concentration B divided by initial concentration A).  $\tau = \frac{C_{A0}X}{-r_A}$ . We are told  $X = 0.9$  (90 percent conversion), and can evaluate  $\tau$  numerically. We are given the  $k$  at 300K.

$$\frac{C_{A0}X}{-r_A} = \frac{C_{A0}X}{kC_{A0}(1-X)C_{A0}(\theta_B - X)} = \frac{16.13 \times 0.9}{0.1 \times 16.13 \times 0.1 \times 16.13 \times (3.441 - 0.9)} = 2.196 \text{ seconds.} \quad (5)$$

The volume of the reactor would be the space time  $\tau$  multiplied by the volumetric flow rate, so here it would be 439.2 L.

For 350K, we need to recalculate  $k$  to adjust for the increase in temperature.

$$k_{new} = k e^{\frac{E}{R} \left( \frac{1}{T_{old}} - \frac{1}{T_{new}} \right)} = 1.99 \frac{dm^3}{mol \times s} \quad (6)$$

For  $R$ , I used the ideal gas constant for units of calories, not joules, since the activation energy was in calories per mole.

I can perform the same calculation as in (5) but using 1.99 instead of 0.1 (or can just multiply 2.196 by  $\frac{0.1}{1.99}$ ) to get 0.1103 seconds. Once again I can multiply this by the volumetric flow rate to get a volume of 22.1 liters.

## 2.4 P4-6<sub>A</sub>

(a) **First order in ONCB AND NH<sub>3</sub>.**

Species	Symbol	Initial	Change	Remaining
ONCB	A	$F_{A0}$	$-F_{A0}X$	$F_{A0}(1-X)$
NH <sub>3</sub>	B	$F_{A0}\theta_B$	$-2F_{A0}X$	$F_{A0}(\theta_B - 2X)$
ONA	C	$F_{A0}\theta_C$	$F_{A0}X$	$F_{A0}X$
NH <sub>4</sub> Cl	D	$F_{A0}\theta_D$	$F_{A0}X$	$F_{A0}X$

(b)  $-r_A = kC_A C_B$ .

(c) For a batch system,  $C_A = N_A/V$  and  $-r_A = kN_A N_B/V^2$ .

(d)  $-r_A = kC_{A0}(1-X)C_{A0}(\theta_B - 2X)$ . This is due to  $C_i = \frac{F_A}{\nu_0} = C_{A0}(1-X)$ , and  $\frac{F_B}{\nu} = C_{A0}(\theta_B - \frac{b}{a}X)$  [This is assuming no phase change, thus allowing us to use equations 4-12 and 4-13 in the textbook].  $\theta_B = 3.67$ ,  $A = 1.8 \text{ kmol/m}^3$ , so  $-r_A = k \times 1.8(1-X) \times 1.8(3.67 - 2X)$

(e) At  $X = 0$ ,  $-r_A$  boils down to  $k \times 1.8(1) \times 1.8(3.67)$ . We know  $k$ , so at 188C (461K)  $-r_{A0} = 0.0202 \frac{\text{kmol}}{\text{m}^3 \text{min}}$ . Need to recalculate  $k$  at 25C and 288C, or 298 and 561K respectively. We can use (6) to find  $k = 2.03 \times 10^{-6}$  and  $0.0152 \frac{\text{m}^3}{\text{kmol} \times \text{min}}$  respectively. Then use the same formula as earlier but with new  $k$ s to get  $2.41 \times 10^{-5}$  and  $0.1807 \frac{\text{kmol}}{\text{m}^3 \times \text{min}}$  respectively.

(f) Exact same process as (e) but  $X = 0.9$ . We can actually easily find all the  $-r_A$  values because they'll all be multiplied by  $[(1-0.9)(3.67-1.8)/(3.67)]$  or 0.051. This leads to (respectively) 0.00103,  $1.23 \times 10^{-6}$ , and  $.00922 \frac{\text{kmol}}{\text{m}^3 \text{min}}$ .

(g)  $\frac{F_{A0}X}{-r_A} = V_{CSTR}$ . The feed rate is 2 dm<sup>3</sup>/min and the conversion is 90 percent, so the rates found in (f) apply. Converting the feed rate into m<sup>3</sup> as those are the units for the rates yields 0.002 m<sup>3</sup>/min. To get the flow rate we need to multiply the feed rate by the concentration, which we get from the problem setup as 1.8 kmol/m<sup>3</sup> ONCB. Therefore the flow rate is 0.0036 kmol/min.

$$\text{At } 25\text{C}, \frac{0.0036 \text{ kmol/min} \times 0.9}{1.23 \times 10^{-6} \text{ kmol/m}^3 \text{ min}} = V_{CSTR} = 2634 \text{ m}^3.$$

$$\text{At } 288\text{C}, \frac{0.0036 \text{ kmol/min} \times 0.9}{0.00922 \text{ kmol/m}^3 \text{ min}} = V_{CSTR} = 0.327 \text{ m}^3.$$