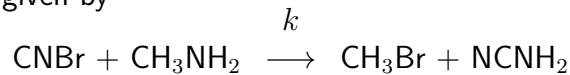


## Computer Simulation of Semibatch Reactors

[Choose one of the problems given in this set and solve it entirely.  
Consultation sessions with the course instructors are available on request.]

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- (1) The production of methyl bromide,  $\text{CH}_3\text{Br}$ , (labelled  $P$ ) is an irreversible, elementary, liquid-phase reaction given by



which is carried out in a semibatch reactor. An aqueous solution of methyl amine,  $\text{CH}_3\text{NH}_2$ , (labelled  $B$ ) at a concentration of  $C_{B0}$  is fed at a volumetric flow rate of  $v$  to an aqueous solution of bromine cyanide,  $\text{CNBr}$ , (labelled  $A$ ) contained in a glass-lined reactor. The initial volume of fluid in the vat is  $V_0$  with a bromine cyanide concentration of  $C_{A0}$ .

*Data:*  $C_{A0} = 0.005$  mol/litre;  $C_{B0} = 0.0025$  mol/litre;  $v = 0.5$  litre/s;  $V_0 = 50$  litre;  $k = 22$  litre/mol.s.

- (i) Starting from the definition of  $x_A$  (conversion of  $A$  defined in terms of the initial amount of  $A$  present in the vat), obtain the following expression for concentration of  $A$  in the vat at time  $t$ :

$$C_A = \frac{C_{A0} V_0 (1 - x_A)}{V_0 + v t}$$

- (ii) Using the stoichiometric relationship among  $A$ ,  $B$  and  $P$ , obtain the following expressions for the concentrations of  $B$  and  $P$  in the vat at time  $t$ :

$$C_B = \frac{C_{B0} v t - C_{A0} V_0 x_A}{V_0 + v t} \quad \text{and} \quad C_P = \frac{C_{A0} V_0 x_A}{V_0 + v t}$$

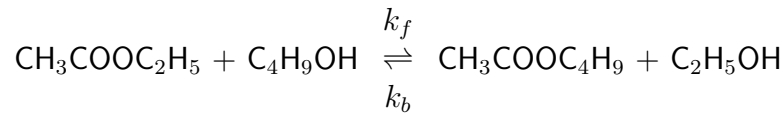
- (iii) Starting from the mass balance for  $A$  over the reactor, obtain the following differential equation:

$$\frac{dx_A}{dt} = \frac{k(1 - x_A)(C_{B0} v t - C_{A0} V_0 x_A)}{V_0 + v t}$$

- (iv) Solve the differential equation of part (iii) using MATLAB™ and plot the following:
- (a)  $x_A$  as function of  $t$  showing  $x_A$  approaching unity
  - (b) volume of the reacting mixture  $V$  as function of  $t$
  - (c)  $C_B$  and  $C_P$  as function of  $t$
  - (d) rate of reaction as function of  $t$
- (v) Explain why the  $C_P$  profile and the rate of reaction profile experience maximums. Also, determine the values of  $V$  at  $x_{Af} = 0.95$  and at the maximum value of  $C_P$  in the reactor.
- (vi) Analyse the sensitivity of  $x_A$  and  $C_P$  to various values of  $v$ . Produce a brief report of the results to help your superior at the industry understand the sensitivity of the reaction system studied.

*Source: Example 4-10 of the Reference (see the end).*

- (2) [Worth a 25% bonus on the marks gained for Set 10] Pure butanol,  $C_4H_9OH$ , (labelled  $B$ ) is to be fed into a semibatch reactor containing pure ethyl acetate,  $CH_3COOC_2H_5$ , (labelled  $A$ ) to produce butyl acetate,  $CH_3COOC_4H_9$ , ( $P$ ) and ethanol,  $C_2H_5OH$ , ( $S$ ). The reaction



is elementary and reversible, and is carried out isothermally at 300 K. Initially, there is  $V_0$  volume of  $A$  in the vat and  $B$  is fed at a volumetric flow rate of  $v$ . The initial concentrations of  $A$  and  $B$  are  $C_{A0}$  and  $C_{B0}$ , respectively.

Data:  $C_{A0} = 0.772$  mol/litre;  $C_{B0} = 1.093$  mol/litre;  $v = 0.5$  litre/s;  $V_0 = 2000$  litre;  $k_f = 9 \times 10^{-4}$  litre/mol.s at 300 K;  $K_{eqm} = k_f/k_b = 1.08$  at 300 K.

- (i) Starting from the definition of  $x_A$  (conversion of  $A$  defined in terms of the initial amount of  $A$  present in the vat), obtain the following expression for concentration of  $A$  in the vat at time  $t$ :

$$C_A = \frac{C_{A0} V_0 (1 - x_A)}{V_0 + v t}$$

- (ii) Using the stoichiometric relationship among  $A$ ,  $B$ ,  $P$  and  $S$ , obtain the following expressions for the concentrations of  $B$ ,  $P$  and  $S$  in the vat at time  $t$ :

$$C_B = \frac{C_{B0} v t - C_{A0} V_0 x_A}{V_0 + v t} \quad \text{and} \quad C_P = C_S = \frac{C_{A0} V_0 x_A}{V_0 + v t}$$

- (iii) Starting from the mass balance for  $A$  over the reactor, obtain the following differential equation:

$$\frac{dx_A}{dt} = \frac{k_f (1 - x_A) (C_{B0} v t - C_{A0} V_0 x_A)}{(V_0 + v t)} - \frac{k_b C_{A0} V_0 x_A^2}{(V_0 + v t)}$$

- (iv) Show that the equilibrium conversion of  $A$  is given by

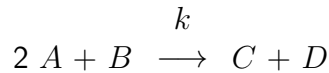
$$x_{A,eqm} = (-b + \sqrt{b^2 + 4ac}) / (2a)$$

where  $a = 1/K_{eqm} - 1$ ;  $b = 1 + C_{B0} v t / (C_{A0} V_0)$  and  $c = C_{B0} v t / (C_{A0} V_0)$ .

- (v) Solve the differential equation of part (iii) using MATLAB™ and plot the following:
- $x_{A,eqm}$  and  $x_A$  as function of  $t$  showing  $x_A$  approaching  $x_{A,eqm}$
  - volume of the reacting mixture  $V$  as function of  $t$
  - $C_B$  and  $C_P$  as function of  $t$
  - rate of reaction as function of  $t$
- (vi) Explain why the  $C_P$  profile and the rate of reaction profile experience maximums. Also, determine the values of  $V$  at  $x_{Af} = 0.85$  and at the maximum value of  $C_P$  in the reactor.
- (vii) Analyse the sensitivity of  $x_A$  and  $C_P$  to various values of  $v$ . Produce a brief report of the results to help your superior at the industry understand the sensitivity of the reaction system studied.

Source: P4-25 of the Reference (see the end).

**(3)** [Worth a 75% bonus on the marks gained for Set 10] The liquid-phase reaction



is carried out in a semibatch reactor of volume  $V_T$ . The reactor initially contains  $N_{B0}$  amount of  $B$  at a concentration of  $C_{B0}$ .  $A$  at an aqueous concentration of  $C_{A0}$  is fed to the reactor at a rate of  $v$ . The reaction rate in terms of  $A$  is first-order in  $A$  and half-order in  $B$ . The feed rate to the reactor is discontinued when the fluid volume in the reactor reaches  $V_s$ .

*Data:*  $C_{A0} = 0.03 \text{ kmol/m}^3$ ;  $C_{B0} = 0.015 \text{ kmol/m}^3$ ;  $N_{B0} = 5 \text{ mol}$ ;  $v = 0.004 \text{ m}^3/\text{min}$ ;  $V_s = 0.533 \text{ m}^3$ ;  $V_T = 1.2 \text{ m}^3$ ;  $k = 6 \text{ (m}^3/\text{kmol)}^{1/2}/\text{min}$

- (i) Show that the feed is stopped at  $t_s = 50 \text{ min}$ .
- (ii) Starting from the definition of  $x_B$  (conversion of  $B$  defined in terms of the initial amount of  $B$  present in the vat), obtain the following expression for concentration of  $B$  in the vat at time  $t$ :

$$C_B = \frac{C_{B0} V_0 (1 - x_B)}{V_0 + v t} \quad \text{for } t < t_s \quad \text{and} \quad C_B = \frac{C_{B0} V_0 (1 - x_B)}{V_s} \quad \text{for } t \geq t_s$$

- (iii) Using the stoichiometric relationship among  $A$ ,  $B$ ,  $C$  and  $D$ , obtain the following expressions for the concentrations of  $A$ ,  $C$  and  $D$  in the vat at time  $t$ :

$$C_A = \frac{C_{A0} v t - 2 C_{B0} V_0 x_B}{V_0 + v t} \quad \text{and} \quad C_C = C_D = \frac{C_{B0} V_0 x_B}{V_0 + v t} \quad \text{for } t < t_s$$

$$C_A = \frac{C_{A0} (V_s - V_0) - 2 C_{B0} V_0 x_B}{V_s} \quad \text{and} \quad C_C = C_D = \frac{C_{B0} V_0 x_B}{V_s} \quad \text{for } t \geq t_s$$

- (iv) Starting from the mass balance for  $A$  over the reactor, obtain the following differential equation:

$$\frac{dx_B}{dt} = \frac{k (C_{A0} v t - 2 C_{B0} V_0 x_B) \sqrt{1 - x_B}}{2 \sqrt{C_{B0} V_0 (V_0 + v t)}} \quad \text{for } t < t_s$$

$$\frac{dx_B}{dt} = \frac{k [C_{A0} (V_s - V_0) - 2 C_{B0} V_0 x_B] \sqrt{1 - x_B}}{2 \sqrt{C_{B0} V_0 V_s}} \quad \text{for } t \geq t_s$$

- (v) Solve the differential equations of part (iv) with appropriate initial conditions using MATLAB™ and plot:
- $x_B$  as function of  $t$  upto  $t = t_s$  and beyond  $t = t_s$
  - volume of the reacting mixture  $V$  as function of  $t$
  - $C_A$  as a function of  $t$
  - $C_B$  and  $C_C$  as functions of  $t$
- (vi) Explain the behaviour of  $C_A$  and  $C_B$  profiles before and after discontinuing the feed to the reactor.

*Source:* P4-27 of the Reference (see below).

Reference: FOGLER, H.S., *Elements of Chemical Reaction Engineering*, Second Edition, Prentice-Hall International Editions.