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Ph.D. Qualifying Examination 05/31/2001
Advanced Chemical Reaction Engineering

(20%) **1.** Hydrocarbon A decomposes as follows to form product molecules R_1, R_2, ..., while X_1^* and X_2^* are free radical intermediates.

$$\begin{cases} A \longrightarrow R_1 + X_1^* \text{ (rate constant} = k_1\text{, the slowest step)} & \text{(i)} \\ A + X_1^* \longrightarrow R_2 + X_2^* \text{ (rate constant} = k_2\text{)} & \text{(ii)} \\ X_2^* \longrightarrow R_3 + X_1^* \text{ (rate constant} = k_3\text{)} & \text{(iii)} \\ 2\,X_1^* \longrightarrow R_4 \text{ (rate constant} = k_4\text{)} & \text{(iv)} \end{cases}$$

(a) Derive expressions for the concentrations of X_1^* ($[X_1^*]$) and X_2^* ($[X_2^*]$) during the reaction.

(b) Derive a rate expression for the disappearance of A.

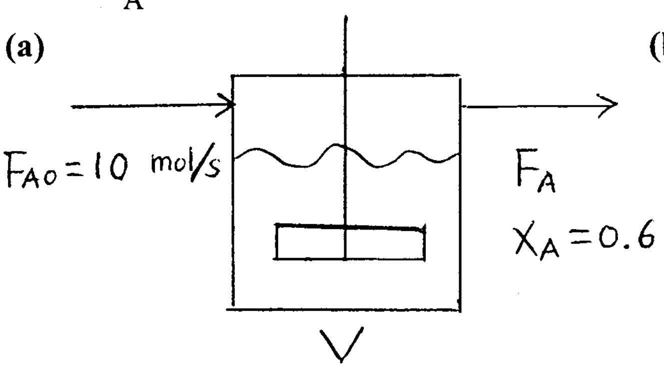
(15%) **2.** Briefly describe the primary characteristics (the reaction rate, residence time distribution (RTD), temperature control and operational flexibility) of **(a)** a batch reaction system, **(b)** a continuous stirred tank reactor (CSTR) and **(c)** a semibatch reaction system.

(15%) **3.** For a particular chemical reaction, the reaction rate ($-r_A$) can be expressed as

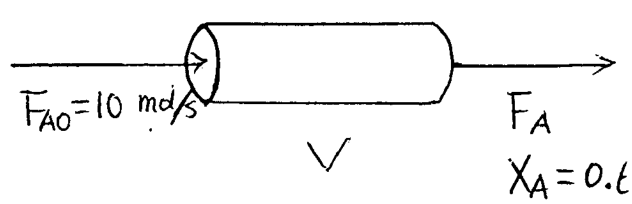
$$-r_A = \begin{cases} 1/(200 + 500\,X_A), & 0 \leqq X_A < 0.4 \\ 1/(1000\,X_A), & 0.4 \leqq X_A \leqq 0.8 \end{cases}$$

where X_A is the fractional conversion of A. Size the following reaction systems:

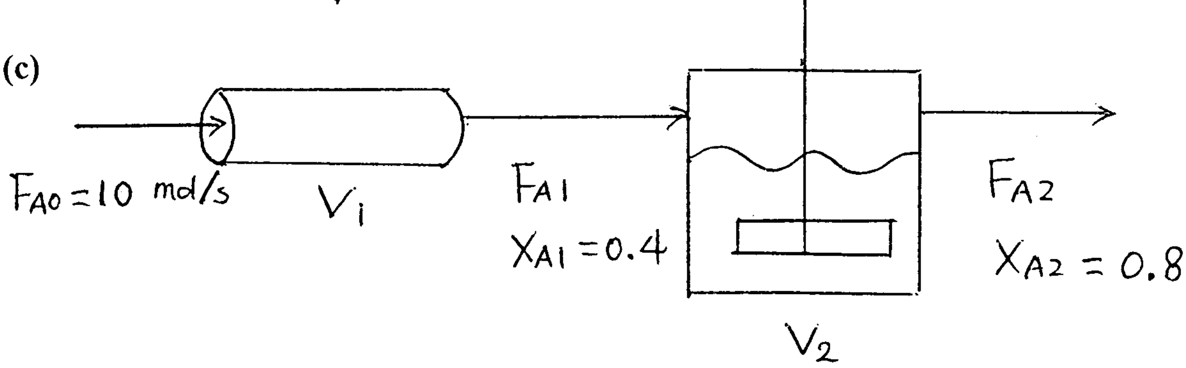
(a)



(b)



(c)



4. For the reaction A + B --> products, immiscible A and B are introduced into a 10-liter batch reactor and after 1 hr conversion of A is found to be 98%. For phase A: C_{A0} = 1 mol/liter, V_A = 6 liters and for phase B: C_{B0} = 2 mol/liter, V_B = 4 liters. Determine the value of the rate constant for $-r_A=kC_AC_B$ (10%)

5. A homogeneous decomposition reaction, A --> R, is carried out in a stainless steel paddle type mixed flow reactor (void volume in the reactor, V = 0.8 liter, Cao = 100 mol/liter, and total surface in the reactor, S = 800 cm^2). Data show that Ca = 20 mol/liter at τ = 40 sec and Ca = 40 mol/liter at τ = 10 sec. However, one suspects that the stainless steel surface would catalyze the reaction. To verify this suspect, additional stainless steel surface is introduced in the reactor (V = 0.75 liter, S = 1500 cm^2). Under such condition, data show that Ca = 20 mol/liter at τ = 26.7 sec and Ca = 40 mol/liter at τ = 7.5 sec. Find the kinetics of these simultaneous homogeneous and catalytic reactions. (10%)

6. A first-order heterogeneous irreversible reaction, A --> B, is taking place within a spherical catalyst pellet. The reactant concentration halfway between the external surface and the center of the pellet is equal to 1/10 of the concentration of the pellet external surface. The concentration at the external surface (Cas) is 0.001 gmol/dm^3, the diameter of the pellet (2R) is $2x10^{-3}$ cm and the diffusion coefficient (De) is 0.1 cm^2/s.
   (a) What is the concentration of reactant at a distance of $7x10^{-4}$ cm in from the external pellet surface? (10%)
   (b) To what diameter should the pellet be reduced if the effectiveness factor (η) is to be 0.8? (10%)
   Please note that for the first-order reaction Thiele modulus $\Phi_1 = k_1 R Sa \rho / De$, and $\eta = 3(\Phi_1 \coth(\Phi_1)-1)/\Phi_1^2$, $Ca/Cas = \sinh(\Phi_1 \lambda)/ \lambda \sinh(\Phi_1)$, $\lambda = r/R$.

7. Please explain why some effectiveness factors (η) are greater than 1. For a single set of Thiele modulus, Arrhenius number and heat-of-reaction parameter, sometimes three values of effectiveness factor exist. What kinds of temperature profile (steep or flat) and reaction-limited step (mass transfer or chemical reaction) correspond to the highest η and to the lowest η, respectively ? (10%)