M. Tech. (Chemical Engg.), Adv. Reaction Engg.
Solution _   (MCH 103)

Q.1.

$$CNBr + CH_3NH_2 \longrightarrow CH_3Br + NCNH_2$$

$$A + B \longrightarrow C + D \qquad \text{(irreversible rea}^n\text{)}$$

Semibatch Reactor_

$C_{B_0} = 0.025 \text{ mol/dm}^3$

$V_0 = 0.05 \text{ dm}^3/s$

$k = 2.2 \text{ dm}^3/s.mol$

$V = 5 dm^3$

$C_{A_0} = 0.05 \dfrac{mol}{dm^3}$

plot C_A and $-r_A$ vs. t

$$\frac{dC_A}{dt} = (-r_A) - \frac{V_0 C_A}{V}$$

$$X_A = 1 - \frac{C_A}{C_{A_0}}$$

$$\frac{dC_A}{dt} = (-kC_A C_B) - \frac{V_0 C_A}{(V_0 + V_0 t)}$$

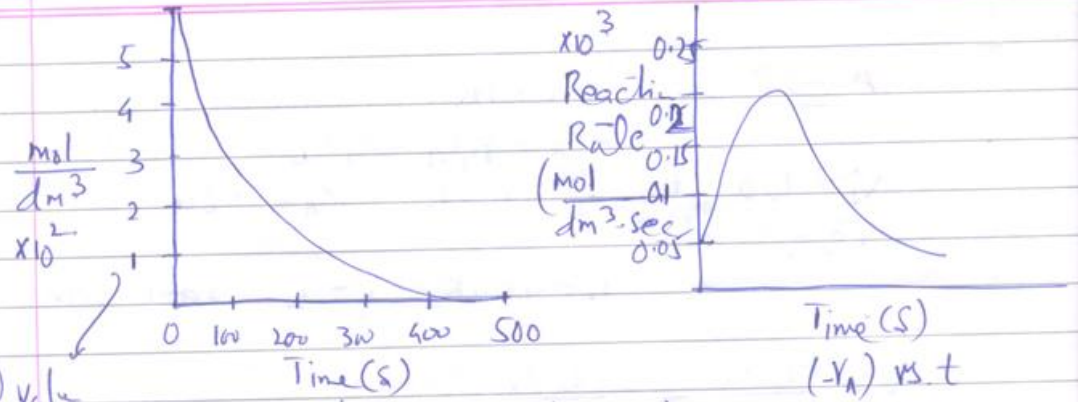$$\frac{dC_A}{dt} = \left\{ kC_{A_0}(1-X_A)C_{B_0}(1-X_B) \right\} - \frac{V_0 C_{A_0}(1-X_A)}{V_0 + V_0 t}$$

$$= \left\{ 2.2 \times 0.05(1-X_A) \, 0.025(1-X_B) \right\} - \frac{0.05 \times 0.05(1-X_A)}{(5 + 0.05t)}$$

$$X_A = \frac{N_{A_0} - N_A}{N_{A_0}} = \frac{C_{A_0}V_0 - C_A V}{C_{A_0} V_0}$$

Initial conditions are t=0, $C_{A_0} = 0.05 \dfrac{mol}{dm^3}$, $C_B = C_C = C_D = 0$
and $V_0 = 5 dm^3$
$k = 2.2 \text{ dm}^3/s.mol$.

Assume t from 0 to 500 Sec and Cal. C_A & $(-r_A)$

$\frac{mol}{dm^3} \times 10^2$

5
4
3
2
1

0   100   200   300   400   500

Time (s)

Actual value is 1×10^{-2}

Conc. of A (methyl cyanide vs t).

$\times 10^3$

Reaction Rate $\left(\frac{mol}{dm^3 \cdot sec}\right)$

0.25
0.2
0.15
0.1
0.05

Time (S)

$(-r_A)$ vs. t

Q.1 b)

$$A \rightleftharpoons B \qquad \text{mixed flow reactor}$$

$$T = 300 \text{ K} \qquad V = 100 \text{ liters} \qquad X_A = 0.60$$
$$T = 400 \text{ K} \qquad V = ? \qquad X_A = 0.60$$

$$V = \frac{F_{A_0} X_A}{-r_A} \qquad \qquad \text{U_0 is same in both the cases}$$

$$V = \frac{F_{A_0} X_A}{k_1 C_A - k_2 C_B} = \frac{C_{A_0} U_0 X_A}{k_1 \left(C_A - \frac{C_B}{K}\right)} = \frac{C_{A_0} U_0 X_A}{k_1 \left(C_{A_0}(1 - X_A) - \frac{C_{A_0} X_A}{K}\right)}$$

$$V = \frac{C_{A_0} U_0 X_A}{C_{A_0} k_1 \left((1 - X_A) - \frac{X_A}{K}\right)}$$

$$\therefore V = \frac{U_0 X_A}{k_1 \left((1 - X_A) - \frac{X_A}{K}\right)}$$

Calculate k_1 and K at 300 K and 400 K using formulae —

$$k_1 = 10^3 \exp\left(\frac{-2416}{T}\right) \qquad \begin{array}{l} \text{at 300 K} \quad k_1 = 0.318 \\ \text{at 400 k} \quad k_1 = 2.38 \end{array}$$

$$K = K(T_1) \exp\left(\frac{\Delta H_R}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

$$K_{400} = 10 \exp\left(\frac{-8000}{1.987}\left(\frac{1}{300} - \frac{1}{T}\right)\right) = \cancel{0.379} \; 9.96$$

$$V_{300} = \frac{U_0 \times 0.60}{0.318\left(0.4 - \frac{0.6}{10}\right)} = 5.549 U_0$$

$$V_{400} = \frac{U_0 \times 0.60}{2.38\left(0.4 - \frac{0.6}{9.96}\right)} = 0.7419 \, U_0$$

$$100 = 5.549 \, V_o$$

$$V_{(4w)} = 0.7419 \, V_o$$

$$\frac{100}{V_{(4w)}} = \frac{5.549}{0.7419} = 7.47 \qquad \boxed{V = 13.37 \, \text{Liter}}$$

Volume of the reactor for the same feed rate & Conversion at 400k is 13.37 Liters

Q. 2. A)

## Kinetic Models for Nonelementary Reactions

To explain the kinetics of nonelementary reactions we assume that a sequence of elementary reactions is actually occurring but that we cannot measure or observe the intermediates formed because they are only present in very minute quantities. Thus, we observe only the initial reactants and final products, or what appears to be a single reaction. For example, if the kinetics of the reaction

$$A_2 + B_2 \rightarrow 2AB$$

$$A_2 \rightleftarrows 2A^*$$

$$A^* + B_2 \rightleftarrows AB + B^*$$

$$A^* + B^* \rightleftarrows AB$$
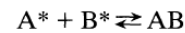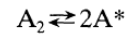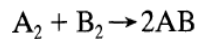
Free Radicals. Free atoms or larger fragments of stable molecules that contain one or more unpaired electrons are called free radicals. The unpaired electron is designated by a dot in the chemical symbol for the substance. Some free radicals are relatively stable, such as triphenylmethyl,
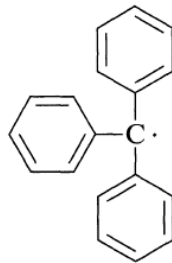
but as a rule they are unstable and highly reactive, such as

$$CH_3\cdot, \quad C_2H_5\cdot, \quad I\cdot, \quad H\cdot, \quad CCl_3\cdot$$
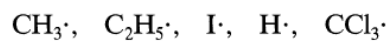
Ions and Polar Substances. Electrically charged atoms, molecules, or fragments of molecules, such as

$$N_3^-, \quad Na^+, \quad OH^-, \quad H_3O^+, \quad NH_4^+, \quad CH_3OH_2^+, \quad I^-$$
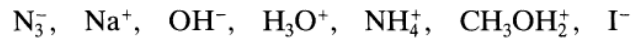
are called ions. These may act as active intermediates in reactions.

Molecules. Consider the consecutive reactions

$$A \rightarrow R \rightarrow S$$

Ordinarily these are treated as multiple reactions. However, if the intermediate R is highly reactive its mean lifetime will be very small and its concentration in the reacting mixture can become too small to measure. In such a situation R may not be observed and can be considered to be a reactive intermediate.

Transition Complexes. The numerous collisions between reactant molecules result in a wide distribution of energies among the individual molecules.
Above model can be explained in brief by giving examples of mechanism

Q. 2 B) Exothermic Reactions in Mixed Flow Reactors

- For exothermic reactions in mixed flow (or close to mixed flow) an interesting situation may develop in that more than one reactor composition may satisfy the governing material and energy balance equations. This means that we may not know which conversion level to expect. van Heerden (1953, 1958) was the first to treat this problem.

- Consider reactant fluid fed at a given rate (fixed r or *VIF,,*) to a mixed flow reactor. At each reactor temperature there will be some particular conversion.

- At low temperature the rate is low so this conversion is low.

- At higher temperature the conversion rises and approaches the equilibrium. At a still higher temperature we enter the region of falling equilibrium so the conversion for given T will likewise fall.

- Figure below shows this behavior for different T values.
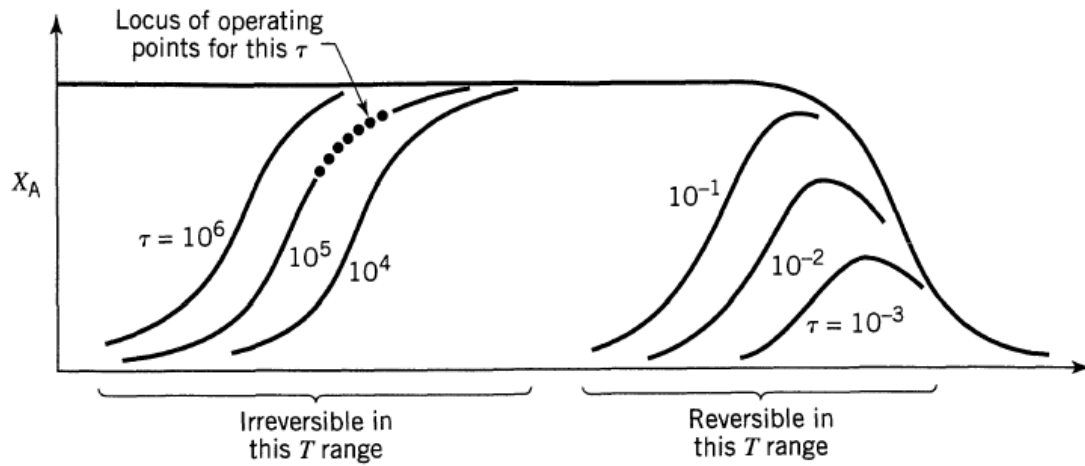
- For a given feed temperature T_1 the intersection of the energy balance line with the S-shaped material balance line for the operating τ gives the conditions within the reactor. Here three cases sare distinguished. These are shown in Fig. below for *irreversible reactions.*
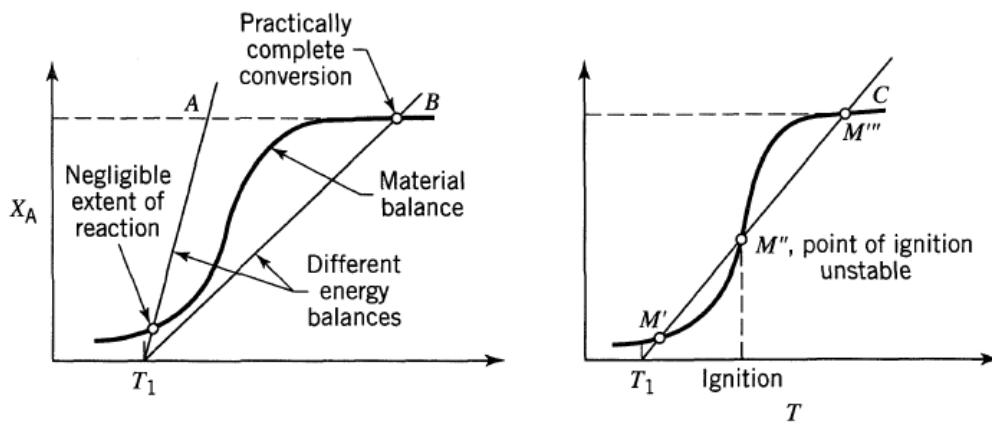
Q.2 c)

$A \longrightarrow R$ Batch Reactor

$C_{A_0} = 2.03$ mol/Lit $\}$ Conc. drop in

$C_{Af} = 1.97$ mol/Lit $\}$ One min.

− Find rate Eq^n for 2nd order reaction?

Design Eq^n for Batch reactor −

(in terms of conc.)

$$t = -\int_{C_{A_0}}^{C_A} \frac{dC_A}{-r_A} = -\int_{C_{A_0}}^{C_A} \frac{dC_A}{kC_A^2} = \frac{-1}{k} \cdot \int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A^2}$$

$$t = -\frac{1}{k} \left[\frac{C_A^{-2+1}}{-2+1} \right]_{C_{A_0}}^{C_{Af}} = -\frac{1}{k} \left[-\frac{1}{C_A} \right]_{C_{A_0}}^{C_{Af}} = \frac{1}{k} \left[\frac{1}{C_{Af}} - \frac{1}{C_{A_0}} \right]$$

$$k = \frac{1}{t} \left[\frac{1}{C_{Af}} - \frac{1}{C_{A_0}} \right] = \frac{1}{1} \left[\frac{1}{1.97} - \frac{1}{2.03} \right]$$

$$k = 0.015 \ min^{-1} con^{-1}$$

$$\boxed{\therefore \text{Rate } Eq^n, \quad -r_A = 0.015 \ (min^{-1} con^{-1}) \ C_A^2}$$

Q.2 d) $-r_{A_1} = k C_{A_1}^n$ $\Rightarrow$ $-3 r_{A_2} = k (2 C_{A_1})^n$

$C_A \Rightarrow 2 C_A$

$-r_A \Rightarrow 3 \ times \ (-r_A)$

$$\frac{-r_{A_1}}{-3 r_{A_1}} = \frac{k C_{A_1}^n}{k \, 2^n \, C_{A_1}^n} \quad \Rightarrow \quad \frac{1}{3} = \frac{1}{2^n}$$

$$2^n = 3 \quad \Rightarrow \quad n = 1.585$$

Order of the reaction