CHEN 416: CHEMICAL REACTION ENGINEERING II

IDEAL REACTORS FOR HOMOGENOUS REACTION AND THEIR PERFORMANCE EQUATIONS

LEARNING OBJECTIVES

- At the end of this week's lecture, students should be able to:
  - Differentiate between the three ideal reactors
  - Develop and apply the performance equation for batch reactor
  - Develop and apply the performance equation for mixed flow reactors.

IDEAL REACTORS

- Ideal reactors usually represents **the best way of contacting the reactants** - no matter the operation. They are relatively easy to treat. They include the BR, Steady-state flow (PFR and MFR)

- In the batch reactor (BR):
  - The operation is unsteady-state
  - composition changes with time;
  - however, the composition is uniform throughout the reactor at any instant. (Why is this so?)

Uniformly mixed

- In the Plug flow reactor (PFR):
  - *aka* slug flow, piston flow, tubular flow, or unmixed flow reactor
  - the flow of fluid through the reactor is orderly with no element of fluid overtaking or mixing with any other element ahead or behind.
  - there may be lateral mixing of fluid but no mixing or diffusion along the flow path.
  - the residence time in the reactor must be the same for all elements of fluid.

Feed   Product

3
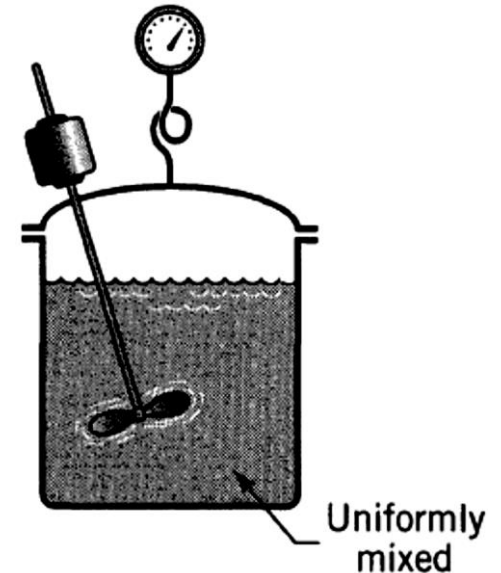
IDEAL REACTORS

- The Mixed flow reactor (MFR):
  - aka the back-mix reactor, the ideal stirred tank reactor, CSTR, or the CFSTR (constant flow stirred tank reactor)
  - contents are well stirred and uniform throughout
  - the exit stream from the reactor has the same composition as the fluid within the reactor.

- Real reactors are often designed so that their flows approach those of the ideals reactors.

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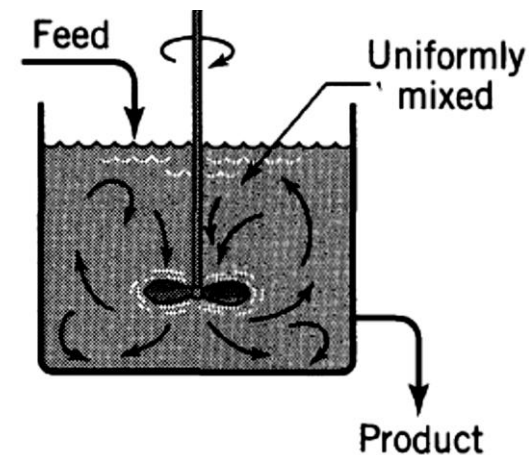
BATCH REACTOR PERFORMANCE EQUATION

❑ Making a material balance for any component A in a BR, since the composition is uniform throughout at any instant of time, and no fluid enters or leaves the reaction mixture during reaction, we have,

$$= 0 \qquad = 0$$

$$\text{input} = \text{output} + \text{disappearance} + \text{accumulation}$$

or

$$+ \begin{pmatrix} \text{rate of loss of reactant A} \\ \text{within reactor due to} \\ \text{chemical reaction} \end{pmatrix} = - \begin{pmatrix} \text{rate of accumulation} \\ \text{of reactant A} \\ \text{within the reactor} \end{pmatrix} \qquad (1)$$

❑ Evaluating the terms of Eq. 1, we find

$$\begin{matrix} \text{disappearance of A} \\ \text{by reaction,} \\ \text{moles/time} \end{matrix} = (-r_A)V = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})} \right) (\text{volume of fluid})$$

$$\begin{matrix} \text{accumulation of A,} \\ \text{moles/time} \end{matrix} = \frac{dN_A}{dt} = \frac{d[N_{A0}(1 - X_A)]}{dt} = -N_{A0}\frac{dX_A}{dt}$$

BATCH REACTOR PERFORMANCE EQUATION

❑ By replacing these two terms in Eq. 1, we obtain

$$(-r_A)V = N_{A0}\frac{dX_A}{dt} \qquad (2)$$

❑ Rearranging and integrating then gives

$$t = N_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)V} \qquad (3)$$

- Eqn.3 is the general equation showing the time required to achieve a conversion X_A for either isothermal or non-isothermal operation.
- The volume of reacting fluid and the reaction rate remain under the integral sign, since they both change as reaction proceeds.

- Eqn.3 may be simplified for a number of situations.

- For fluid of constant density, we obtain

$$t = C_{A0}\int_0^{X_A}\frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_A}\frac{dC_A}{-r_A} \qquad \text{for } \varepsilon_A = 0 \qquad (4)$$
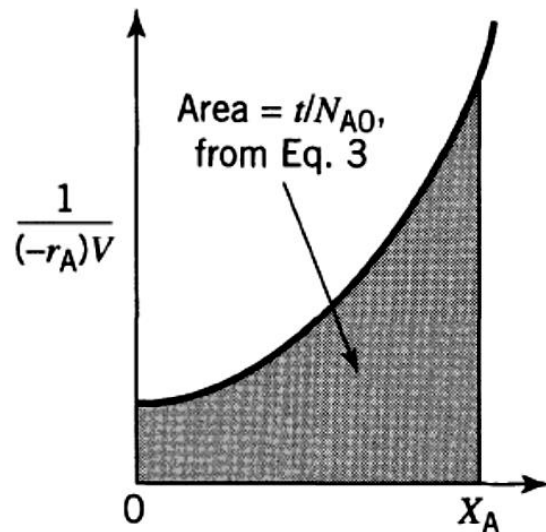
BATCH REACTOR PERFORMANCE EQUATION

- For reactions in which the volume of fluid vary with conversion (i.e. density changes, gas-phase reactions), Eqn.**3** becomes
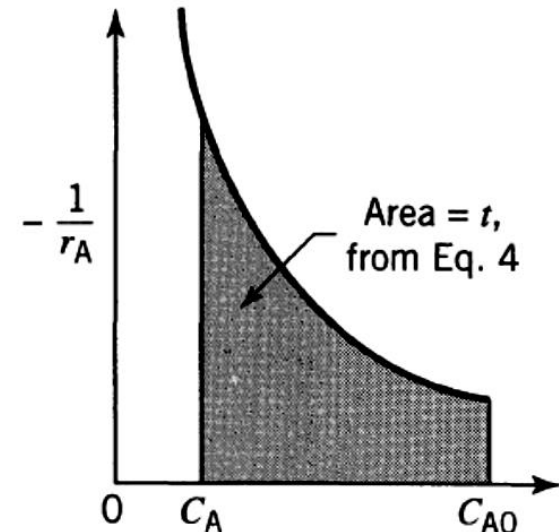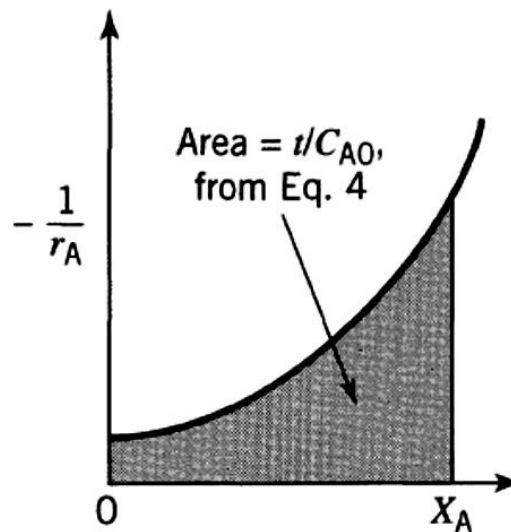
$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)V_0(1 + \varepsilon_A X_A)} = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)(1 + \varepsilon_A X_A)} \qquad (5)$$

- Eqns.3-5, the performance equations for BRs are applicable to both isothermal and non-isothermal operations.

General case

Constant-density systems only

Area = t/N_{AO}, from Eq. 3

Area = t/C_{AO}, from Eq. 4

Area = t, from Eq. 4

SPACE-TIME AND SPACE-VELOCITY

- As reaction time t is to batch reactor, so are the space-time and space-velocity the proper performance measures of flow reactors.

- They are defined as follows:

- Space-time:

$$\tau = \frac{1}{s} = \left(\begin{array}{c} \text{time required to process one} \\ \text{reactor volume of feed measured} \\ \text{at specified conditions} \end{array} \right) = [\text{time}] \qquad (6)$$

- Space velocity:

$$s = \frac{1}{\tau} = \left(\begin{array}{c} \text{number of reactor volumes of} \\ \text{feed at specified conditions which} \\ \text{can be treated in unit time} \end{array} \right) = [\text{time}^{-1}] \qquad (7)$$

- A space-time of 2 min means that every 2 min one reactor volume of feed at specified conditions is being treated by the reactor.

- A space-velocity of 5 hr-l means that five reactor volumes of feed at specified conditions are being fed into the reactor per hour.

SPACE-TIME AND SPACE-VELOCITY

❑ Space-velocity or space-time depends on the conditions selected.

❑ If they are of the stream entering the reactor, the relation between **s** and τ and the other pertinent variables is

$$\tau = \frac{1}{s} = \frac{C_{A0}V}{F_{A0}} = \frac{\left(\dfrac{\text{moles A entering}}{\text{volume of feed}}\right)(\text{volume of reactor})}{\left(\dfrac{\text{moles A entering}}{\text{time}}\right)} \qquad (8)$$

$$= \frac{V}{v_0} = \frac{(\text{reactor volume})}{(\text{volumetric feed rate})}$$

❑ The relation between the space-velocity and space-time for actual feed conditions (unprimed symbols) and at standard conditions (designated by primes) is given by

$$\tau' = \frac{1}{s'} = \frac{C'_{A0}V}{F_{A0}} = \tau\frac{C'_{A0}}{C_{A0}} = \frac{1}{s}\frac{C'_{A0}}{C_{A0}} \qquad (9)$$

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MIXED FLOW REACTOR PERFORMANCE EQUATION

❑ Making a material balance for component A in a MFR, since the composition is uniform throughout, we have,

$$= 0$$

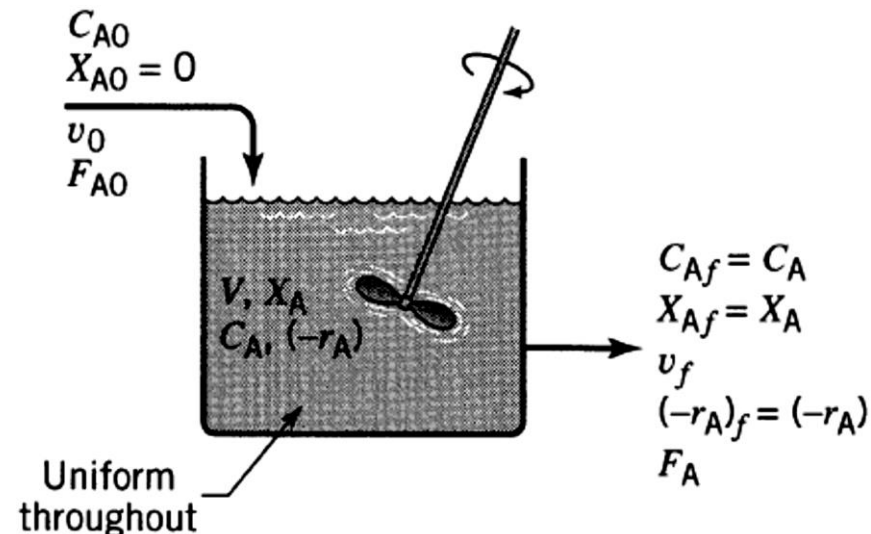$$\text{input} = \text{output} + \text{disappearance by reaction} + \text{accumulation} \qquad (10)$$

❑ From the figure,

✓ input of A, moles/time $= F_{A0}(1 - X_{A0}) = F_{A0}$

✓ output of A, moles/time $= F_A = F_{A0}(1 - X_A)$

disappearance of A by reaction, moles/time $= (-r_A)V$

$$= \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})}\right)\left(\begin{array}{c}\text{volume of}\\\text{reactor}\end{array}\right)$$

C_{A0}
$X_{A0} = 0$
v_0
F_{A0}

V, X_A
$C_A, (-r_A)$

Uniform throughout

$C_{Af} = C_A$
$X_{Af} = X_A$
v_f
$(-r_A)_f = (-r_A)$
F_A

MIXED FLOW REACTOR PERFORMANCE EQUATION

- Introducing these three terms into Eq. 10, we obtain

$$F_{A0}X_A = (-r_A)V$$

- which on rearrangement becomes

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{\Delta X_A}{-r_A} = \frac{X_A}{-r_A}$$

-     or

$$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{-r_A}$$

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  - for any ε_A and where X_A and r_A are measured at exit stream conditions, which are the same as the conditions within the reactor.

- For constant density system,

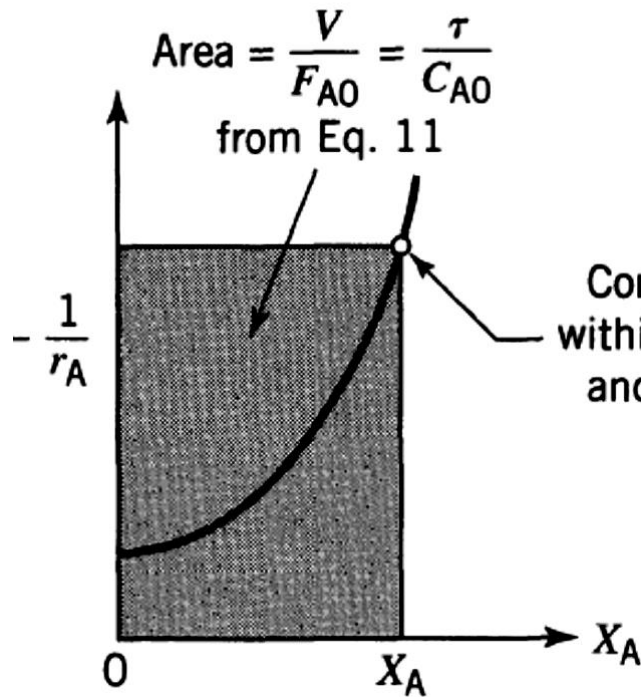$$\frac{V}{F_{A0}} = \frac{X_A}{-r_A} = \frac{C_{A0} - C_A}{C_{A0}(-r_A)}$$

-     or   for $\varepsilon_A = 0$

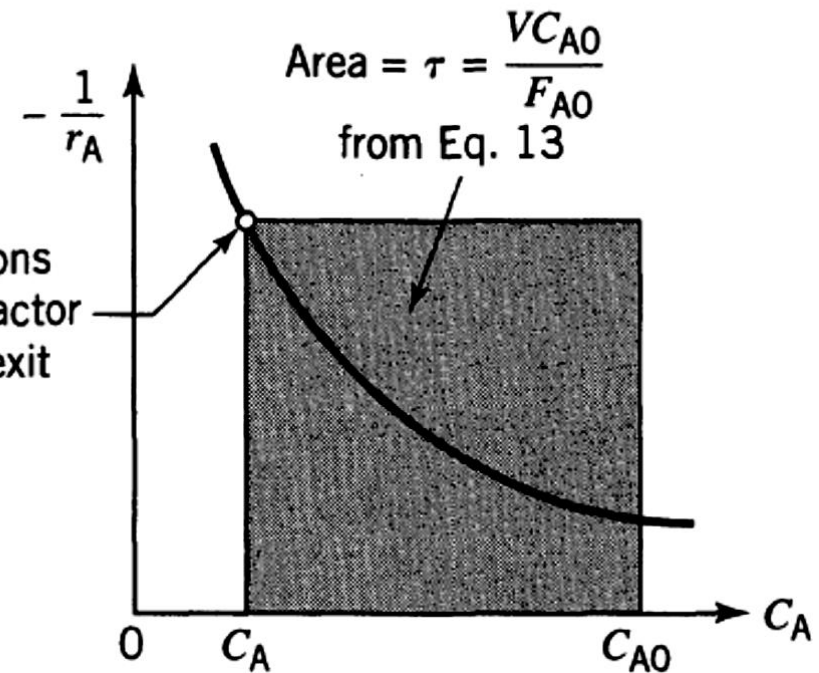$$\tau = \frac{V}{v} = \frac{C_{A0}X_A}{-r_A} = \frac{C_{A0} - C_A}{-r_A}$$

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GRAPHICAL REPRESENTATION OF MFR

SPECIAL CASES

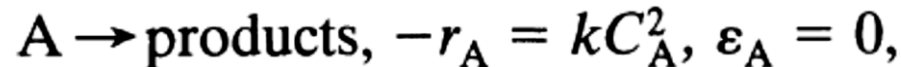- For *first-order reaction* constant density systems, the performance expression is

$$k\tau = \frac{X_A}{1 - X_A} = \frac{C_{A0} - C_A}{C_A} \qquad \text{for } \varepsilon_A = 0$$

13a

- for any ε_A, Eqn.11 for *first-order reaction* becomes

$$k\tau = \frac{X_A(1 + \varepsilon_A X_A)}{1 - X_A}$$

13b

for $\quad V = V_0(1 + \varepsilon_A X_A) \quad$ and $\quad \dfrac{C_A}{C_{A0}} = \dfrac{1 - X_A}{1 + \varepsilon_A X_A}$

- For *second-order reaction*,

$$A \rightarrow \text{products}, \ -r_A = kC_A^2, \ \varepsilon_A = 0,$$

- the performance equation of Eq. 11 becomes

$$k\tau = \frac{C_{A0} - C_A}{C_A^2} \quad \text{or} \quad C_A = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau}$$

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SPECIAL CASES

- If the feed on which conversion is based (i.e. with subscript 0), enters the reactor partially converted (with subscript i), and leaves at conditions given by subscript *f*, we have

$$\frac{V}{F_{A0}} = \frac{\Delta X_A}{(-r_A)_f} = \frac{X_{Af} - X_{Ai}}{(-r_A)_f}$$
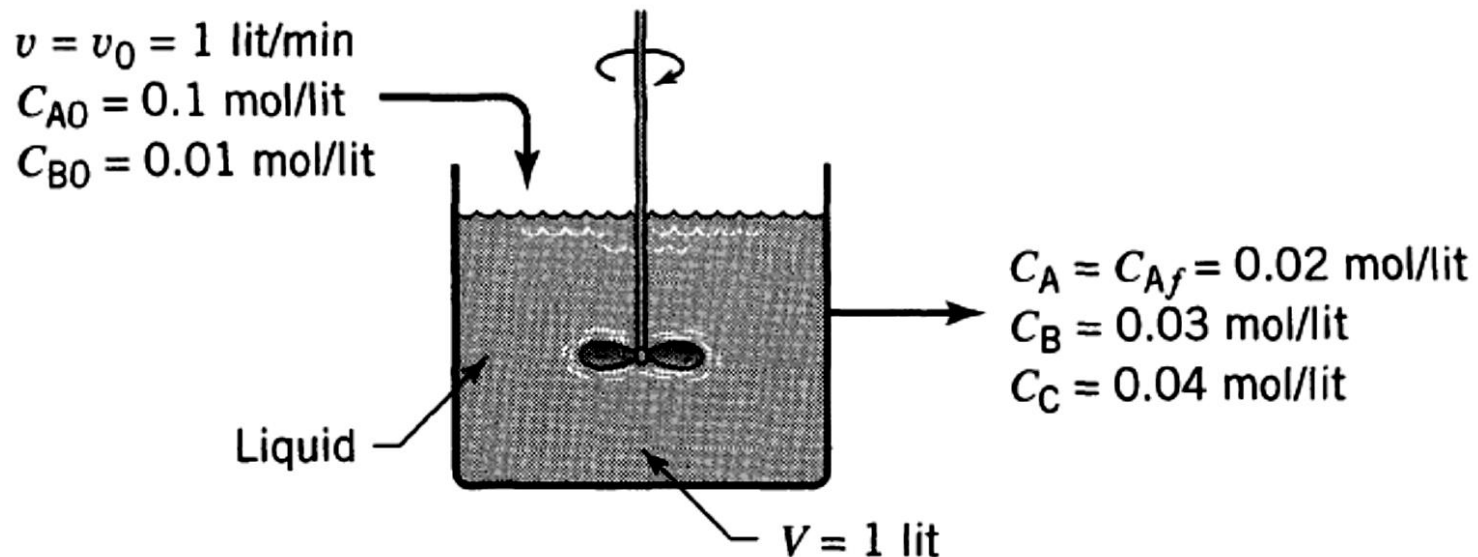
or

$$\tau = \frac{V C_{A0}}{F_{A0}} = \frac{C_{A0}(X_{Af} - X_{Ai})}{(-r_A)_f}$$

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EXAMPLE 1

- One liter per minute of liquid containing A and B (C_{A0} = 0.10 mol/liter, C_{B0} = 0.01 mol/liter) flow into a mixed reactor of volume V = 1 liter. The materials react in a complex manner for which the stoichiometry is unknown. The outlet stream from the reactor contains A, B, and C (C_{Af} = 0.02 mol/liter, C_{Bf} = 0.03 mol/liter, C_{Cf} = 0.04 mol/liter), as shown in the Figure below. Find the rate of reaction of A, B, and C for the conditions within the reactor.

$v = v_0$ = 1 lit/min
C_{A0} = 0.1 mol/lit
C_{B0} = 0.01 mol/lit

$C_A = C_{Af}$ = 0.02 mol/lit
C_B = 0.03 mol/lit
C_C = 0.04 mol/lit

Liquid

V = 1 lit

SOLUTION

- For a liquid in a mixed flow reactor $\varepsilon_A = 0$ and Eq. 12 applies to each of the reacting components, giving for the rate of disappearance:

- For $-r_A$

$$-r_A = \frac{C_{A0} - C_A}{\tau} = \frac{C_{A0} - C_A}{V/v}$$

- Substituting, we have:

$$= \frac{0.10 - 0.02}{1/1} = 0.08 \text{ mol/liter} \cdot \text{min}$$

- For $-r_B$

$$-r_B = \frac{C_{B0} - C_B}{\tau}$$

- Substituting, we have:

$$= \frac{0.01 - 0.03}{1} = -0.02 \text{ mol/liter} \cdot \text{min}$$

- For $-r_B$

$$-r_C = \frac{C_{C0} - C_C}{\tau}$$
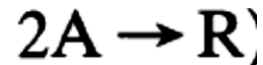
- Substituting, we have:

$$= \frac{0 - 0.04}{1} = -0.04 \text{ mol/liter} \cdot \text{min}$$

- Thus A is disappearing while B and C are being formed.

EXAMPLE 2

Pure gaseous reactant A (C_{A0} = 100 millimol/liter) is fed at a steady rate into a mixed flow reactor (V = 0.1 liter) where it dimerizes

$$2A \rightarrow R$$

For different gas feed rates the following data are obtained:

Run number	1	2	3	4
v_0, liter/hr	10.0	3.0	1.2	0.5
C_{Af}, millimol/liter	85.7	66.7	50	33.4

Find a rate equation for this reaction.

SOLUTION

For the stoichiometry, the expansion factor is

$$\varepsilon_A = \frac{1-2}{2} = -\frac{1}{2}$$

the corresponding relation between concentration and conversion is

$$\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A} = \frac{1 - X_A}{1 - \frac{1}{2} X_A}$$

EXAMPLE 2 SOLUTION

- or

$$X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/C_{A0}} = \frac{1 - C_A/C_{A0}}{1 - C_A/2C_{A0}}$$

- The conversion for each run is then calculated and tabulated

Run	Given v_0	C_A	$\overline{X_A}$
1	10.0	85.7	0.25
2	3.0	66.7	0.50
3	1.2	50	0.667
4	0.5	33.3	0.80

- From the performance equation, Eqn. *11,* the rate of reaction for each run is given by

$$(-r_A) = \frac{v_0 C_{A0} X_A}{V}, \qquad \left[\frac{\text{millimol}}{\text{liter} \cdot \text{hr}}\right]$$

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EXAMPLE 2 SOLUTION

- $-r_A$, log C_A and log $(-r_A)$ are then calculated for each of the run and tabulated as shown below to test for the kinetics of the reaction,

$(-r_A)$	log C_A	log $(-r_A)$
2500	1.933	3.398
1500	1.824	3.176
800	1.699	2.903
400	1.522	2.602

- Testing for nth-order kinetics. For this take logarithms of

$$-r_A = kC_A^n$$

- Yielding

$$\log(-r_A) = \log k + n \log C_A$$

- For nth-order kinetics this data should give a straight line on a log $(-r_A)$ vs. log C_A plot.

EXAMPLE 2 SOLUTION

- From the Table four data points are reasonably represented by a straight line of slope 2, as shown in the graph
- so the rate equation for this dimerization is

$$-r_A = \left(0.36\,\frac{\text{liter}}{\text{hr}\cdot\text{millimol}}\right) C_A^2, \qquad \left[\frac{\text{millimol}}{\text{liter}\cdot\text{hr}}\right]$$

Slope $= \dfrac{3.398 - 2.602}{1.933 - 1.522}$

$= 1.93 \cong 2$

Fit the lowest point
$400 = k\,(33.3)^2$
$\therefore k = 0.36$

$\log(-r_A)$

$\log C_A$