\[(CH_3)_2COOC(CH_3)_3 \rightarrow C_2H_4 + 2CH_3COCH_3\]

Elementary gas phase reaction, isothermal, no \(\Delta P\)

\[A(g) \rightarrow B(g) + 2C(g)\]

\[k = 10^{-4} \text{ m}^3 \text{ mol}^{-1} \text{ min}^{-1}\] at \(50^\circ C = 323K\)

\[-\Gamma_A = k\left[\frac{P_A}{P_0}\right] \quad \text{E} = 2\]

\[E_A = 85 \text{ kJ/mol}\]

Pure \(A\) enters reactor at 10 atm, \(127^\circ C = 400K\)

\[F_{A0} = 2.5 \text{ mol/min}\]

Calculate the reactor volume and space-time \((\tau)\) to achieve 70% conv.

a) CSTR

\[V = \frac{F_{A0}X}{-\Gamma_A} \quad \tau = \frac{V}{V_0}\]

\[k_2 = \frac{e^{E - RT}}{k_2} \quad k_1 = \frac{e^{E - RT}}{k_1}\]

\[k_2 = 10^{-4} e^{32.65 - 25.56} \quad k_2 = 10^{-4} e^{4.441.4} = 4.441.4 \times 10^{-2} \text{ min}^{-1}\]

\[-\Gamma_A = k \cdot C_{A0} \left(\frac{1 - X}{1 + X}\right) = \left(4.441.4 \cdot 10^{-2}\right) \cdot \left(\frac{0.305 \text{ mol/L}}{1 + 1.8}\right) = 4.84 \times 10^{-4} \text{ mol/min L}\]

\[C_{A0} = \frac{P}{RT} = \frac{10 \text{ atm}}{0.0821(400)} = 0.305 \text{ mol/L}\]

\[V = \frac{\left(2.5 \text{ mol/min}\right)(0.9)}{4.84 \times 10^{-4} \text{ mol/min L}} = 4700 \text{ L} \quad \boxed{V = 4700 \text{ L}}\]

\[\tau = \frac{V}{V_0} = \frac{4700 \text{ L}}{572.47 \text{ min}} = 8.21 \text{ L/min}\]

\[V_0 = \frac{P \cdot KT}{F_{A0}} = \frac{(2.5 \text{ mol/min})(0.9)}{8.21 \text{ L/min}} = 8.21 \text{ L/min}\]
b) PFR

\[ V = \frac{F_{A0}}{kCA_0} \int_0^x \frac{dx}{1 - \frac{x}{1 + \xi}} \]

\[ V = \frac{F_{A0}}{kCA_0} \left[ (1 + \frac{x}{1 + \xi}) \ln \left( \frac{1 - x}{1 - \xi} \right) \right] \]

\[ V = \frac{F_{A0}}{kCA_0} \left[ \frac{1}{kCA_0} \left( 1 + \frac{x}{1 + \xi} \right) \ln \left( \frac{1 - x}{1 - \xi} \right) \right] \]

\[ V = \frac{2.5 \text{ mol/min}}{(0.4 \times 10^{-3})(305 \text{ mol/L})} \left[ \frac{3}{\ln(10)} - 1.8 \right] \]

\[ V = 185.47 \text{ L} \]

\[ V = 949.4 \text{ L} \]

\[ \frac{V}{V_0} = \frac{949.4 \text{ L}}{8.21 \text{ L/min}} = 115.44 \text{ min } \times \frac{5}{4} \]

C) Batch reactor (constant volume)

\[ t = \frac{N_{A0} x}{V_0} \int_0^x \frac{dx}{1 - \frac{x}{1 + \xi}} \]

\[ t = \frac{N_{A0}}{V_0} \int_0^x \frac{dx}{kCA_0 (1-x)} = \frac{1}{k} \ln \left( \frac{1 - x}{1 - \xi} \right) \]

\[ t = 0.4 \ln \left( \frac{1}{1.9} \right) = 52.3 \text{ min} \]

\[ t = 52.3 \text{ min} + 4 \text{ hr for turn over} \]

\[ t = 5 \text{ hrs} \]

3600 mol and we can do \( \frac{2.4 \text{ hrs}}{4 \text{ hrs}} = 4.8 = 4 \) batches per day

\[ \frac{3600}{4} = 900 \text{ mol/batch} \]

\[ V = \frac{900 \text{ mol}}{5} \text{ and must account for 8.2} \]

\[ V = \frac{(2700)(0.0821)(400)}{10} = 8867 \text{ L} \]
d) Assume the reaction is reversible \( K_c = 0.025 \text{ mol}^{-1} \text{L}^2 \)

\[
\gamma_A' = k \left( \frac{C_A}{K_c} \right) \text{ mol}^{-1} \text{L}^2 \\
K_p = \frac{P_0 X}{P_A}
\]

Need to find \( x_c \) for a flow system and a constant volume batch system.

### Stechiometric Table: Batch

<table>
<thead>
<tr>
<th>Species</th>
<th>Symbol</th>
<th>Initial</th>
<th>Change</th>
<th>Remaining</th>
<th>Corr</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NaO</td>
<td></td>
<td>-NaOx</td>
<td>NaO ( (1-x) )</td>
<td>CaO ( (1-x) )</td>
</tr>
<tr>
<td>B</td>
<td>O</td>
<td></td>
<td>+NaOx</td>
<td>NaO ( x )</td>
<td>CaOx</td>
</tr>
<tr>
<td>C</td>
<td>O</td>
<td></td>
<td>+2NaOx</td>
<td>NaO ( 2x )</td>
<td>2CaOx</td>
</tr>
</tbody>
</table>

\[ C_{NaO} = 0.305 \text{ mol/L} \]

\[
\gamma_A' = k \left( \frac{C_{NaO}(1-x)}{C_{NaO}} \right) - \frac{4C_{NaO}^2x^3}{0.025} \\
K_c = \frac{4C_{NaO}x^3}{C_{NaO}(1-x)} \\
K_c = \frac{C_{CaO}X^3}{4C_{NaO}} \\
K_c = \frac{0.025}{4(3.05)} \cdot \frac{X^3}{1-x} \\
0.020 = \frac{X^3}{1-x} \\
x_c = 0.247
d) For a flow system

\[
\frac{C_A}{v} = \frac{F_{A0}(1-x)}{v} = \frac{F_{A0}(1-x)}{v_x(1+ex)} = \frac{C_A(1-x)}{(1+ex)}
\]

\[
C_B = \frac{C_A0x}{(1+ex)}
\]

\[
C_C = \frac{2C_A0x}{(1+ex)}
\]

\[
K_C = \frac{4C_A0^2x^2}{(1+ex)^2} = \frac{4C_A0x^3}{(1+ex)^2(1-x)}
\]

\[
K_C = \frac{x^3}{4C_A0(1+ex)^2(1-x)}
\]

\[
x_{CSTR} = 0.283
\]

CSTR:

\[
V = \frac{F_{A0}x}{k \left[ C_A0(1-x) - \frac{4C_A0^2x^2}{(1+ex)} \right]}
\]

\[
= \frac{2.5 (0.283)}{0.044 \left[ 385 (0.717) - \frac{4(305)^2(0.283)^3}{1.566 \cdot 0.025 (1.566)^3} \right]}
\]

\[
V = \frac{16.08}{0.1596 - 0.198} = 311 L
\]

\[
V_{CSTR} = 311 L
\]
d) PFR:

\[ V = F_A \int_0^{x_e} \frac{dx}{1 - C_A} \]

\[ V = F_A \int_0^{x_e} \frac{dx}{1 - C_A} \left[ \frac{C_A (1-x)}{C_A (1+2x)^2} \right] \]

Plot \( \frac{F_A}{C_A} \) vs. \( x \) \( (x_e = 0.28) \)

Area under curve = \( V \)

\[ V = 130.4 \text{ L} \]

Batch Reactor:

\[ t = \frac{N_A}{V} \int_0^{x_e} \frac{dx}{1 - C_A} \]

Plot \( \frac{C_A}{C_A^0} \) vs. \( x \) \( (x_e = 0.25) \)

\( t = 10.93 \text{ min} \)

This does not impact \( t_{\text{total}} \) very much, so batch reactor size is not much different.
%this program solves problem 5-3
% A ---> B  Batch reactor

clear
%enter raw data
time = [0 3 5 8 10 12 15 17.5];
ca = [4.0 2.89 2.25 1.45 1.0 0.65 0.25 0.07];

% fit a polynomial
coeff = polyfit(time,ca,2);
% take derivative
dercoeff = polyder(coeff);
% evaluate derivative at each time point
dcadt = polyval(dercoeff,time);
% find natural logs for plotting
lnnder = log(-1*dcadt);
lnca = log(ca);
plot(lnca,lnnder)

%determine alpha and k
parameters = polyfit(lnca,lnnder,1);
alpha = parameters(1);
k = exp(parameters(2))

\( \alpha = 0.51 \)

\[ k = 0.20 \left( \frac{\text{mol}}{L \text{min}} \right)^2/\text{min} \]

Note: you can check your answer for \( \alpha \) by making sure your units match.
\[ \text{Et}_2 \text{In} + \text{AsH}_3 \rightarrow \text{aduct} \]
\[ \text{A}_2 + \text{As} \rightarrow \text{C} \]

**PFR data**

\[ P_r = 152.0 \text{ torr} \]

1) **Rewrite design equation for PFR in terms of measurement variables**

\[ V = A \text{sec} \theta \]

\[ \frac{dx}{d\theta} = \frac{-rt A_T}{F_{\text{no}}} \]

Reaction is isothermal with no pressure drop

\[ C_A = C_{A_0} \frac{1-x}{1+ex} \quad C_A = \frac{P_A}{RT} \]

\[ P_A = P_{A_0} \frac{1-x}{1+ex} \]

Solve for \( x \)

\[ x = \frac{1-P_{A_0}P_A}{1+\exp P_A P_{A_0}} \]

Now we can write the differential mole balance in terms of \( P_A \) and \( \theta \)

\[ d \left( \frac{1-P_{A_0}P_A}{1+\exp P_A P_{A_0}} \right) \]

\[ \frac{d}{d\theta} = -\frac{rt A_T}{F_{\text{no}}} \]

2) **Postulate rate law**

\[ -C_A = k \left( P_{A}^{2} P_{\text{e}}^{3} - P_{\text{e}}^{2} \right) \]

Can we simplify?

\[ \varepsilon = \gamma_{\text{Ar}} = \frac{0.1217}{152} (-1) = 8 \times 10^{-2} \Rightarrow 0 \quad \varepsilon = 0 \]
Now \[ \frac{\Delta P_a}{dz} = \frac{P_{a0} k A}{P_{a0}} \left[ \frac{P_a^n P_b^m}{K_p} \right] \]

We can neglect reverse reaction because in runs:

\(-C_A = k_1 P_a^2 P_b^3\)

Thus in equation (1) put \(n = 1\) and \(m = 3\) to further simplify:

\(-C_A = k_1 P_a^2\)

\[-\frac{dP_a}{dz} = k_1 P_a^2\]

Calculate \(-\frac{\Delta P_a}{dz}\):

Plot \(\ln \left( -\frac{\Delta P_a}{dz} \right)\) vs \(\ln (P_a)\) for runs 1 and 2.

Note: The raw data is noisy at the end of the reactor.

If you use the differential method to solve this, you should leave out the last two data points for each run.

The integral method might be better in this case.

- See next page for plot \(\alpha = 1\).

Now we need to solve for \(\beta\).

We can use the ratio of \(-\frac{dP_a}{dz}\) at \(P_a = 1.5\) to \(-\frac{dP_a}{dz}\) at \(P_a = 2.0\)

\(\alpha = 0\)

\[-\frac{dP_a}{dz} = k_1 P_a^2 (0.5)^\beta\]

\[-\frac{dP_a}{dz} = 0.0826\]

\[-\frac{dP_a}{dz} = 0.0424\]

\(\frac{0.0826}{0.0424} = \left( \frac{3.0}{1.5} \right)^\beta\)

\(\ln 1.945 = \ln (2^\beta)\)
Integral method: assume 1st order

\[ \alpha = 1 \]

\[ -\frac{d\rho_n}{dZ} = k' \rho_n \]

\[ -\frac{d\rho_n}{\rho_n} = k' dZ \]

\[ \int_{\rho_0}^{\rho_n} \frac{d\rho_n}{\rho_n} = \int k' dZ \]

\[ \ln \frac{\rho_n}{\rho_0} = k' Z \]

Run #3

![Graph showing \( \ln(\rho_n/\rho_0) \) vs. \( Z \)](image-url)
Decay of aqueous bromine

Br₂ (aq) → decay product
A → B

a) Determine whether the reaction rate is zero, first, or second order in Bromine and calculate the reaction rate constant.

By differential method and linear regression

\[ \alpha = 1.28 \quad \ln \kappa = -3.53 \]

\[ k = 0.029 \]

clear
%enter data
time = [10 20 30 40 50 60]
conc = [2.45 1.74 1.23 0.88 0.62 0.44]
plot(time,conc)
coeff = polyfit(time,conc,2)
plot(time,polyval(coeff,time),time,conc, 'o')
dercoeff = polyder(coeff)
der = polyval(dercoeff,time)
lncon = log(-1*der)
inca = log(conc)
plot(inca,lncon)
parameters = polyfit(inca,lncon,1)

b) \[ F_0 \rightarrow \]

\[ \frac{dN_A}{dt} = -v_r = F_0 \]

\[ F_A = \frac{0.029 \text{ ppm}}{\text{min}} = \frac{0.029 \text{ mg}}{\text{L min}} \cdot C_A \cdot 1 \text{ ppm} \]

\[ F_0 = 25000 \cdot 0.029 \text{ ppm} \cdot \left( \frac{1 \text{ hr}}{60 \text{ min}} \right) \cdot \left( \frac{1 \text{ L}}{1 \text{ min}} \right) \cdot \frac{1}{455 \cdot 302} \cdot \frac{1}{3.785]_1} \cdot 1 \text{ L/hr} = 0.363 \text{ hr/hr} \]

\[ F_0 = (25000 \cdot 0.029 \text{ ppm} \cdot \left( \frac{1 \text{ hr}}{60 \text{ min}} \right) \cdot \left( \frac{1 \text{ L}}{1 \text{ min}} \right) \cdot \frac{1}{455 \cdot 302} \cdot \frac{1}{3.785]_1} \cdot 1 \text{ L/hr} = 0.363 \text{ hr/hr} \]
$$\ln 1.948 = \ln (2^A)$$

$$0.667 = \beta (1.693)$$

$$\beta = .96 \sim 1$$

Plugging \( a \) and \( \beta \) into our rate equation,

$$-r_A = k \left[ P_c P_a^a P_b^a - \frac{P_c^a}{k_p} \right] \quad A + B \rightarrow C$$

$$-r_A = k \left[ P_c P_a P_b - \frac{P_c^a}{k_p} \right]$$

at equilibrium,

$$k_p = \frac{P_c}{P_a P_b} \quad \text{and} \quad -r_A = 0 \quad \frac{P_c^a}{k_p} = P_a P_b$$

Combine,

$$\frac{P_c^a}{P_a P_b} = P_a P_b$$

$$P_c^a = P_c \quad \text{so} \ a \ \text{must be} \ 1$$

$$-r_A = k \left[ \frac{P_a P_b}{k_p} - \frac{P_c}{k_p} \right]$$

Evaluate \( k^a \) and \( k_p \)

From run #3, equilibrium is reached at \( P_{ac} = .01 \)

$$P_{ce} = 0.129 - 0.01 = .119$$

$$P_{be} = 3.0 - .119 = 2.881$$

$$k_p = \frac{.119}{.01(2.881)} = 4.13 \ \text{torr}^{-1}$$

From initial rate

$$-\frac{dP_a}{dz} = 9.0 \times 10^{-5} \ \text{torr cm} = k^a (1.129 \ \text{torr}) (3.0 \ \text{torr})$$

$$k^a = 0.23 \ \text{(torr cm)}^{-1}$$
Oxidation of propene to acrolein over no-Pr-Bi catalyst

\[ \text{CH}_2\text{CH} = \text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_2\text{CH} = \text{CHCHO} + \text{H}_2\text{O} \]

Proposed rate law:

\[ r_{\text{reaction}} = k p_p^a p_{o_2}^b \]

Differential reactor with 0.5 g of catalyst at 623 K

Determine reaction orders with respect to propene (\(a\)) and oxygen (\(b\)) and \(k\)

You are given the exit molar flow rate of acrolein as a function of \(p_p\) and \(p_{o_2}\)

Convert \(F_A\) to rate using:

\[ -r_A = \frac{F_A}{w} \]

Use the two runs with equal \(p_p\) to find \(b\)

\[
\begin{align*}
    r_{A_{0.05}} &= k p_p^{0.05} p_{o_2}^b \\
    r_{A_{0.14}} &= \frac{0.14}{5} = 0.028 \\
    r_{A_{0.05}} &= \frac{0.09}{5} = 0.018 \\
    \frac{0.028}{0.018} &= \left( \frac{k p_p^{0.05} p_{o_2}^b}{r_{A_{0.05}}} \right) \left( \frac{r_{A_{0.14}}}{0.05} \right) \left( \frac{0.14}{0.05} \right) \\
    \quad \ln \left( \frac{1.56}{r_{A_{0.05}}} \right) &= 8 \beta \\
    0.44 &= \beta (2.08) \\
    \beta &= 0.21
\end{align*}
\]

%plot ln(rate) vs ln(Pp) assuming o2 in excess. Use runs 1, 2, 6, 7

pp = [0.05, 0.1, 0.2, 0.5]
fa = [0.14, 0.21, 0.48, 1.44]
rate = fa / 5
lnpp = log(pp)
lnrate = log(rate)
parameters = polyfit(lnpp, lnrate, 1)
\[ x = 1.03 - x = 1 \]

For run 1:

\[-r_N = k \cdot P_e^2 \cdot P_o \cdot x^3\]

\[
\frac{0.21}{5} = k \cdot (0.1)^3 \cdot (0.3)^{21}
\]

\[1.42 = 0.681 \cdot k\]

\[k = 1.617\]

For run 2:

\[
\frac{1.44}{3} = k \cdot (0.5)^2 \cdot (0.5)^{21}
\]

\[0.184 = k \cdot (1.432)\]

\[k = 0.67 \text{ mmol atm}^{-1/21} \text{ mol g}^{-1}\]

\[x = 1\]

\[\beta = 0.21\]

\[k = 0.67 \text{ mmol L}^{-1} \text{ g}^{-1} \text{ atm}^{-1/21}\]