Chemical Reaction Engineering I

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What is chemical reaction engineering

A core course in all chemical engineering curriculums that distinguish chemical engineering students from other engineering majors and chemistry major.

It is the field that provides information for large scale productions of chemicals from lab scale.

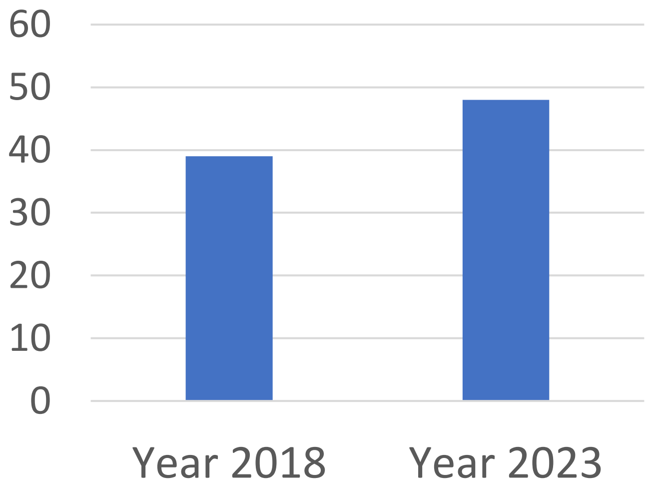
The primary purpose of chemical reaction engineering is *optimization of chemical reactors*, *feed composition* and *operating conditions*.

Example 1.1

Ethyl benzene (EB) is an organic compound with the formula ($C_6H_5CH_2CH_3$). It is mainly used as a chemical intermediate for the manufacture of:

- Styrene monomer
- Building block for many plastics.
- Used as a solvent for coatings
- Making of rubber and plastic wrap
- Production of acetophenone, diethyl benzene, etc..

Global Production



Global market, 2021

US$ 21.3 Billion

Lab scale reaction

$$C_6H_6 + C_2H_4 \longrightarrow C_6H_5C_2H_5$$

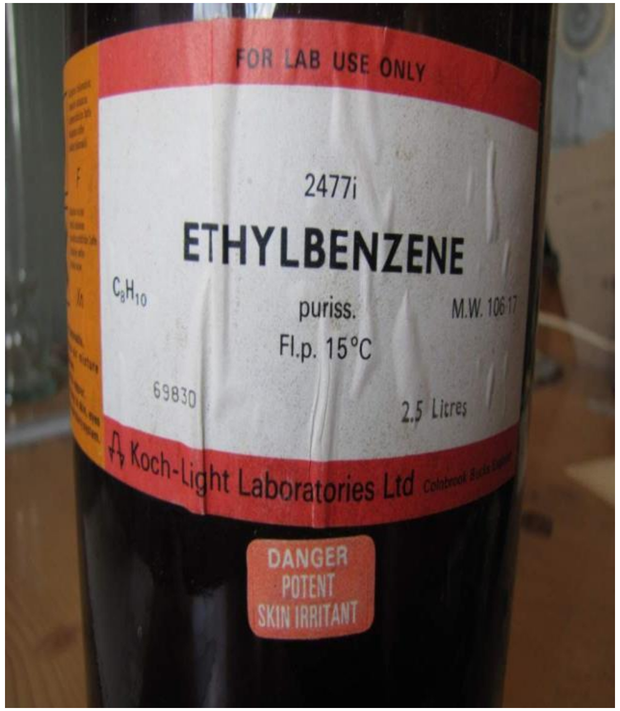
Reaction conditions:

- This reaction is carried out at high temperatures (380 – 420 ^oC) and medium pressure (20 atm)
- This reaction requires acidic catalyst like ZMS-5 zeolite
- There are unimportant side reactions that takes place which results diethyl benzene as:

$$C_6H_6 + 2C_2H_4 \longrightarrow C_6H_4(C_2H_5)_2$$

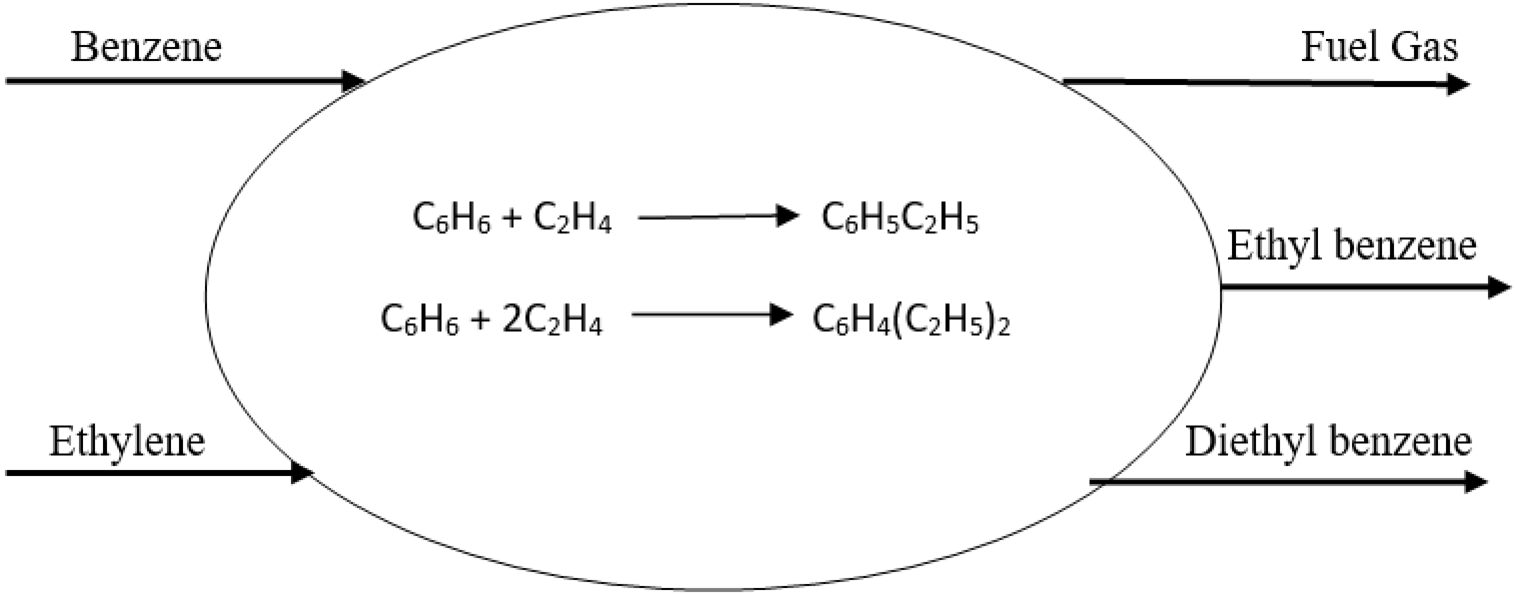
Therefore, excess benzene can minimize these side reactions.

- The reaction is exothermic



Why large scale production?

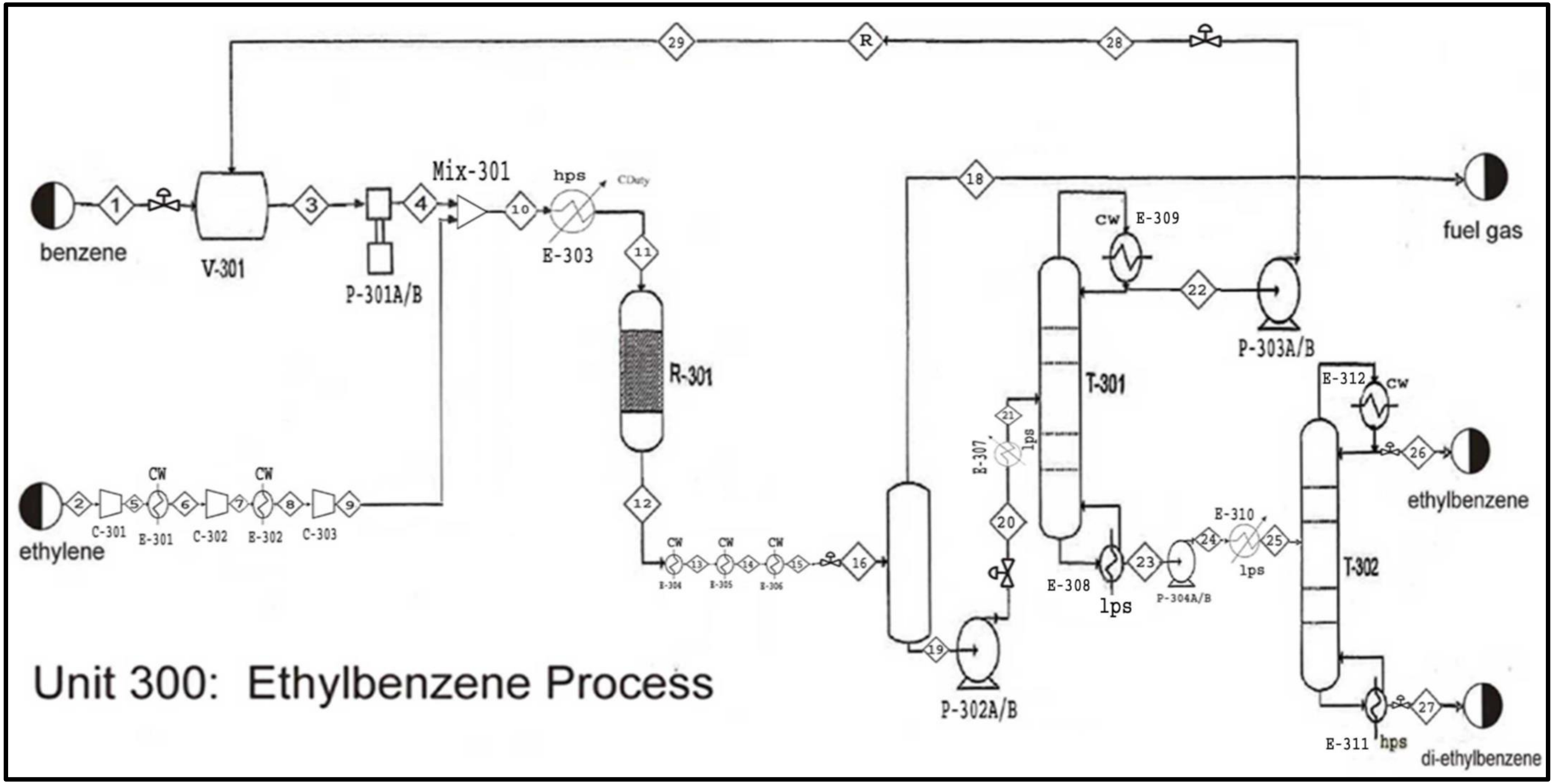
- Achieve the desired production rate, hence the need for global consumption
- Continuous production rate
- Better controlling the reaction conditions
- Minimize the effect of side reactions
- Increase the conversion
- Safe process



$$C_6H_6 + C_2H_4 \longrightarrow C_6H_5C_2H_5$$

$$C_6H_6 + 2C_2H_4 \longrightarrow C_6H_4(C_2H_5)_2$$

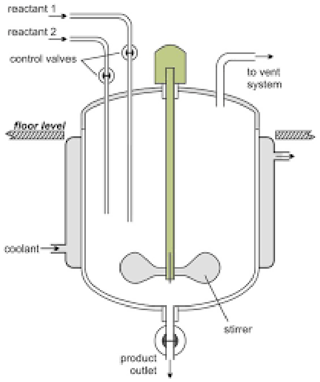
What is process for EB production?



Unit 300: Ethylbenzene Process

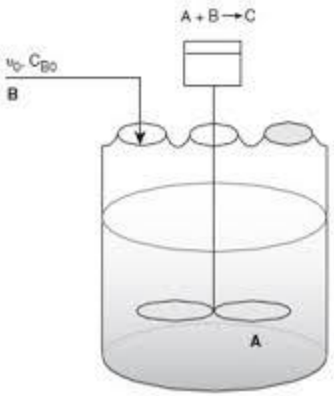
What type of reactor should be used?

Batch reactor

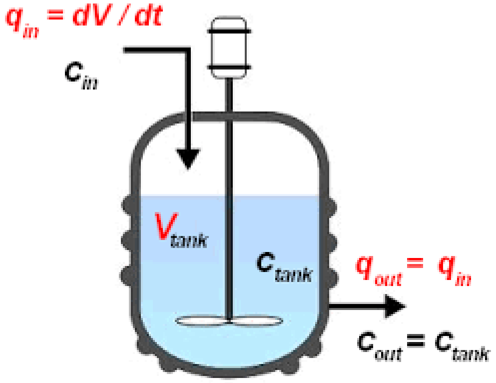


Semi-batch reactor

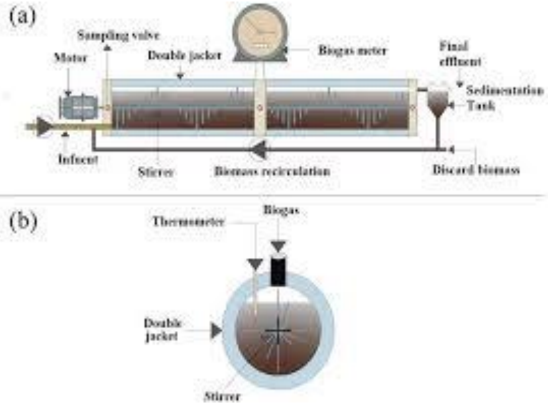
$A + B \rightarrow C$



Continuous stirred tank reactor



Plug flow reactor



Industrial Reactors

Chemical Engineering Department
Chemical Reaction Engineering 1
Fall 2022

Course Syllabus

Instructors:

Dr. Reyad A. Shawabkeh

Course Description:

Rate equations and conservation equation applied to homogeneous reaction system in batch, continuous stirred tank and tubular reactors. Conversion, yield and selectivity for isothermal reactors with multiple reactions: Choice of reactor for various reactions. Non-isothermal reactors

Outcomes:

By the end of this course students will be able to achieve the following objectives:

Objective 1

1. Understand the performance characteristics and the advantages and disadvantages of major reactor types (O1)
2. Set up material and energy balances and identify known and unknowns (O1).
3. Make comparisons of ideal reactor types (batch, plug flow, mixed flow, etc.) and be able to determine the best choice for simple objectives when using a single reactor or a set of reactors (O1).

Course Syllabus

Objective 2

1. Analyze experimental data to obtain rate equations and kinetic and thermodynamic data (O1)
2. Develop rate laws (reaction order and specific reaction rate) for use in reactor design based on reaction data from a reactor or set of reactors (O1).
3. Describe the steps in a catalytic mechanism and how one goes about deriving a rate law, mechanism, and rate-limiting step that are consistent with experimental data (O1).

Objective 3

1. Describe the algorithm that allows the student to solve chemical reaction engineering problems through logic rather than memorization (O1).
2. Predict reactor performance in situations where a reacting gas has a significantly changing density, including the case of variable pressure within an ideal plug flow reactor.
3. Identify design alternatives and evaluate these alternatives (O1, O2).
4. Determine optimal ideal reactor design for multiple reactions for yield or selectivity (O1, O2).
5. Predict reactor performance for reactors when the temperature is not uniform within the (O1, O2).
6. Analyze multiple reactions carried out non-isothermally in flow, batch and semi batch reactors to determine selectivity and yield (O1, O2).
7. Transform calculation problems in chemical reaction engineering into mathematical models and, if necessary choose a numerical method for solving those models and, if necessary, choose suitable ready-made software and carry out the calculations on a computer (O1, O2).

Course Syllabus

Relationship to Program outcome:

NEW ABET 1 -7	1	2	3	4	5	6	7
	x	x					

Relationship to CHE Program Objectives:

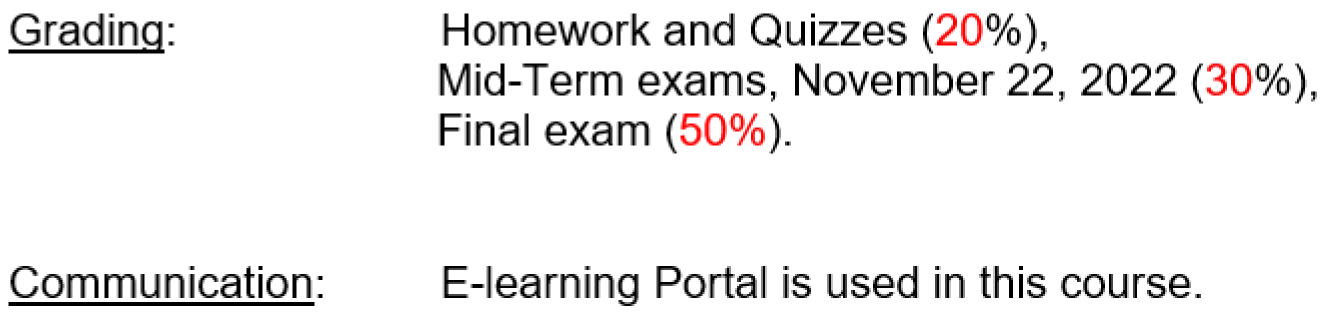
PEO1	PEO 2	PEO 3	PEO 4
x		x	

Textbook:	Fogler, H. S., "Elements of Chemical Reaction Engineering", 4th ed., Prentice Hall (2005).
Key Reference:	Levenspiel, O., "Chemical Reaction Engineering", 3rd ed., John Wiley & Sons (1999).

Course Syllabus

Topics

1. Rate Laws, Stoichiometry and Mole Balances (Chapter 1 & 3)
2. Conversion and Reactor Sizing (Chapter 2)
3. Isothermal Reactor Design (Chapter 4)
4. Collection and Analysis of Rate Data (Chapter 5)
5. Multiple Reactions (Chapter 6)
6. Non-Isothermal Reactor Design (Chapter 8)



Grading: Homework and Quizzes (20%),
Mid-Term exams, November 22, 2022 (30%),
Final exam (50%).

Communication: E-learning Portal is used in this course.

Topic 2, Rate law

Last lecture

- ✓ Introduction to chemical reaction engineering.
- ✓ Why Chemical Engineers need to scale up the production rate of a chemical reaction.
- ✓ Effect of operating conditions on conversion, yield, and selectivity.

This lecture

- ✓ Types of reactions
- ✓ Rate law
- ✓ Reaction order

Note: Parts of this lecture was obtained from notes of my Professor David Rockstraw – New Mexico State University

Definitions

- **Homogeneous Reaction:** Involves one phase
- **Heterogeneous Reaction:** In multiple phases, a reaction usually occurs at the interface between phases.
- **Irreversible Reaction:** Proceeds in only one direction and continues in that direction until the reactants are exhausted.
- **Reversible Reaction:** Can proceed in either direction, depending on the concentrations of reactants and products present relative to the corresponding equilibrium constants.

Rate Laws

For a general chemical reaction:

$$a\,\boldsymbol{A} + b\,\boldsymbol{B} \leftrightarrow c\,\boldsymbol{C} + d\,\boldsymbol{D}$$

The rate of disappearance of the number of moles of ***A*** equals that of ***B***, and equals the rate of appearance of the number of moles of ***C*** and of ***D*** according to the expressions:

$$-\frac{1}{a}\frac{dN_A}{dt} = -\frac{1}{b}\frac{dN_B}{dt} = +\frac{1}{c}\frac{dN_C}{dt} = +\frac{1}{d}\frac{dN_D}{dt}$$

The rate of the chemical reaction with respect to species ***i***, r_i:

$$\boxed{r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid})\,(\text{time})}}$$

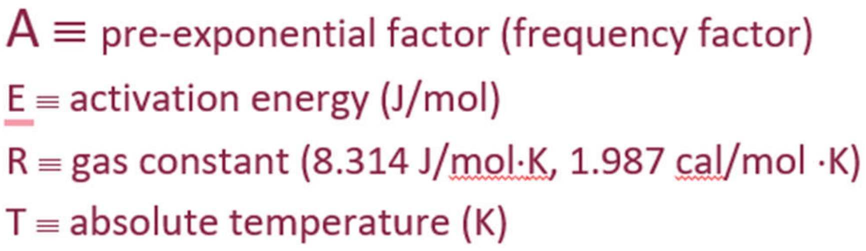
A rate law is an algebraic equation that relates $-r_i$ to species concentrations.

$$-r_A = k_f(T)\, f(C_A, C_B, C_C, C_D, \ldots)$$

$k_f(T)$ is the reaction rate constant:

- Species specific, therefore subscripted to reflect which species constant is making reference
- NOT really a constant, but is not a function of concentrations
- Described by kinetic theory of gases:

$$k_f(T) = Ae^{-E/RT}$$



A ≡ pre-exponential factor (frequency factor)

E ≡ activation energy (J/mol)

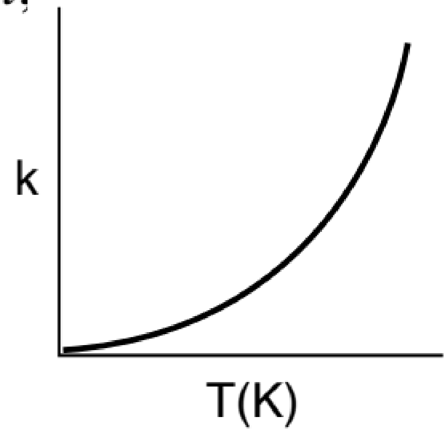
R ≡ gas constant (8.314 J/mol·K, 1.987 cal/mol ·K)

T ≡ absolute temperature (K)

Activation Energy:

Arrhenius equation,

$$k = Ae^{-E/RT}$$



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A ≡ pre-exponential factor (frequency factor)

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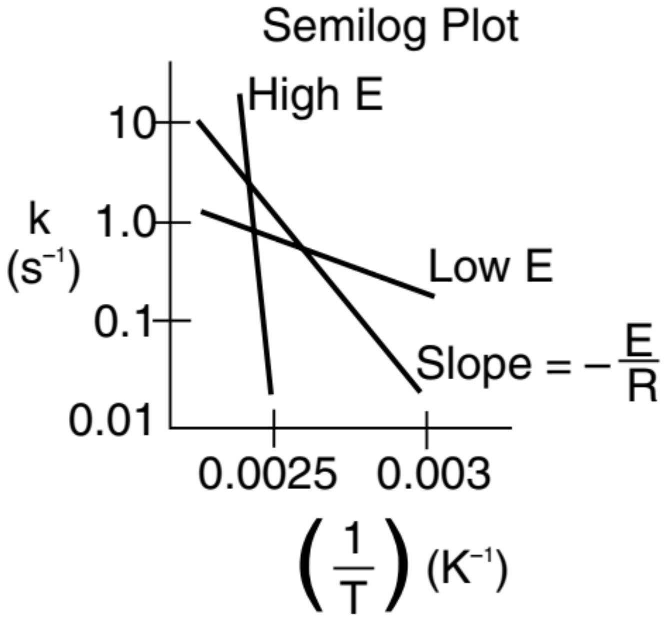
$$\ln(k) = \ln(A) - \frac{E}{R}\left(\frac{1}{T}\right)$$

Form suggests a plot of ln(k) vs (1/T)

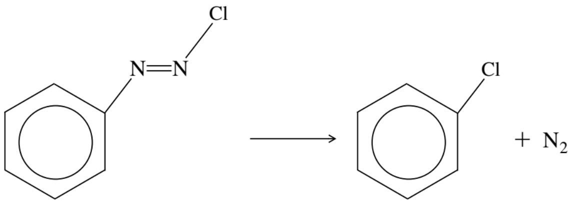
$$slope = -\frac{E}{R}$$

$$Intercept = \ln(A)$$



Example 2.1 Determination of the Activation Energy

Calculate the activation energy for the decomposition of benzene diazonium chloride to give chlorobenzene and nitrogen



k (s^{-1})	0.00043	0.00103	0.00180	0.00355	0.00717
T (K)	313.0	319.0	323.0	328.0	333.0

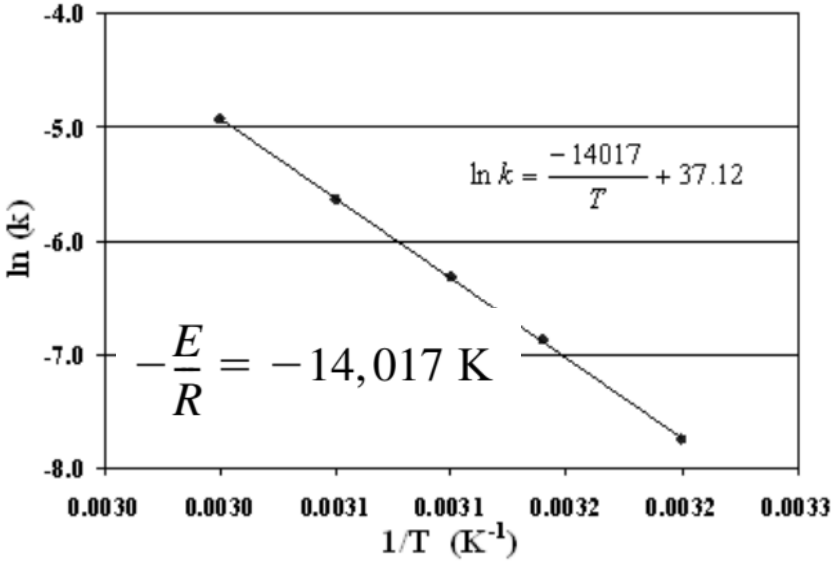
Solution

$$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right)$$

$$E = (14{,}017\ \text{K})R = (14{,}017\ \text{K})\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)$$

$$E = 116.5\ \frac{\text{kJ}}{\text{mol}}$$

$$k = 1.32\times 10^{16}\ exp\left[-\frac{14{,}017\ \text{K}}{\text{T}}\right]$$



$$-\frac{E}{R} = -14{,}017\ \text{K}$$

Special Case 1: irreversible, homogeneous reaction

$$a\,\boldsymbol{A} + b\,\boldsymbol{B} \overset{\boldsymbol{k_f}}{\rightarrow} c\,\boldsymbol{C} + d\,\boldsymbol{D}$$

The rate of the chemical reaction with respect to species ***A***, r_A:

$$r_A = -\frac{1}{V}\frac{dN_A}{dt} = -\boldsymbol{k_f}\ \boldsymbol{C_A^a}\,\boldsymbol{C_B^b}$$

The rate of the chemical reaction with respect to species ***B***, r_B:

$$r_B = -\frac{1}{V}\frac{dN_B}{dt} = -\frac{b}{a}\boldsymbol{k_f}\ \boldsymbol{C_A^a}\,\boldsymbol{C_B^b}$$

$$\boxed{-\frac{r_A}{a} = -\frac{r_B}{b} = +\frac{r_C}{c} = +\frac{r_D}{d}}$$

Special Case 2: reversible, homogeneous reaction

$$a\,\boldsymbol{A} + b\,\boldsymbol{B} \overset{\boldsymbol{k_{eq}}}{\Leftrightarrow} c\,\boldsymbol{C} + d\,\boldsymbol{D}$$

The rate of the chemical reaction with respect to species ***A (key)***, r_A:

$$r_A = -\frac{1}{V}\frac{dN_A}{dt} = -\boldsymbol{k_f}\ \boldsymbol{C_A^a}\,\boldsymbol{C_B^b} + \boldsymbol{k_b}\ \boldsymbol{C_C^c}\,\boldsymbol{C_D^d}$$

The rate of the chemical reaction with respect to species ***D (key)***, r_D:

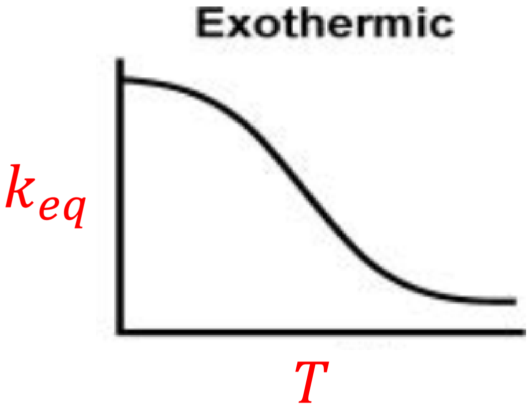
$$r_D = \frac{1}{V}\frac{dN_D}{dt} = \boldsymbol{k_f}\ \boldsymbol{C_A^a}\,\boldsymbol{C_B^b} - \boldsymbol{k_b}\ \boldsymbol{C_C^c}\,\boldsymbol{C_D^d}$$

The equilibrium constant $$\boldsymbol{k_{eq}} = \frac{\boldsymbol{k_f}}{\boldsymbol{k_b}}$$

Reversible, homogeneous reaction $a\,\boldsymbol{A} + b\,\boldsymbol{B} \overset{\boldsymbol{k_{eq}}}{\Leftrightarrow} c\,\boldsymbol{C} + d\,\boldsymbol{D}$

At equilibrium, $r_A = r_B = r_C = r_D = 0$:

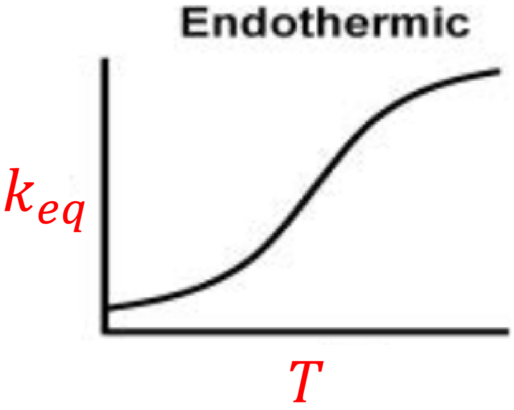
$$k_{eq} = \frac{k_f}{k_b} = \frac{C_C^c\,C_D^d}{C_A^a\,C_B^b}$$



Generally

$$k(T_0) = Ae^{-E/RT_0} \quad \text{and} \quad k(T) = Ae^{-E/RT}$$

$$\boxed{K_{eq}(T) = K_{eq}(T_1)\exp\left[\frac{\Delta H^\circ_{\text{Rx}}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]}$$



Example 2.2 Reversible reaction

Consider the dehydrogenation reaction of benzene to produce Heptalene. What is the net rate of reaction?

$$2C_6H_6 \underset{k_{-B}}{\overset{k_B}{\rightleftarrows}} C_{12}H_{10} + H_2$$

Solution

$$2B \underset{k_{-B}}{\overset{k_B}{\rightleftarrows}} D + H_2$$

Benzene (B) is being depleted by the forward reaction

$$2C_6H_6 \xrightarrow{k_B} C_{12}H_{10} + H_2 \quad ⇨ \quad r_{B,\text{forward}} = -k_B C_B^2$$

For the reverse reaction between heptalene (D) and hydrogen (H_2),

$$C_{12}H_{10} + H_2 \xrightarrow{k_{-B}} 2C_6H_6 \quad ⇨ \quad r_{B,\text{ reverse}} = k_{-B} C_D C_{H_2}$$

$$r_B \equiv r_{B,\text{ net}} = r_{B,\text{ forward}} + r_{B,\text{ reverse}} \quad ⇨ \quad r_B = -k_B C_B^2 + k_{-B} C_D C_{H_2}$$

Reaction Order

$$-r_A = kC_A^{\alpha}C_B^{\beta}$$

order in A = α
order in B = β
overall order = $\alpha + \beta$

$$-r_A = \frac{kC_A}{1 + k'C_B}$$

Low C_B: n = 1 (w.r.t. A)

High C_B: $n_A = 1$, $n_B = -1$
(*apparent* orders)

Units of reaction constants

The unit of the reaction constant depends on the order of reaction whether is it zero, first, second or higher order.

$$\mathrm{A} \longrightarrow \text{Products}$$

with an overall reaction order *n*. The units of rate, $-r_A$, and the specific reaction rate, k are

$$\{-r_{\mathrm{A}}\} = [\text{concentration/time}]$$

$$\{k\} = \frac{[\text{concentration}]^{1-n}}{\text{time}}$$

Example 2.3 Reaction order and unit of reaction constant

What is the unit of zero order, first order, second order, and third order reaction?

Solution

Zero-order ($n = 0$): $-r_A = k_A$: $\{k\} = \text{mol/dm}^3\text{/s}$

First-order ($n = 1$): $-r_A = k_A C_A$: $\{k\} = \text{s}^{-1}$

Second-order ($n = 2$): $-r_A = k_A C_A^2$: $\{k\} = \text{dm}^3\text{/mol/s}$

Third-order ($n = 3$): $-r_A = k_A C_A^3$: $\{k\} = (\text{dm}^3\text{/mol})^2\text{/s}$

Key reactant

The reaction equation $aA + bB \rightarrow cC + dD$

can be written in terms of a key reactant such as A as

$$\mathrm{A} + \frac{b}{a}\mathrm{B} \rightarrow \frac{c}{a}\mathrm{C} + \frac{d}{a}\mathrm{D}$$

The relative rates of reaction can be written either as

$$\boxed{\frac{-r_{\mathrm{A}}}{a} = \frac{-r_{\mathrm{B}}}{b} = \frac{r_{\mathrm{C}}}{c} = \frac{r_{\mathrm{D}}}{d}} \quad \text{or} \quad \boxed{\frac{r_{\mathrm{A}}}{-a} = \frac{r_{\mathrm{B}}}{-b} = \frac{r_{\mathrm{C}}}{c} = \frac{r_{\mathrm{D}}}{d}}$$

Key reactant and reacton conversion

If the reaction takes place in a batch vessel and reactant A is the basis of calculation

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

- N_{Ao} is the number of moles of A initially present in the reactor
- N_A is the number of moles of A left after the reaction

Then, the number of male of A consumed during reaction with B to form C and D is

$$N_{consumed} = N_{Ao} - N_A$$

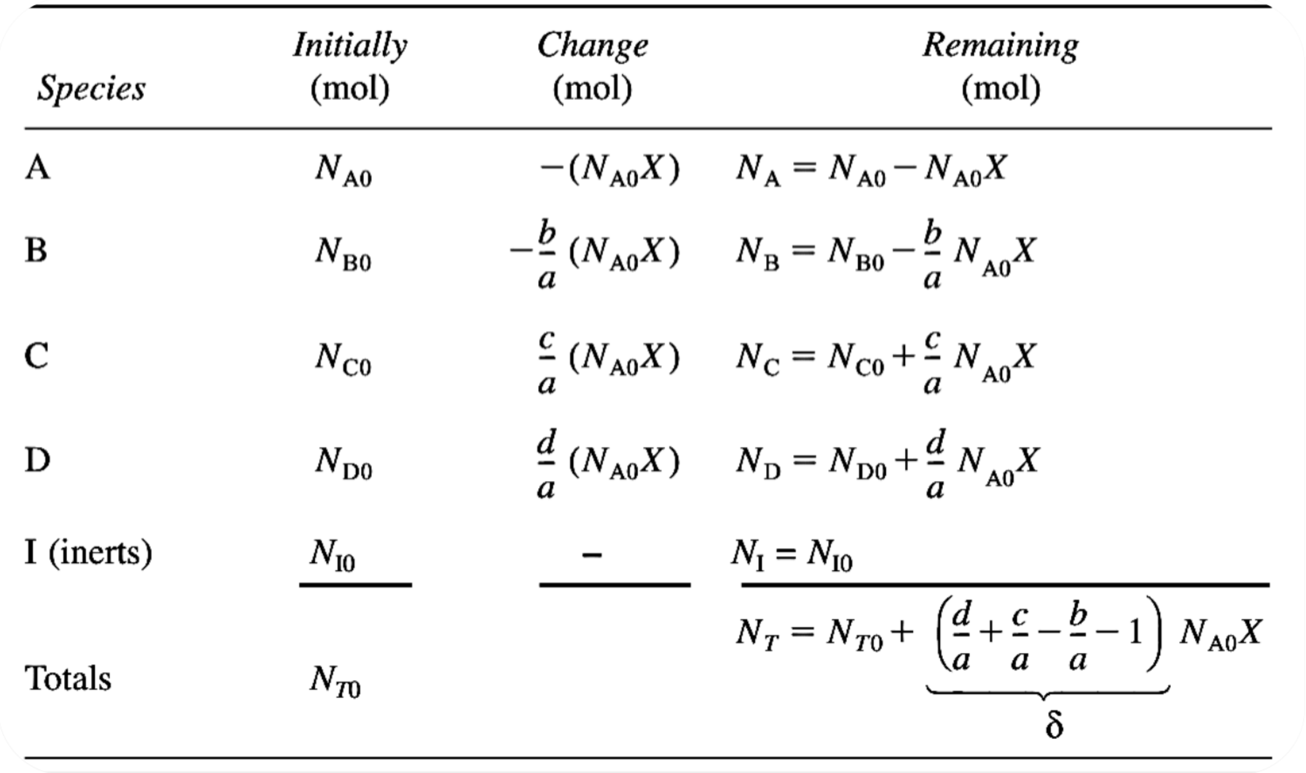
The reaction conversion, x is the ratio of the number of moles of A consumed to that initially presented.

$$\boxed{x = \frac{N_{consumed}}{N_{Ao}} = \frac{N_{Ao} - N_A}{N_{Ao}}}$$

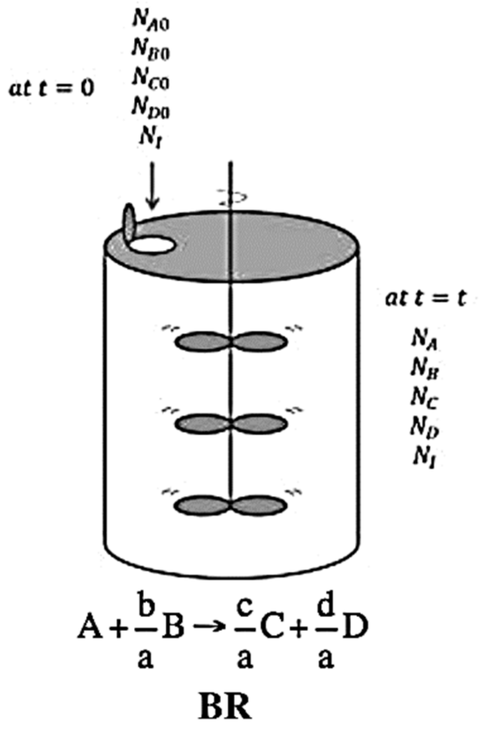
Relating conversion to number of moles of other species in reactor

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

$$\boxed{x = \frac{N_{consumed}}{N_{Ao}} = \frac{N_{Ao} - N_A}{N_{Ao}}}$$



Species	*Initially* (mol)	*Change* (mol)	*Remaining* (mol)
A	N_{A0}	$-(N_{A0}X)$	$N_A = N_{A0} - N_{A0}X$
B	N_{B0}	$-\frac{b}{a}(N_{A0}X)$	$N_B = N_{B0} - \frac{b}{a}N_{A0}X$
C	N_{C0}	$\frac{c}{a}(N_{A0}X)$	$N_C = N_{C0} + \frac{c}{a}N_{A0}X$
D	N_{D0}	$\frac{d}{a}(N_{A0}X)$	$N_D = N_{D0} + \frac{d}{a}N_{A0}X$
I (inerts)	N_{I0}	–	$N_I = N_{I0}$
Totals	N_{T0}		$N_T = N_{T0} + \underbrace{\left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)}_{\delta} N_{A0}X$



BR

Extent of reaction

$$\boxed{(-\nu_A)\mathrm{A} + (-\nu_B)\mathrm{B} \longrightarrow \nu_C\mathrm{C} + \nu_D\mathrm{D}}$$

$$\mathrm{A} + \frac{(-\nu_B)}{(-\nu_A)}\mathrm{B} \longrightarrow \frac{\nu_C}{(-\nu_A)}\mathrm{C} + \frac{\nu_D}{(-\nu_A)}\mathrm{D}$$

$$\frac{r_A}{\nu_A} = \frac{r_B}{\nu_B} = \frac{r_C}{\nu_C} = \frac{r_D}{\nu_D}$$

Extent of Reaction

$$\xi = \frac{\mathrm{d}\,N_i}{\nu_i} = \frac{N_i - N_{i,0}}{\nu_i}$$

$$\xi = \frac{N_{Ao}\ x}{\nu_{key}}$$

$$N_i = N_{i,0} + \nu_i \xi$$

This can also be written in terms of a molar flow as, $\dot{n}_i = \dot{n}_{i,0} + \nu_i \xi$

Extent of reaction

$$\mathrm{A} + \frac{(-\nu_B)}{(-\nu_A)}\mathrm{B} \longrightarrow \frac{\nu_C}{(-\nu_A)}\mathrm{C} + \frac{\nu_D}{(-\nu_A)}\mathrm{D}$$

$$\xi = \frac{\mathrm{d}\,N_i}{\nu_i} = \frac{N_i - N_{i,0}}{\nu_i}$$

$$X_i = \frac{-\mathrm{d}\,N_i}{N_{i,0}} = \frac{N_{i,0} - N_i}{N_{i,0}}$$

$$\xi = \frac{N_{Ao}\,x}{\nu_{key}}$$

$$\boxed{0 \le \xi \le n_A^o/a \text{ and } 0 \le \chi \le 1}$$

$$N_A = N_{Ao} - N_{Ao}\,x$$

$$N_B = N_{Bo} - \frac{b}{a}\,N_{Ao}\,x$$

$$N_C = N_{Co} + \frac{c}{a}\,N_{Ao}\,x$$

$$N_D = N_{Do} + \frac{d}{a}\,N_{Ao}\,x$$

$$N_A = N_{Ao} - \xi$$

$$N_B = N_{Bo} - b\,\xi$$

$$N_C = N_{Co} + c\,\xi$$

$$N_D = N_{Do} + d\,\xi$$

Example 2.4 Reaction rate in terms of the extent of reaction

Consider the simple reaction A $\longrightarrow$ B, if this is first order, then the rate can be given by

$$-r_i = kC_i$$

C_i is the concentration of i and can be related to the number of moles, N_i, by

$$N_i = C_i V$$

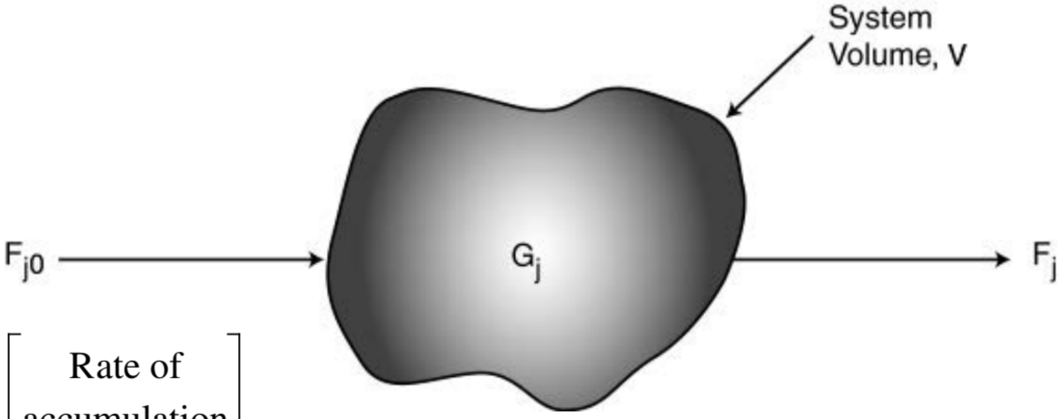
for a constant volume reactor, V, or, to the molar flow rate, $\dot{n}_i$, by

$$\dot{n}_i = C_i v \qquad ⇨ \qquad -r_i = \frac{k}{v}\dot{n}_i$$

$$\dot{n}_i = \dot{n}_{i,0} + \nu_i \xi \qquad ⇨ \qquad -r_i = \frac{k}{v}\left(\dot{n}_{i,0} + \nu_i \xi\right)$$

The general mole balance equation

$$aA + bB \rightarrow cC + dD$$



$$\begin{bmatrix}\text{Rate of flow}\\ \text{of } j \text{ into}\\ \text{the system}\\ \text{(moles/time)}\end{bmatrix} - \begin{bmatrix}\text{Rate of flow}\\ \text{of } j \text{ out of}\\ \text{the system}\\ \text{(moles/time)}\end{bmatrix} + \begin{bmatrix}\text{Rate of generation}\\ \text{of } j \text{ by chemical}\\ \text{reaction within}\\ \text{the system}\\ \text{(moles/time)}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\\ \text{of } j \text{ within}\\ \text{the system}\\ \text{(moles/time)}\end{bmatrix}$$

$$\textbf{In} \quad - \quad \textbf{Out} \quad + \quad \textbf{Generation} \quad = \quad \textbf{Accumulation}$$

$$F_{j0} \quad - \quad F_j \quad + \quad G_j \quad = \quad \frac{dN_j}{dt}$$

$$\boxed{F_{j0} - F_j + \int^V r_j \, dV = \frac{dN_j}{dt}}$$

$$G_j = \int^V r_j \, dV$$

$$\frac{moles}{time} = \frac{moles}{time \cdot volume} \cdot volume$$

$$G_j = r_j \cdot V$$

Batch reactor

$$\boxed{F_{j0} - F_j + \int^V r_j \, dV = \frac{dN_j}{dt}}$$

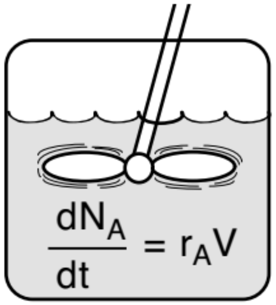
$$F_{j0} = F_j = 0 \quad \Rightarrow \quad \frac{dN_j}{dt} = \int^V r_j \, dV$$

If the reaction mixture is perfectly mixed there is no variation in the rate of reaction throughout the reactor volume

$$\boxed{\frac{dN_j}{dt} = r_j V}$$

Example 2.5 Estimation of reaction time in batch reactor

consider the isomerization of species A in a batch reactor. As the reaction proceeds, the number of moles of A decreases, and the number of moles of B increases. What is the time needed to decrease the concentration of A from N_{Ao} to N_{A1} ?



Batch Reactor

Solution

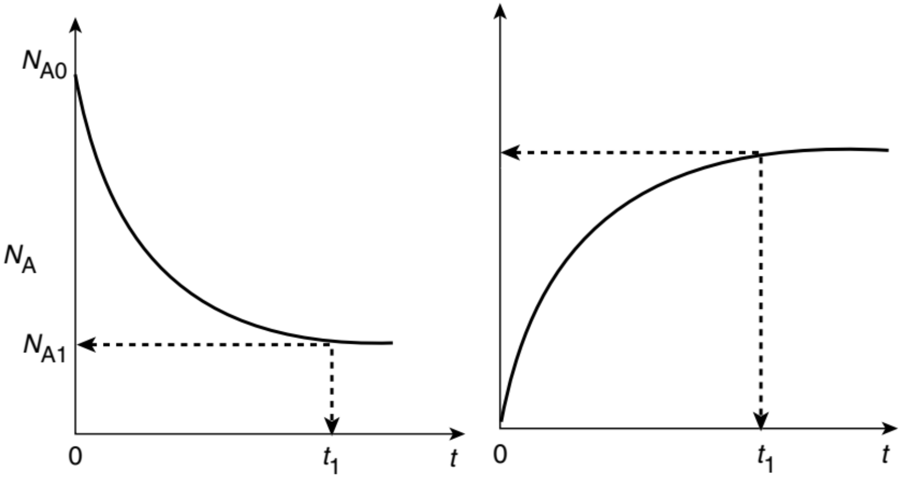
$$A \longrightarrow B$$

$$\frac{dN_A}{dt} = r_A V \quad \Rightarrow \quad dt = \frac{dN_A}{r_A V}$$

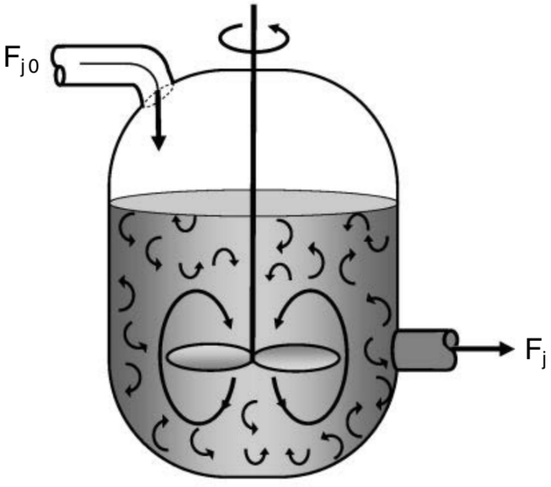
$$t_1 = \int_{N_{A1}}^{N_{Ao}} \frac{dN_A}{-r_A V} \qquad t_1 = \int_{N_{A1}}^{N_{Ao}} \frac{dN_A}{k N_A}$$

$$r_A = -k\, C_A \quad \Rightarrow \quad t_1 = \frac{1}{k}\, ln \frac{N_{Ao}}{N_{A1}}$$

$$C_A = \frac{N_A}{V}$$



Continuous-Stirred Tank Reactor (CSTR)



$$\boxed{F_{j0} - F_j + \int^V r_j \, dV = \frac{dN_j}{dt}}$$

CSTR operated at a steady state and constant volume

$$F_{j0} - F_j + \int^V r_j \, dV = \frac{dN_j}{dt} \quad \Rightarrow \quad \frac{dN_j}{dt} = 0 \quad \text{and} \quad \int^V r_j \, dV = V r_j$$

$$\boxed{V = \frac{F_{j0} - F_j}{-r_j}}$$

The molar flow rate F_j is just the product of the concentration of species j and the volumetric flow rate v

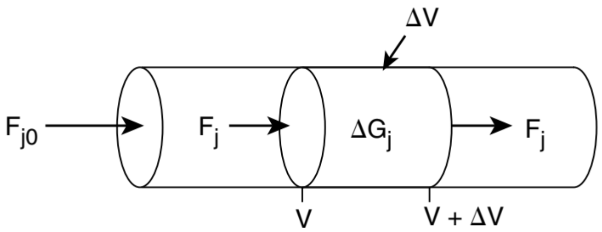
$$F_j = C_j \cdot v$$

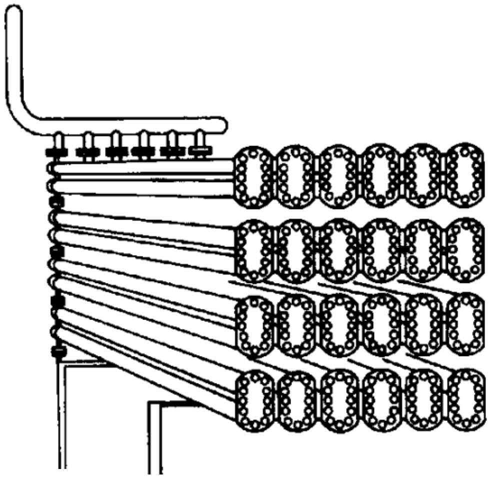
$$\boxed{\begin{array}{c} F_j = C_j \cdot v \\ \dfrac{\text{moles}}{\text{time}} = \dfrac{\text{moles}}{\text{volume}} \cdot \dfrac{\text{volume}}{\text{time}} \end{array}}$$

$$V = \frac{F_{j0} - F_j}{-r_j} \quad \Rightarrow \quad V = \frac{v_0 C_{\mathrm{A}0} - v C_{\mathrm{A}}}{-r_{\mathrm{A}}}$$

Tubular Reactor (PFR)

$$\boxed{F_{j0} - F_j + \int^{V} r_j \, dV = \frac{dN_j}{dt}}$$





$$\left[\begin{array}{c}\text{Molar flow}\\ \text{rate of species } j\\ \textit{In} \text{ at V}\\ \textit{moles/time}\end{array}\right] - \left[\begin{array}{c}\text{Molar flow}\\ \text{rate of species } j\\ \textit{Out} \text{ at } (V+\Delta V)\\ \textit{moles/time}\end{array}\right] + \left[\begin{array}{c}\text{Molar rate of}\\ \textit{Generation}\\ \text{of species } j\\ \text{within } \Delta V\\ \textit{moles/time}\end{array}\right] = \left[\begin{array}{c}\text{Molar rate of}\\ \textit{Accumulation}\\ \text{of species } j\\ \text{within } \Delta V\\ \textit{moles/time}\end{array}\right]$$

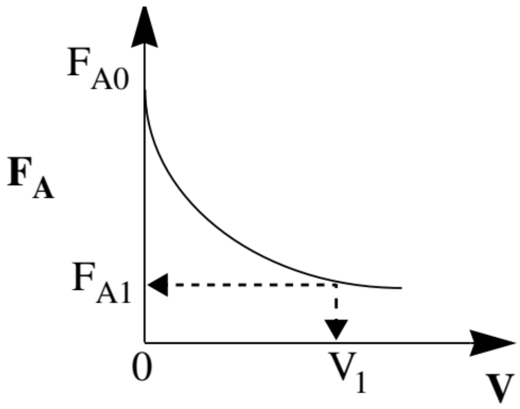
In – Out + Generation = Accumulation

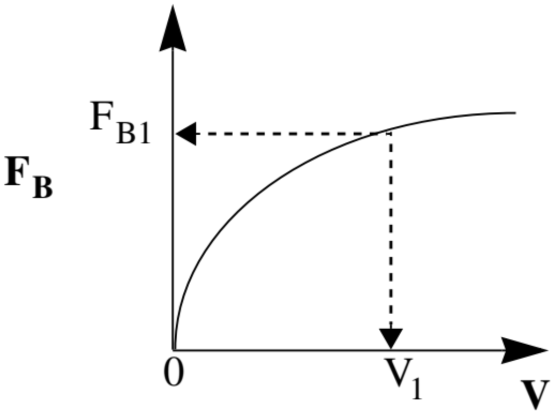
$$F_j\big|_{V} \quad - \quad F_j\big|_{V+\Delta V} \quad + \quad r_j \Delta V \quad = \quad 0$$

$$\boxed{F_j\big|_V \quad - \quad F_j\big|_{V+\Delta V} \quad + \quad r_j\Delta V \quad = \quad 0}$$

Dividing by ΔV and rearranging $\Rightarrow$ $\left[\dfrac{F_j\big|_{V+\Delta V} - F_j\big|_V}{\Delta V}\right] = r_j$

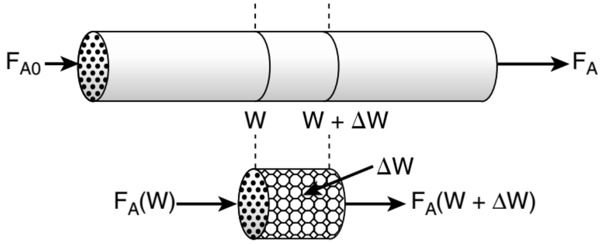
$$\boxed{\frac{dF_j}{dV} = r_j} \quad \Rightarrow \quad V = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r_A}$$

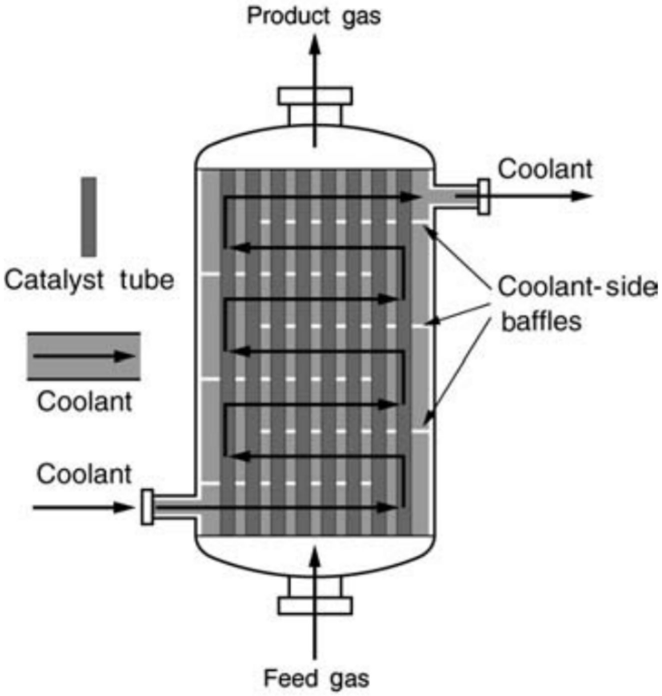




Packed-Bed Reactor (PBR)

$$\boxed{F_{j0} - F_j + \int^{V} r_j \, dV = \frac{dN_j}{dt}}$$





$$\textbf{\textit{In}} - \textbf{\textit{Out}} + \textbf{\textit{Generation}} = \textbf{\textit{Accumulation}}$$

$$F_{A|W} - F_{A|(W+\Delta W)} + r'_A \, \Delta W = 0$$

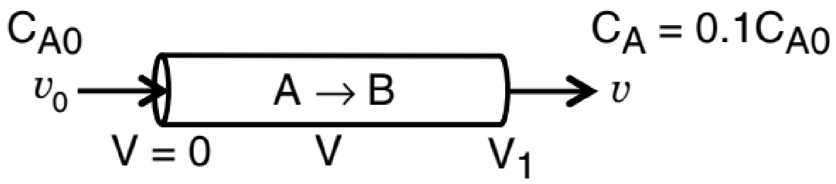
$$(r'_A)\,\Delta W \equiv \frac{moles\ A}{(time)(mass\ of\ catalyst)} \cdot (mass\ of\ catalyst) \equiv \frac{moles\ A}{time}$$

$$\boxed{\frac{dF_A}{dW} = r'_A} \quad \Rightarrow \quad W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r'_A}$$

Example 2.5 Sizing of reactors

The bellow reaction is first order in A, $-r_A = k\, C_A$, and is carried out in a tubular reactor in which the volumetric flowrate, $v = 10\ \mathrm{L/min}$, is constant, i.e., $v_o = v$. What will be the volume of this reactor needed to reduce the initial concentration to 10%?

$$k = 0.23\ \mathrm{min}^{-1}$$



Solution

$$A \longrightarrow B$$

$$\frac{dF_A}{dV} = r_A \qquad \text{and} \qquad -r_A = kC_A$$

$$\frac{dF_A}{dV} = \frac{d(C_A v)}{dV} = \frac{d(C_A v_0)}{dV} = v_0 \frac{dC_A}{dV} = r_A \quad \Rightarrow \quad -\frac{v_0\, dC_A}{dV} = -r_A = kC_A$$

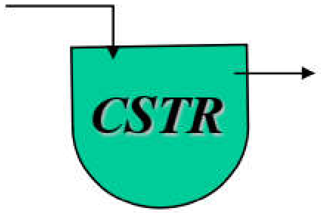
$$-\frac{v_0}{k}\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^V dV$$

$$\boxed{V = \frac{v_0}{k}\, ln\, \frac{C_{A0}}{C_A}} \quad \Rightarrow \quad V = \frac{10\ \mathrm{dm^3/min}}{0.23\ \mathrm{min}^{-1}} \ln \frac{C_{A0}}{0.01C_{A0}} = \frac{10\ \mathrm{dm}^3}{0.23} \ln 100 = 200\ \mathrm{dm}^3$$

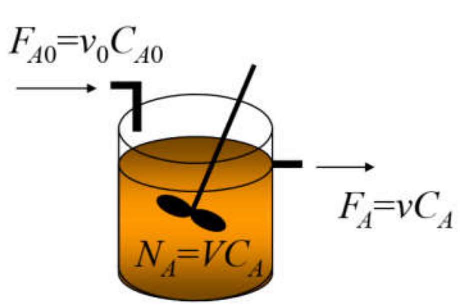
Summary - Design Equations of Ideal Reactors

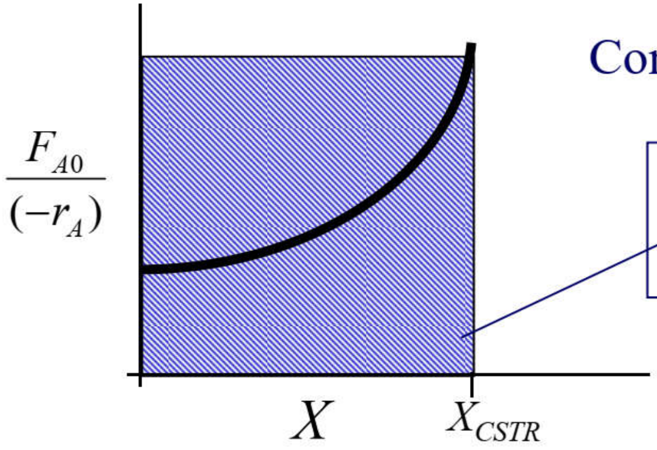
	Differential Equation	Algebraic Equation	Integral Equation	Remarks
Batch (well-mixed)	$\frac{dN_j}{dt} = (r_j)V$		$t = \int_{N_{j0}}^{N_j} \frac{dN'_j}{(r_j)V}$	Conc. changes with time but is uniform within the reactor. Reaction rate varies with time.
CSTR (well-mixed at steady-state)		$V = \frac{F_{j0} - F_j}{-(r_j)}$		Conc. inside reactor is uniform. (r_j) is constant. Exit conc = conc inside reactor.
PFR (steady-state flow; well-mixed radially)	$\frac{dF_j}{dV} = r_j$		$V = \int_{F_{j0}}^{F_j} \frac{dF'_j}{(r_j)}$	Concentration and hence reaction rates vary spatially (with length).

Summary - Design Equations as a function of conversion

IDEAL REACTOR	DIFFERENTIAL FORM	ALGEBRAIC FORM	INTEGRAL FORM
	$N_{A0}\frac{dX_A}{dt}=(-r_A)V$		$t=N_{A0}\int_0^{X_A}\frac{dX'_A}{-r_AV}$
		$V=\frac{F_{A0}(X_A)}{(-r_A)}$	
	$F_{A0}\frac{dX_A}{dV}=(-r_A)$		$V=F_{A0}\int_0^{X_A}\frac{dX'_A}{-r_A}$

Determination of Reactor volume – A plot of $\frac{F_{Ao}}{-r_A}$ vs. x

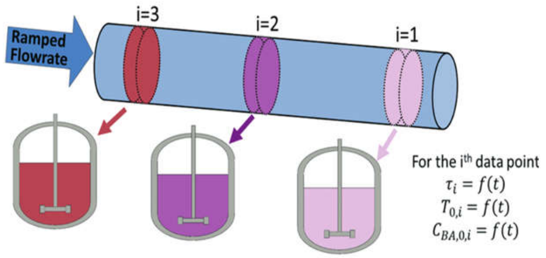


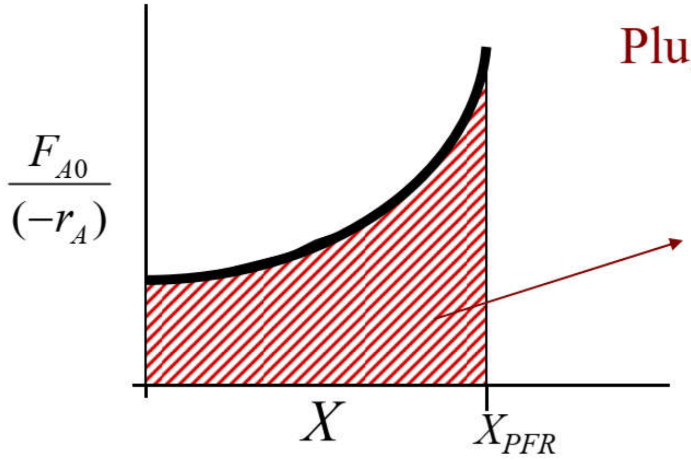


Continuous Stirred Tank Reactor (CSTR)

$$V_{CSTR} = \left[\frac{F_{A0}}{(-r_A)}\right] \times [X_{CSTR}]$$

Evaluated at X=X_{CSTR}





Plug Flow Reactor (PFR)

$$V_{PFR} = \int_0^{X_{PFR}} \frac{F_{A0}}{-r_A} dX$$

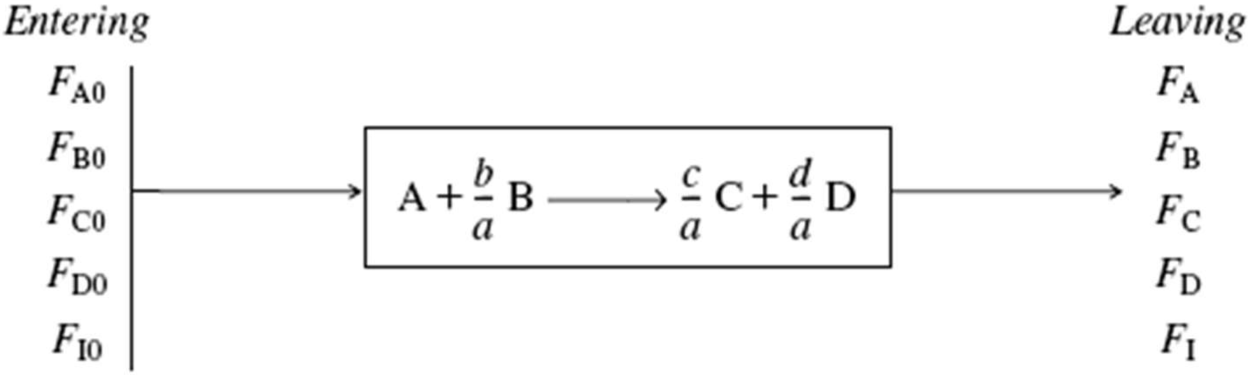
Stoichiometry in liquid and gas systems

Concentration Flow System can be presented in term of molar flowrate, F_A and volumetric flowrate, v as :

$$C_A = \frac{F_A}{\upsilon}$$

However, for liquid phase Flow System the initial volumetric flowrate is equal to the final volumetric flowrate: $\upsilon = \upsilon_0$

For the chemical reaction:



The concentration of *A* becomes $$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}\left(1-X\right)}{\upsilon_0} = C_{A0}\left(1-X\right)$$

The concentration of *B* becomes $$C_B = \frac{N_B}{V} = \frac{N_{A0}}{V_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

Where: $$\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$$ and $$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

For liquid Systems

$F_A = F_{A0}\,(1 - X)$

$F_B = F_{A0}\,(\Theta_B - b/a\ X)$

$F_C = F_{A0}\,(\Theta_C + c/a\ X)$

$F_D = F_{A0}\,(\Theta_D + d/a\ X)$

If Inert material exisits then $F_I = F_{A0}\Theta_I$

$F_T = F_{T0} + \delta\ F_{A0}\,X$

Example: Liquid Systems

Consider the liquid phase reaction bellow; what is the concentration of each species in term of conversion

$$\mathrm{NaOH} + \tfrac{1}{3}(\mathrm{C_{17}H_{35}COO})_3\mathrm{C_3H_5} \longrightarrow \mathrm{C_{17}H_{35}COONa} + \tfrac{1}{3}\mathrm{C_3H_5(OH)_3}$$

$$\mathrm{A} \quad + \quad \tfrac{1}{3}\mathrm{B} \quad \longrightarrow \quad \mathrm{C} \quad + \quad \tfrac{1}{3}\mathrm{D}$$

Solution

The concentration of each species are

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \qquad \Theta_B = \frac{C_{B0}}{C_{A0}} \quad \Theta_C = \frac{C_{C0}}{C_{A0}} \quad \Theta_D = \frac{C_{D0}}{C_{A0}}$$

$$C_B = C_{Ao}\left(\theta_B - \frac{1}{3}x\right) \qquad C_C = C_{Ao}\left(\theta_C + x\right) \qquad C_D = C_{Ao}\left(\theta_D + \frac{1}{3}x\right)$$

$$C_{Inert} = C_{Ao}\left(\theta_{Inert}\right)$$

For gas phase Systems

The reaction takes place in tubular or packed bed reactor. This will lead to variation volumetric flowrate of the total species with distance from the inlet of the reactor. The volumetric flowrate is related to total molar flowrates, pressure and temperature according

$$\upsilon = \upsilon_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

Therefore, the concentration of species A at these conditions can be expressed by

$$C_A = F_A / \upsilon = \frac{F_A}{\upsilon_0 \left(\frac{F_T}{F_0} \right)} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right) = \frac{F_{T0}}{\upsilon_0} \frac{F_A}{F_T} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

$$C_A = F_A / \upsilon = C_{T0} \frac{F_A}{F_T} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

For species B

$$C_B = C_{T0}\left(\frac{F_B}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

The total molar flow rate is: $F_T = F_{T0} + F_{A0}\delta X$

Substitute F_T gives:

$$\upsilon = \upsilon_0\left(\frac{F_{T0} + F_{A0}\delta X}{F_{T0}}\right)\frac{T}{T_0}\frac{P_0}{P} = \upsilon_0\left(1 + \frac{F_{A0}}{F_{T0}}\delta X\right)\frac{T}{T_0}\frac{P_0}{P}$$

$$= \upsilon_0\left(1 + y_{A0}\delta X\right)\frac{T}{T_0}\frac{P_0}{P} = \upsilon_0\left(1 + \varepsilon X\right)\frac{T}{T_0}\frac{P_0}{P}$$

Where $\varepsilon = y_{A0}\delta$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}\left(1-X\right)}{\upsilon_0\left(1+\varepsilon X\right)\frac{T}{T_0}\frac{P_0}{P}} = \frac{C_{A0}\left(1-X\right)}{\left(1+\varepsilon X\right)}\frac{T_0}{T}\frac{P}{P_0}$$

$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{\upsilon_0\left(1+\varepsilon X\right)\frac{T}{T_0}\frac{P_0}{P}} = \frac{C_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{\left(1+\varepsilon X\right)}\frac{T_0}{T}\frac{P}{P_0}$$

If $-r_A = kC_AC_B$

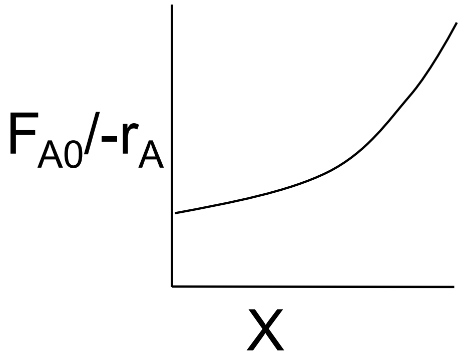
Then $$-r_A = k_A C_{A0}^2\left[\frac{\left(1-X\right)}{\left(1+\varepsilon X\right)}\frac{\left(\Theta_B - \frac{b}{a}X\right)}{\left(1+\varepsilon X\right)}\left(\frac{P}{P_0}\frac{T_0}{T}\right)^2\right]$$

where

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

$$\delta = \frac{\text{change in total number of moles}}{\text{mole of A reacted}}$$

This gives



$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) \frac{F_{A0}}{F_{T0}} = y_{A0}\delta$$

$$\varepsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}}$$

Example:

Calculate the equilibrium conversion (X_{ef}) for gas phase reaction in a flow reactor

Consider the following elementary reaction $2\text{A} \Leftrightarrow \text{B}$
Where K_C=20 dm^3/mol and C_{A0}=0.2 mol/dm^3.

Calculate the equilibrium conversion for both a batch reactor (X_{eb}) and a flow reactor (X_{ef}).

Solution:

$$-r_A = k_A\left[C_A^{\ 2} - \frac{C_B}{K_C}\right]$$

$$\text{A} \rightarrow \frac{1}{2}\text{B}$$

<u>Species</u>	<u>Fed</u>	<u>Change</u>	<u>Remaining</u>
A	F_{A0}	$-F_{A0}X$	$F_A=F_{A0}(1-X)$
B	0	$+F_{A0}X/2$	$F_B=F_{A0}X/2$
	$F_{T0}=F_{A0}$		$F_T=F_{A0}-F_{A0}X/2$

A	F_{A0}	$-F_{A0}X$	$F_A=F_{A0}(1-X)$
B	0	$F_{A0}X/2$	$F_B=F_{A0}X/2$

Stoichiometry: Gas isothermal $T=T_0$

Gas isobaric

$P=P_0$

$$\upsilon=\upsilon_0\left(1+\varepsilon X\right)$$

$$C_A=\frac{F_{A0}\left(1-X\right)}{\upsilon_0\left(1+\varepsilon X\right)}=\frac{C_{A0}\left(1-X\right)}{\left(1+\varepsilon X\right)}$$

$$C_B=\frac{F_{A0}\,X/2}{\upsilon_0\left(1+\varepsilon X\right)}=\frac{C_{A0}\left(1-X\right)}{2\left(1+\varepsilon X\right)}$$

$$-r_A = k_A\left[\left(\frac{C_{A0}(1-X)}{(1+\varepsilon X)}\right)^2 - \frac{C_{A0}X}{2(1+\varepsilon X)K_C}\right]$$

Pure A → $y_{A0}=1$, $C_{A0}=y_{A0}P_0/RT_0$, $C_{A0}=P_0/RT_0$

$$\varepsilon = y_{A0}\delta = (1)\left(\frac{1}{2}-1\right) = -\frac{1}{2}$$

At equilibrium: $-r_A=0$

$$2K_C C_{A0} = \frac{X_e(1+\varepsilon X_e)}{(1-X_e)^2}$$

$$2K_C C_{A0} = 2\left(20\frac{dm^3}{mol}\right)\left(0.2\frac{mol}{dm^3}\right) = 8$$

$$\varepsilon = y_{A0}\delta = 1\left(\frac{1}{2} - 1\right) = -\frac{1}{2}$$

$$8 = \frac{X_e - 0.5X_e{}^2}{\left(1 - 2X_e + X_e{}^2\right)}$$

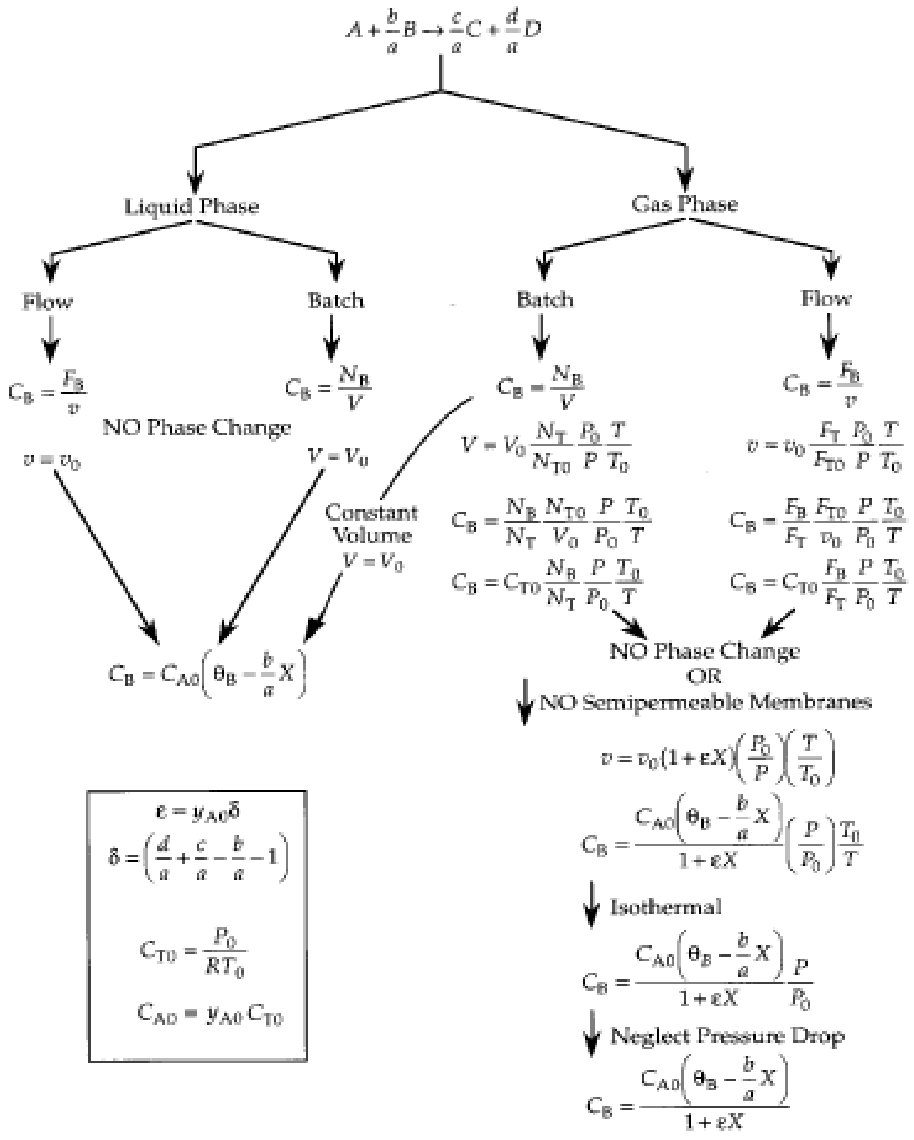
$$8.5X_e{}^2 - 17X_e + 8 = 0$$

Flow: $X_{ef} = 0.757$

Re-call

Batch: $X_{eb} = 0.70$

Summary



$$A+\frac{b}{a}B \rightarrow \frac{c}{a}C+\frac{d}{a}D$$

Liquid Phase

Flow

$$C_B=\frac{F_B}{v}$$

$$v=v_0$$

Batch

$$C_B=\frac{N_B}{V}$$

$$V=V_0$$

NO Phase Change

$$C_B=C_{A0}\left(\theta_B-\frac{b}{a}X\right)$$

Gas Phase

Batch

$$C_B=\frac{N_B}{V}$$

Constant Volume $V=V_0$

$$V=V_0\frac{N_T}{N_{T0}}\frac{P_0}{P}\frac{T}{T_0}$$

$$C_B=\frac{N_B}{N_T}\frac{N_{T0}}{V_0}\frac{P}{P_0}\frac{T_0}{T}$$

$$C_B=C_{T0}\frac{N_B}{N_T}\frac{P}{P_0}\frac{T_0}{T}$$

Flow

$$C_B=\frac{F_B}{v}$$

$$v=v_0\frac{F_T}{F_{T0}}\frac{P_0}{P}\frac{T}{T_0}$$

$$C_B=\frac{F_B}{F_T}\frac{F_{T0}}{v_0}\frac{P}{P_0}\frac{T_0}{T}$$

$$C_B=C_{T0}\frac{F_B}{F_T}\frac{P}{P_0}\frac{T_0}{T}$$

NO Phase Change
OR
NO Semipermeable Membranes

$$v=v_0(1+\varepsilon X)\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)$$

$$C_B=\frac{C_{A0}\left(\theta_B-\frac{b}{a}X\right)}{1+\varepsilon X}\left(\frac{P}{P_0}\right)\frac{T_0}{T}$$

Isothermal

$$C_B=\frac{C_{A0}\left(\theta_B-\frac{b}{a}X\right)}{1+\varepsilon X}\frac{P}{P_0}$$

Neglect Pressure Drop

$$C_B=\frac{C_{A0}\left(\theta_B-\frac{b}{a}X\right)}{1+\varepsilon X}$$

$$\varepsilon=y_{A0}\delta$$

$$\delta=\left(\frac{d}{a}+\frac{c}{a}-\frac{b}{a}-1\right)$$

$$C_{T0}=\frac{P_0}{RT_0}$$

$$C_{A0}=y_{A0}C_{T0}$$

Stoichiometry in liquid and gas systems

Examples & Damköhler Number

Last lecture dealt with the relation between number of moles, concentration or molar flowrate of each species that taken out of the reactor as a funcion of conversion. In this leacture, some examples will be presented for each reactor.

To summurize what was presented last time, the table aside shows the relations mentioned above.

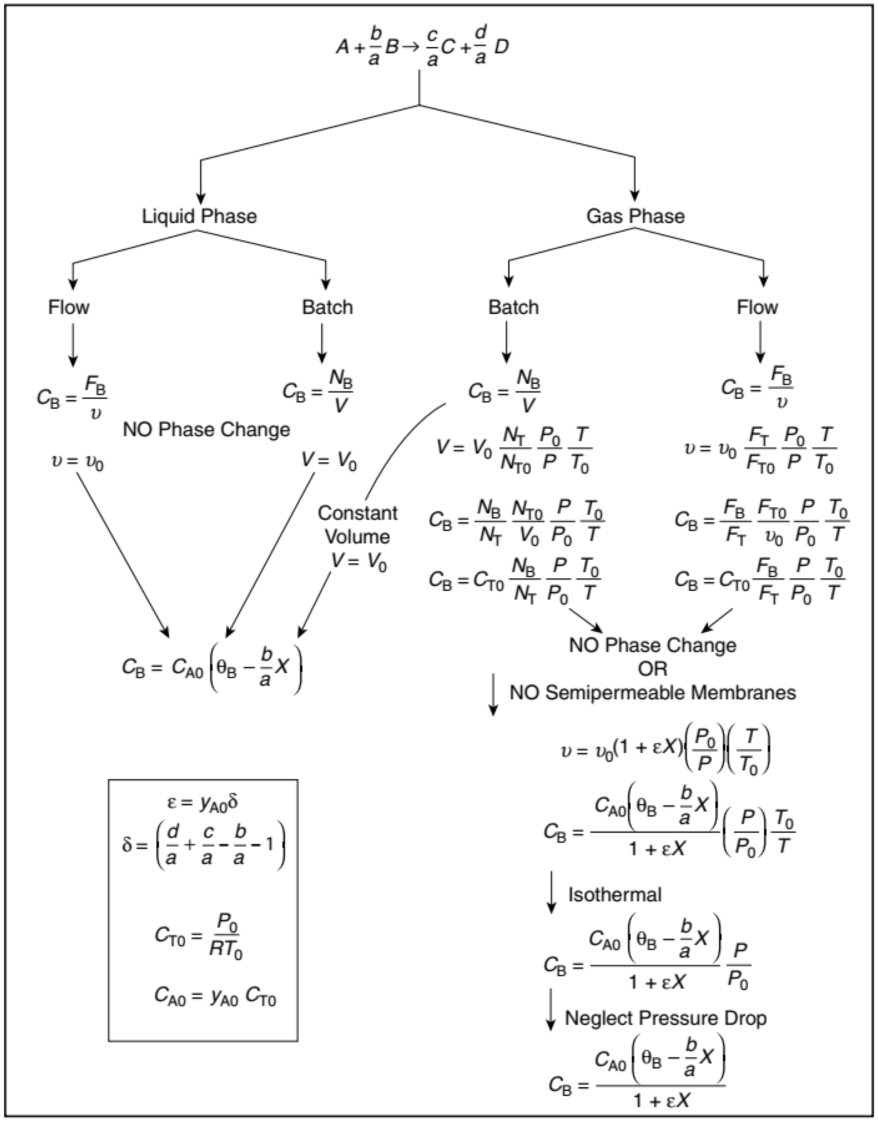


Figure 4-3 Expressing concentration as a function of conversion.

Example

The formation of ammonia is to be carried out isothermally at 227°C in packed bed reactor and with a pressure of 16.4 atm. This is an isobaric (constant pressure) flow system with equimolar feeds of N_2 & H_2. Assume the gas mixture behaves like an ideal gas.

$$H_2 + \tfrac{1}{3}N_2 \rightarrow \tfrac{2}{3}NH_3$$

Solution

The variation in molar flowrate for the reactant and product species across the reactor is listed in the Table bellow

Compound	Symbol	In	Change	Out
H_2	A	F_{A0}	$-F_{A0}X_A$	$F_{A0}-F_{A0}X_A$
N_2	B	$F_{B0}=F_{A0}$	$-(\tfrac{1}{3}F_{A0}X_A)$	$F_{A0}-(\tfrac{1}{3}F_{A0}X_A)$
NH_3	C	0	$\tfrac{2}{3}F_{A0}X_A$	$\tfrac{2}{3}F_{A0}X_A$
Total		$2F_{A0}$	$-\tfrac{2}{3}F_{A0}X_A$	$F_{A0}(2-\tfrac{2}{3}X_A)$

$$\delta = \nu_c + \nu_b - 1 = \frac{2}{3} - \frac{1}{3} - 1 \qquad \boxed{\rightarrow \delta = -\tfrac{2}{3}}$$

$$H_2 + \tfrac{1}{3}N_2 \rightarrow \tfrac{2}{3}NH_3$$

Equimolar feeds of N_2 & H_2 → $F_{B0} = F_{A0}$

$$y_{A0} = \frac{x}{2x} = \frac{1}{2}$$

$$\varepsilon = \delta y_{A0} = \left(-\frac{2}{3}\right)\left(\frac{1}{2}\right) = -\frac{1}{3} = \varepsilon$$

$$C_{A0} = \frac{N_{A0}}{V} = \frac{\text{mol}}{\text{volume}} = \frac{F_{A0}}{\upsilon_0}$$

If you don't have F_{A0} or υ_0

And do have P & T

→

Then relate P&T to C_{A0}:

$$PV = N_{T0}RT \rightarrow \frac{P}{RT} = \frac{N_{T0}}{V} = C_{T0}$$

N_2 & H_2 are equimolar in the feed: →

$$N_{A0} = \frac{1}{2}N_{T0}$$

$$\rightarrow C_{A0} = \frac{N_{A0}}{V} = \frac{0.5N_{T0}}{V} = \frac{0.5P}{RT}$$

P= 16.4 atm
T= 227°C = 500 K

$$\rightarrow C_{A0} = \frac{16.4\text{atm}}{2\left(0.082\frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}\right)500\text{K}} \rightarrow C_{A0} = 0.2\frac{\text{mol}}{\text{L}}$$

What are the concentrations of H_2, N_2, and NH_3 when H_2 is 60% consumed?

$$C_j = \frac{C_{j0}+\nu_j C_{A0}X_A}{1+\varepsilon X_A}\cancelto{1}{\left(\frac{P}{P_0}\right)}\cancelto{1}{\left(\frac{T_0}{T}\right)}\cancelto{1}{\left(\frac{Z_0}{Z}\right)}$$

isothermal
isobaric
ideal

$$\rightarrow C_j = \frac{C_{j0}+\nu_j C_{A0}X_A}{1+\varepsilon X_A}$$

$$X_A = 0.6 \quad \varepsilon = -\frac{1}{3} \quad C_{A0} = 0.2\frac{\text{mol}}{\text{L}} = C_{B0} \quad C_{C0}=0$$

$$C_{H_2} = \frac{0.2-1(0.2)(0.6)}{1+(-1/3)(0.6)} = 0.1\frac{\text{mol}}{\text{L}}$$

$$C_{N_2} = \frac{0.2+(-1/3)(0.2)(0.6)}{1+(-1/3)0.6} = 0.2\frac{\text{mol}}{\text{L}}$$

$$C_{NH_3} = \frac{0+(2/3)(0.2)(0.6)}{1+(-1/3)(0.6)} = 0.1\frac{\text{mol}}{\text{L}}$$

Damköhler Number

A Damköhler number (Da) is a useful ratio for determining whether diffusion rates or reaction rates are more ‘important’ for defining a steady-state chemical distribution over the length and time scales of interest.

$$\mathrm{Da} = \frac{\text{Reaction rate}}{\text{Diffusion rate}} = \frac{\text{Diffusion time}}{\text{Reaction time}}$$

$$\mathrm{Da} = \frac{-r_{A0} V}{F_{A0}} = \frac{\text{Rate of reaction at entrance}}{\text{Entering flow rate of A}} = \frac{\text{"A reaction rate"}}{\text{"A convection rate"}}$$

$$Da = k\, C_o^{n-1}\, \tau$$

- K = kinetics reaction rate constant
- C_0 = initial concentration
- n = reaction order
- τ = mean residence time or space time

Example

Consider the following second order reaction takes place in a tubular reactor at isothermal condition. What will be the volume of this reactor if (a) is a liquid phase (b) gas phase reaction is considered.

$$2A \rightarrow B$$

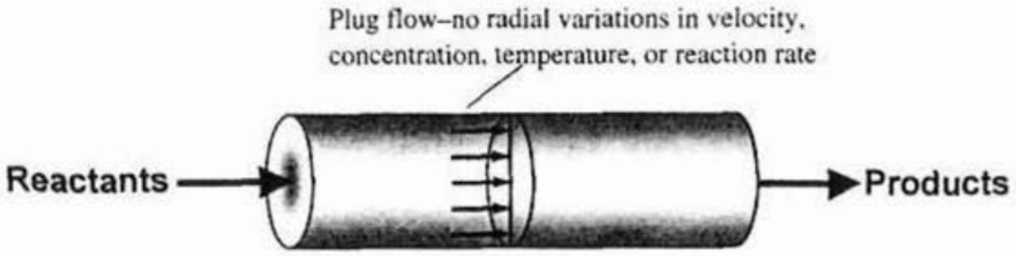


Figure 1-9 (Revisited) Tubular reactor.

Solution

(a) Liquid phase reaction

$2A \rightarrow B$

Liquid Phase $v = v_0$

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$

$$-r_A = kC_A^2$$

$$C_A = C_{A0}(1 - X)$$

$$\frac{dX}{dV} = \frac{kC_A^2}{F_{A0}}$$

$$V = \frac{F_{A0}}{kC_{A0}^2} \int_0^x \frac{dx}{(1-X)^2} = \frac{v_0}{kC_{A0}}\left(\frac{X}{1-X}\right)$$

$$(\tau = V/v_0)$$

$$X = \frac{\tau k C_{A0}}{1 + \tau k C_{A0}} = \frac{\mathrm{Da}_2}{1 + \mathrm{Da}_2}$$

(b) Gas phase reaction $\quad 2A \rightarrow B$

Assumption: Isothermal and Isobaric conditions

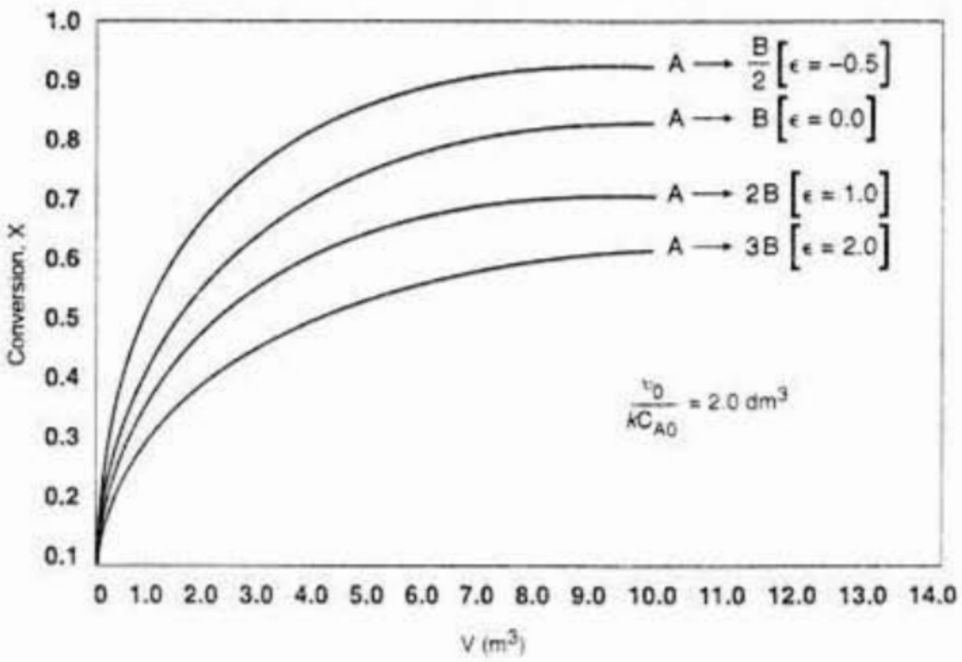
$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0(1+\varepsilon X)} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0}\frac{(1-X)}{(1+\varepsilon X)}$$

$$\frac{dX}{dV} = \frac{kC_A^2}{F_{A0}}$$

$$V = F_{A0}\int_0^X \frac{(1+\varepsilon X)^2}{kC_{A0}^2(1-X)^2}\,dX$$

$$V = \frac{F_{A0}}{kC_{A0}^2}\int_0^X \frac{(1+\varepsilon X)^2}{(1-X)^2}\,dX$$

$$V = \frac{v_0}{kC_{A0}}\left[2\varepsilon(1+\varepsilon)\ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X}\right]$$



Conversion as a function of distance down the reactor.

Calculation of equilibrium conversion

Example

The reversible gas-phase decomposition of nitrogen tetroxide N_2O_4, to nitrogen dioxide NO_2 is to be carried out isothermally at 340 K and pressure of 202.6 kpa (2 atm) [This pressure is for inlet feed]. the conc. equil. const. $K_c = 0.1$ mol/L

$$N_2O_2 \rightleftharpoons 2\,NO_2$$

a) Calc. the equil. conversion of N_2O_4 in a const. vol. batch Rxr.

$$A \rightleftharpoons 2\,B$$

In batch Rxr

$$N_A = N_{A0}(1-X)$$

$$N_B = N_{A0}(\Theta_B + 2X)$$

$$N_T = N_{T0} + N_{A0}X$$

also $C_A = C_{A0}(1-X)$, $C_B = 2\,C_{A0}X$

and

$$C_{A0} = \frac{y_{A0}P_0}{RT_0} = \frac{(1)(202.6\ \text{kPa})}{\left(8.314\ \frac{\text{kPa.L}}{\text{mol.K}}\right)(340\,\text{K})} = 0.071\ \frac{\text{mol}}{\text{L}}$$

$$K_c = \frac{C_{Beq}^2}{C_{Aeq}} = \frac{(2\,C_{A0}X_{eq})^2}{C_{A0}(1-X_{eq})} = \frac{4\,C_{A0}X_e^2}{1-X_{eq}} = 0.1$$

$$X_{eq} = 0.44$$

using of polymath software

The above equation can be written in the form

$$x_{eq} = \sqrt{\frac{K_c(1-x_e)}{4 C_{A0}}}$$

or $f(x_{eq}) = xeq - (Kc*(1-xeq)/(4*Cao))^0.5 = 0$

Explicite Equation

$K_c = 0.1$

$C_{A0} = 0.07174$

b) Calculate the equil. conv. of N_2O_4 in a flow reactor

In a flow reactor $\quad v = v_0(1+\epsilon x)$

and

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-x)}{v} = \frac{F_{A0}(1-x)}{v_0(1+\epsilon x)}$$

$$= C_{A0}\frac{(1-x)}{(1+\epsilon x)}$$

Similarly $\quad C_B = \frac{2 C_{A0} x}{1+\varepsilon x}$

$$\therefore \; K_c = \frac{C_{Beq}^2}{C_{Aeq}} = \frac{\left[2 C_{A0} x_{eq}/(1+\varepsilon x_{eq})\right]^2}{C_{A0}(1-x_{eq})/(1+\varepsilon x)} = \frac{4 C_{A0} x_{eq}^2}{(1-x_{eq})(1+\varepsilon x_{eq})} = 0.1$$

For $\varepsilon = y_{A0}\delta = (1)[2-1] = 1 \Rightarrow x_{eq} = 0.51$

using polymath

$$X_{eq} = \sqrt{\frac{K_c(1-X_{eq})(1+\varepsilon X_{eq})}{4C_{A0}}}$$

$$f(X_e) = X_{eq} - [kc*(1-X_{eq})*(1+eps*X_{eq})/(4*C_{A0}))^{\wedge}0.$$

c) what will be the rate for this Rxn in a batch and flow Rxr?

$$+r_A = -k_{Af}C_A + k_{Ab}C_B^2 \qquad A \underset{k_{Ab}}{\overset{k_{Af}}{\rightleftharpoons}} B_2$$

$$\therefore -r_A = k_{Af}\left[C_A - \frac{C_B^2}{K_c}\right]$$

For batch : $-r_A = k_{Af}\left[C_{A0}(1-X) - \frac{4C_{A0}^2X^2}{K_c}\right]$

For flow : $-r_A = k_{Af}\left[\frac{C_{A0}(1-X)}{(1+\varepsilon X)} - \frac{4C_{A0}^2X^2}{K_c(1+\varepsilon X)^2}\right]$

d) Determine the CSTR volume necessary to achieve 80% of the equil. conversion if $F_A = 3$ mol/min , $k_{Af} =$ ~~0.0036~~ 0.5/min

$X = 80\%$ of X_{eq}

$\therefore \quad X = 0.8\,(0.5) = 0.4$

$$-r_A = k_{Af}\left[\frac{C_{A0}(1-X)}{(1+\epsilon X)} - \frac{4\,C_{A0}^2 X^2}{K_c(1+\epsilon X)^2}\right]$$

$$= 0.5\left[0.072\frac{(1-X)}{(1+X)} - \frac{4(0.072)^2 X^2}{0.1\,(1+X)^2}\right]$$

$$= 0.0036\left[\frac{(1-X)}{(1+X)} - \frac{2.88\,X^2}{(1+X)}\right] \quad \frac{\text{mol}}{\text{L.min}}$$

$$V = \frac{F_{A0}X}{-r_A|_X} = \frac{(3\ \text{mol/min})(0.4)}{-r_A|_{X=0.4}}$$

@ $X = 0.4 \Rightarrow -r_A = 0.0007\ \frac{\text{mol}}{\text{L.min}}$

$$\therefore \quad V = \frac{3\times 0.4}{0.0007} = 1714\ \text{L} = 1.71\ \text{m}^3$$

Collection and analysis of Rate Data

In this class we will study the determination rate order and constant using:

1. Method of Excess (initial rate method)
2. Method of half-lives
3. Integral Method
4. Differential Method

1. Method of Excess (isolation method)

This method assumes one reactant as limiting and considers the other reactants are in excess. Therefore, these excess reactants will constantly affect the rate of reaction. Therefore, the whole terms related to these excess reactants' concentration are constant. Hence, the rate of reaction is the only function of the concentration of the limiting reactant with its stoichiometric power. As a result, the rate constant and stoichiometric power will be determined. Then the procedure is repeated, but their corresponding coefficients will be determined for the other reactants that were considered in excess.

To illustrate this, let us assume the following reaction with its rate law

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{Products} \qquad\qquad -r_{\mathrm{A}} = k_{\mathrm{A}} C_{\mathrm{A}}^{\alpha} C_{\mathrm{B}}^{\beta}$$

First, we will assume B is in excess, therefore, it will not affect the rate of reaction as it have constant (but not varied) effect. Therefore, the rate of reaction becomes:

$$-r_{\mathrm{A}} = k' C_{\mathrm{A}}^{\alpha}$$

Where the concentration of B at any time is assumed to equal its initial concentration; $C_B \approx C_{B0}$

Therefore, the rate of reaction becomes $\boxed{-r_A = k' C_A^{\alpha}}$

Where $k' = k_A C_B^{\beta} \approx k_A C_{B0}^{\beta}$

Having the natural log of rate of reaction versus that of concentration of A yields a straight line with a slope of $\propto$ and intercept of lnk' as

$$ln\, r_A = lnk' + \propto lnC_A$$

Similarly, to obtain the stoichiometric coefficient of B, the reactant A is considered in excess and concentration of B is varied as

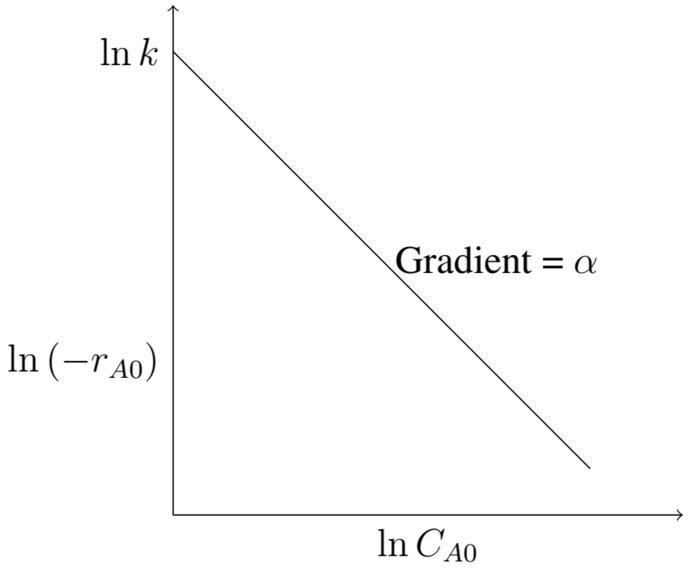
$-r_A = k'' C_B^{\beta}$ Where $k'' = k_A C_A^{\alpha} \approx k_A C_{A0}^{\alpha}$

Once and are determined, the rate constant, k_A the can be calculated from the measurement of $-r_A$ at known concentrations of A and B

$$-r_{\mathrm{A}} = k_{\mathrm{A}} C_{\mathrm{A}}^{\alpha} C_{\mathrm{B}}^{\beta}$$

$$k_{\mathrm{A}} = \frac{-r_{\mathrm{A}}}{C_{\mathrm{A}}^{\alpha} C_{\mathrm{B}}^{\beta}} = \frac{(\mathrm{dm}^3/\mathrm{mol})^{\alpha+\beta-1}}{s}$$

If the rate law is, $-r_A = kC_A^\alpha$ then a plot of $\ln(-r_{A0})$ against $\ln C_{A0}$



Example

Given the following data for variation of concentration of species with the rate of their reaction. Determine the order of reaction using the initial rate method.

$$A + B + 2C \rightarrow D + 2E$$

Experiment	[A] mol dm^{-3}	[B] mol dm^{-3}	[C] mol dm^{-3}	Rate mol dm^{-3} s^{-1}
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

Solution

$A + B + 2C \rightarrow D + 2E$

In order to calculate the order for a particular reactant it is easiest to compare two experiments where **only that reactant** is being changed

If conc is doubled and rate stays the same: order= 0

If conc is doubled and rate doubles: order= 1

If conc is doubled and rate quadruples : order= 2

For reactant A compare between experiments **1 and 2**

- For reactant A as the concentration **doubles** (B and C staying constant) so does the rate. Therefore the order with respect to reactant **A is first order**

For reactant B compare between experiments **1 and 3** :

- As the concentration of B **doubles** (A and C staying constant) the rate **quadruples**. Therefore the order with respect to **B is 2nd order**

Experiment	[A] mol dm^{-3}	[B] mol dm^{-3}	[C] mol dm^{-3}	Rate mol $\text{dm}^{-3}\ \text{s}^{-1}$
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

$A + B + 2C \rightarrow D + 2E$

For reactant C compare between experiments **1 and 4** :

- As the concentration of C **doubles** (A and B staying constant) the rate **stays the same**. Therefore the order with respect to **C is zero order**

Experiment	[A] mol dm^{-3}	[B] mol dm^{-3}	[C] mol dm^{-3}	Rate mol dm^{-3} s^{-1}
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

The overall rate equation is $r = k [A] [B]^2$

The reaction is 3rd order overall and the unit of the rate constant is $\frac{L^6}{mol^2.s}$

2. Method of half-lives

$$-\frac{\mathrm{d}\,C_A}{\mathrm{d}\,t} = -r_A = kC_A^{\alpha}$$

Integrating the design equation with $C_A = C_{A0}$ when $t = 0$ yields:

$$t = \frac{1}{k\left(\alpha - 1\right)}\left(\frac{1}{C_A^{\alpha-1}} - \frac{1}{C_{A0}^{\alpha-1}}\right)$$

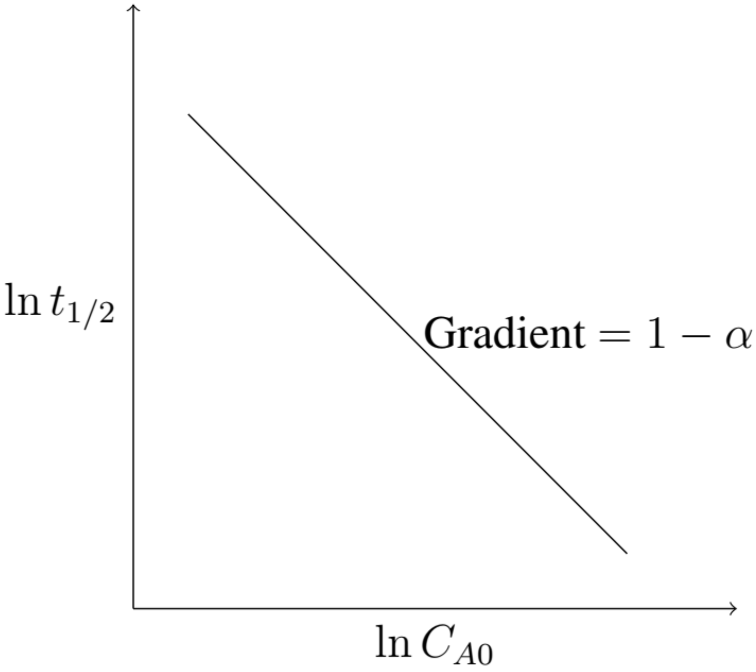
$$t = \frac{1}{kC_{A0}^{\alpha-1}\left(\alpha - 1\right)}\left[\left(\frac{C_{A0}}{C_A}\right)^{\alpha-1} - 1\right]$$

We then use the definition of half-life, $t = t_{1/2}$ when $C_A = 1/2C_{A0}$

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k\left(\alpha - 1\right)}\frac{1}{C_{A0}^{\alpha-1}}$$

$$t_{1/2} = \frac{2^{\alpha-1}-1}{k\,(\alpha-1)}\frac{1}{C_{A0}^{\alpha-1}} \quad \Rightarrow \quad \ln t_{1/2} = \ln\frac{2^{\alpha-1}-1}{k\,(\alpha-1)} + (1-\alpha)\ln C_{A0}$$

Plotting $\ln t_{1/2}$ against $\ln C_{A0}$ gives a line with a slope equal to $(1-\alpha)$



Example

Based on the following concentration data as a function of time, determine the behavior of the half-life as the reaction progresses. Use this information to determine if the following reaction is 0 order, 1 order, or 2 order in A. Also, use the data to estimate the rate constant for the reaction.

time (s)	[A] (M)
0	1.200
10	0.800
20	0.600
30	0.480
40	0.400
50	0.343
60	0.300
70	0.267
80	0.240
90	0.218
100	0.200

Solution

If the original concentration is taken as 1.200 M, half of the original concentration is 0.600 M. The reaction takes 20 seconds to reduce the concentration to half of its original value. If the original concentration is taken as 0.800 M, it clearly takes 30 seconds for the concentration to reach half of that value. Based on this methodology, the following table is easy to generate:

$[A]_o$ (M)	1.200	0.800	0.600	0.400
$t_{1/2}$ (s)	20	30	40	60

The rate constant can be calculated using any of these values:

$$k = \frac{1}{[A]t_{1/2}} = \frac{1}{(0.8\,M)(30\,s)} = 0.0417\,M^{-1}s^{-1}$$

3. Integral Method

The integral method is the quickest method to use to determine the rate law if the order turns out to zero, first, or second order. This method uses a trial-and-error procedure to find the reaction order. The reaction order is assumed (guessed) in a combined batch reactor mole balance and the equation is integrated as a concentration versus time

First assume a zero-order reaction, $r_A = -k$, and the combined rate law and mole balance is $\frac{dC_A}{dt} = -k$

Integrating with $C_A = C_{A0}$ at $t = 0$, we have

$$\boxed{C_A = C_{A0} - kt}$$

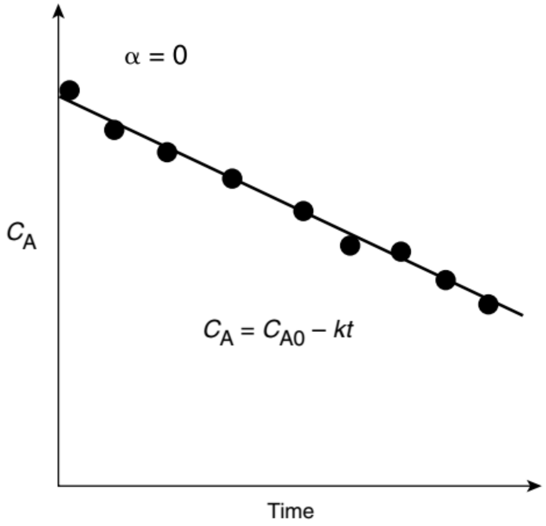


Figure 7-1 Zero-order reaction.

First-order reaction

Now assume a first-order reaction with rate equation of

$$-\frac{dC_A}{dt} = kC_A$$

The integration of this equation

with the limit $C_A = C_{A0}$ at $t = 0$ gives

$$\ln\frac{C_{A0}}{C_A} = kt$$

A plot of $ln\frac{C_{A0}}{C_A}$ with time yield a

straight line with slope of k

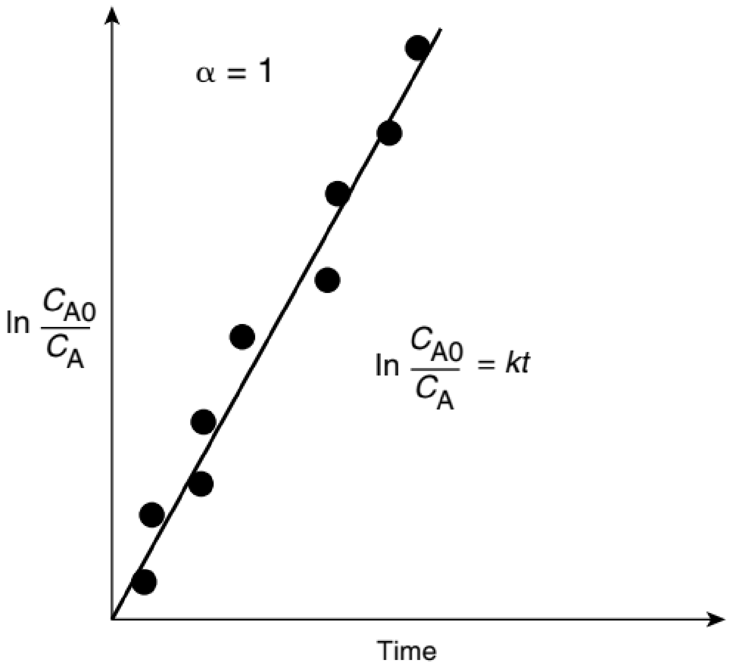


Figure 7-2 First-order reaction.

Second-order reaction

Now assume a second-order reaction with type of

$$2A \rightarrow product$$

The rate equation is

$$-\frac{dC_A}{dt} = kC_A^2$$

with the limit $C_A = C_{A0}$ at $t = 0$ gives

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

A plot of $\frac{1}{C_A}$ with time yield a straight line with slope of k

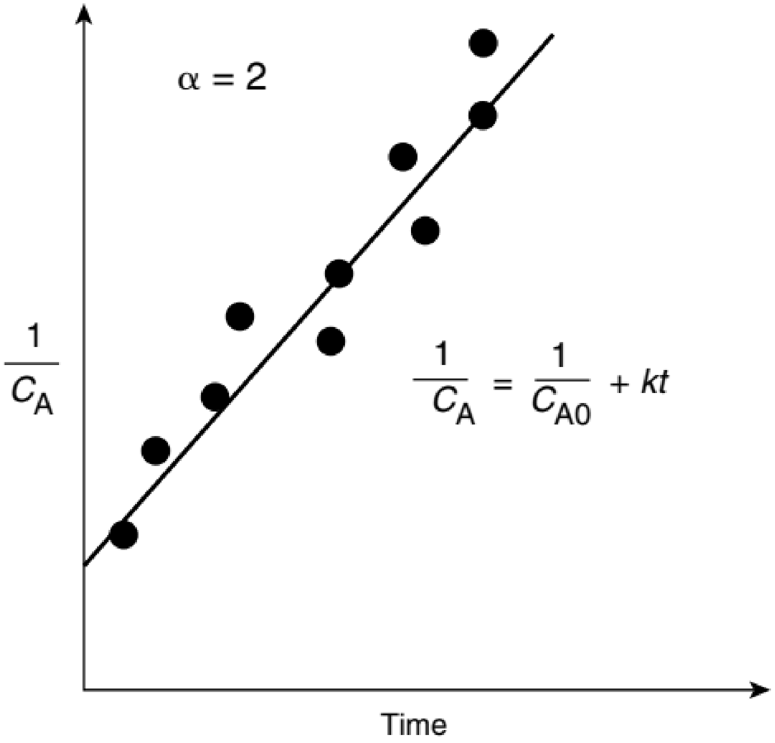


Figure 7-3 Second-order reaction.

4. Differential Method

In this method here we consider a reaction carried out isothermally in a constant-volume batch reactor and the concentration of *A*, is recorded as a function of time. By combining the mole balance with the rate law given by

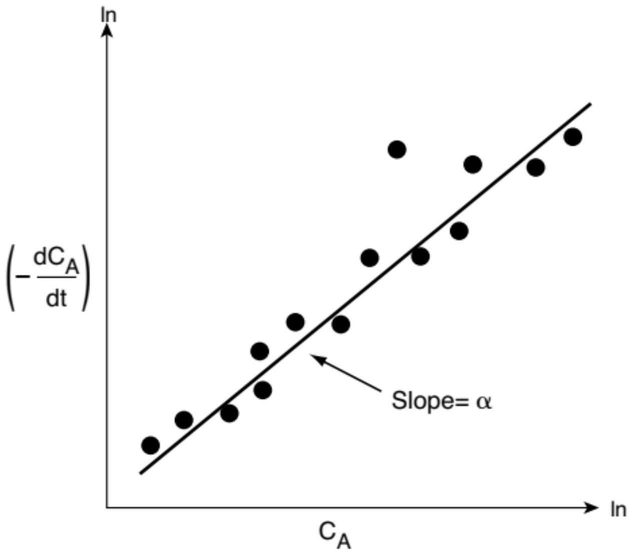
$$-\frac{dC_A}{dt} = k_A C_A^{\alpha}$$

If the natural logarithmic is taken for the above equation we get

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k_A + \alpha \ln C_A$$

Or in difference form

$$ln\left(\frac{\Delta C_A}{\Delta t}\right) = ln\ k_A + \propto ln\ C_A$$



The slope of a plot of $ln\left(\frac{\Delta C_A}{\Delta t}\right)$ as a function of $ln\ C_A$ yields the slope $\propto$ and intercept $ln\ k_A$. Then the reaction order $\propto$ will be defined .

Example

Liquid phase reaction between trimethylamine(A) and n-propyl bromide (B) was studied by Winkler & Hinshelwood. The results at 139.4 C are shown below. Initial solutions of A and B in benzene is 0.1 molar each, were mixed and placed in constant temperature bath. After certain times, they were cooled to stop the reaction. Determine the first order and second order specific rates, k1 and k2, assuming the reaction is irreversible. Use integration and differential methods.

Run	t, min	x (%)
1	13	11.2
2	34	25.7
3	59	36.7
4	120	55.2

Solution

$A + B \rightarrow C^{+} + D^{-}$

Volume is constant

1st order $\quad -r_A = \frac{dC_A}{dt} = k_1 \cdot C_A$

2nd order $\quad -r_A = \frac{dC_A}{dt} = k_2 \cdot C_A \cdot C_B$

Integration Method

1st order $\quad -\ln \frac{C_A}{C_{A0}} = k_1 \cdot t \quad \Rightarrow \quad k_1 = \frac{1}{t} \cdot \ln \frac{C_{A0}}{C_A} \quad \Rightarrow \quad C_A = C_{A0}(1 - x)$

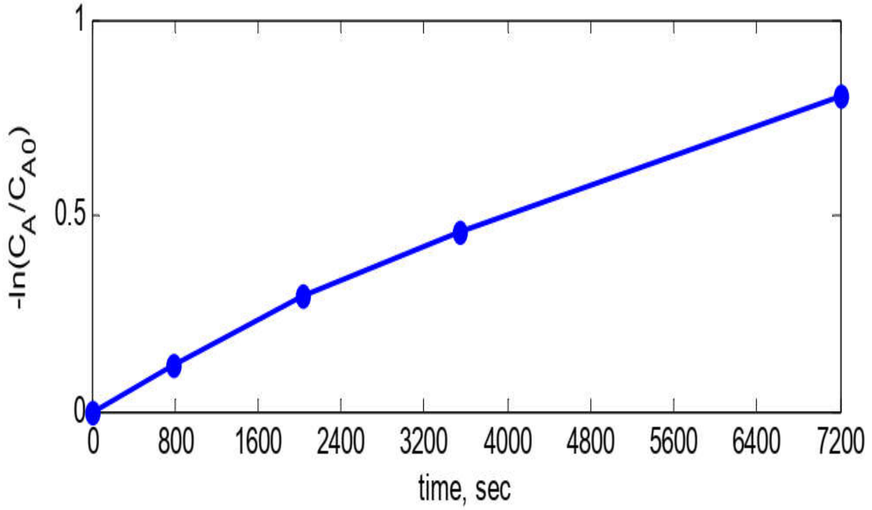
For the first run $\quad x = 0.112 \quad \Rightarrow \quad C_A = 0.1(1 - 0.112) = 0.0888$

$$k_1 = \frac{1}{t} \cdot \ln \frac{C_{A0}}{C_A} = \frac{1}{13 \cdot 60} \ln \frac{0.1}{0.0888} = 1.54 \times 10^{-4}\, sn^{-1}$$

If you repeat for four of the runs:

Run	t, sec	$k_1 \times 10^{-4}$ (s^{-1})
1	780	1.54
2	2040	1.46
3	3540	1.30
4	7200	1.12

⇨



2nd order

Stoichiometric coefficients are equal and $C_{A0} = C_{B0} = 0.1$ molal

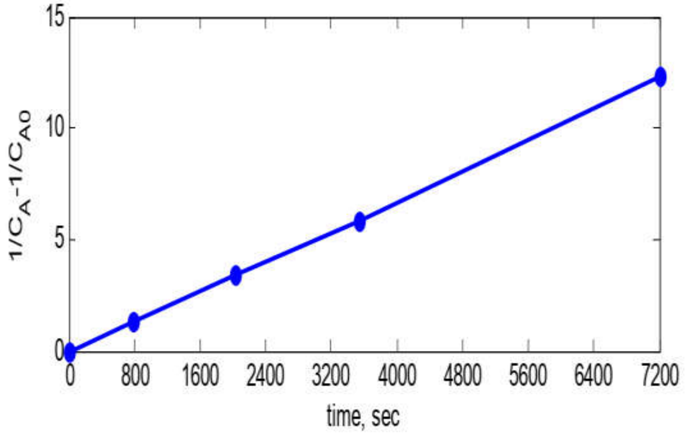
$$-\frac{dC_A}{dt} = k_2 \cdot C_A^{\,2} \quad \Rightarrow \quad \frac{1}{C_A} - \frac{1}{C_{A0}} = k_2 \cdot t \quad \Rightarrow \quad k_2 = \frac{1}{t \cdot C_{A0}} \cdot \left(\frac{1}{1-x} - 1 \right)$$

$$C_A = C_{A0}(1-x)$$

$$k_2 = \frac{1}{t \cdot C_{A0}} \cdot \left(\frac{1}{1-x} - 1 \right) = \frac{0.112}{(13 \cdot 60) \cdot 0.1 \cdot (1 - 0.112)} = 1.63 \times 10^{-3} \frac{L}{gmol \cdot s}$$

If you repeat for four of the runs:

Run	t, sec	$k_1 \times 10^{-4}$ (s^{-1})	$k_2 \times 10^{-3}$ (L/mol s)
1	780	1.54	1.63
2	2040	1.46	1.70
3	3540	1.30	1.64
4	7200	1.12	1.71

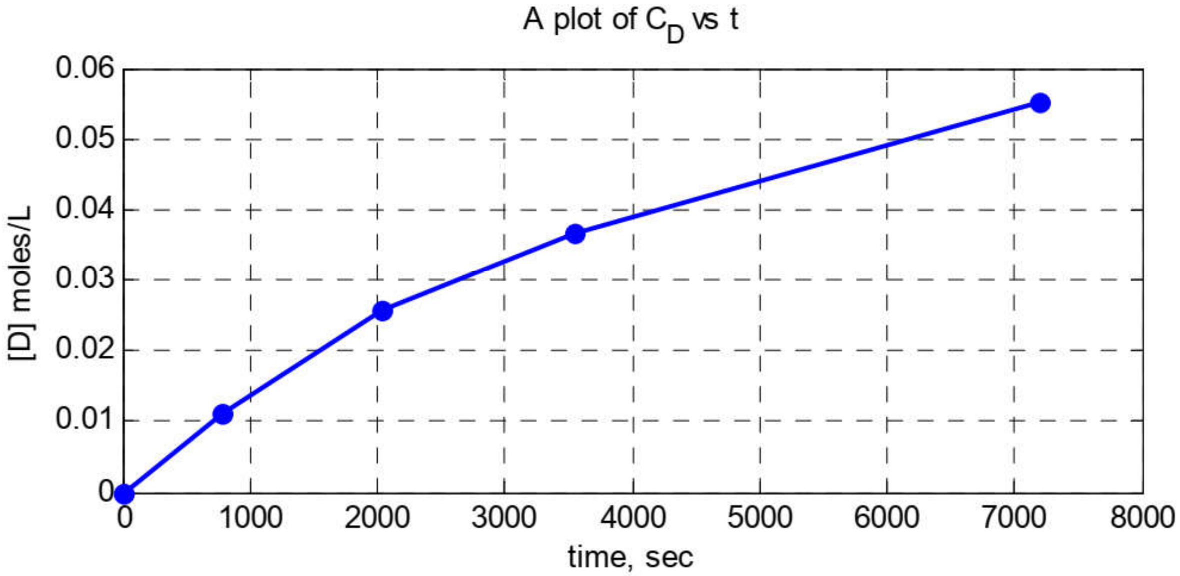


So, it is SECOND ORDER

Differential Method

$C_D = C_{A0} - C_A$ (moles of D produced = moles of A reacted)

$C_D = x\, C_{A0}$



$$r = -\frac{dC_A}{dt} = \frac{dC_D}{dt} \quad \text{(the slope of the curve)}$$

Slopes determined from the curve are given as follows

C_D	C_A	$r = dC_D/dt$ (10^5 gmol/L)
0.0	0.10	1.58
0.01	0.09	1.38
0.02	0.08	1.14
0.03	0.07	0.79
0.04	0.06	0.64
0.05	0.05	0.45

$\log r_A = \log k_1 + \log C_A$ (from $-r_A = k_1 C_A$)

$\log r_A = \log k_2 + \log C_A^2 = \log k_2 + 2 \log C_A$ (from $-r_A = k_2 C_A^2$)

1st: log r vs log C_A should yield a straight line with a slope of 1.0.

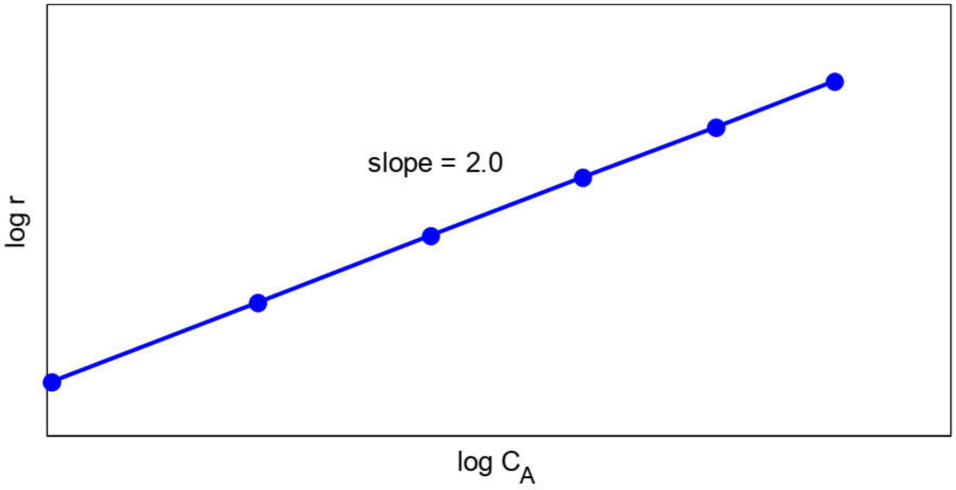
2nd: log r vs log C_A should yield a straight line with a slope of 2.0.

$\log r = -2.76 + 2.0 \log C_A$

The data suggest a slope of 2!

$\log k_2 = -2.76$

$k_2 = 1.73 \times 10^{-3}$ L / mol s



Comparison between reactors

In this class we will study the determination rate order and constant using:

1. Graphical interpretation of reactor sizing
2. Reactors in series

Note: Part of this topic is obtained from lecture notes of professor Özlem Keskin -Koç University, Turkey
http://home.ku.edu.tr/~okeskin/ChBI502/chbi_502.htm

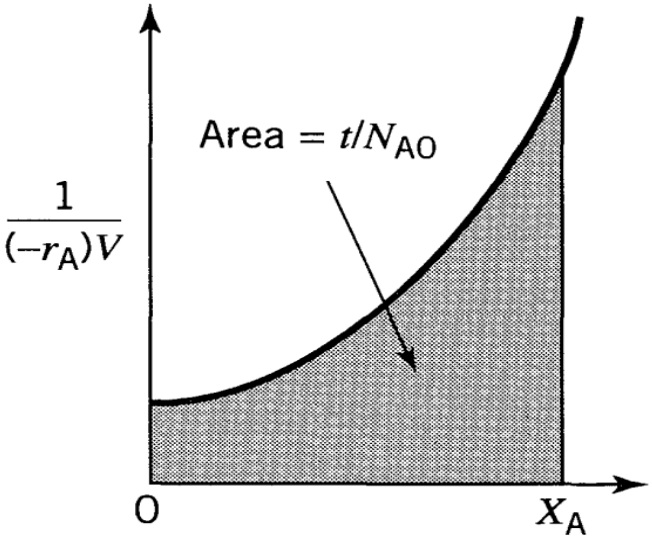
Batch Reactor

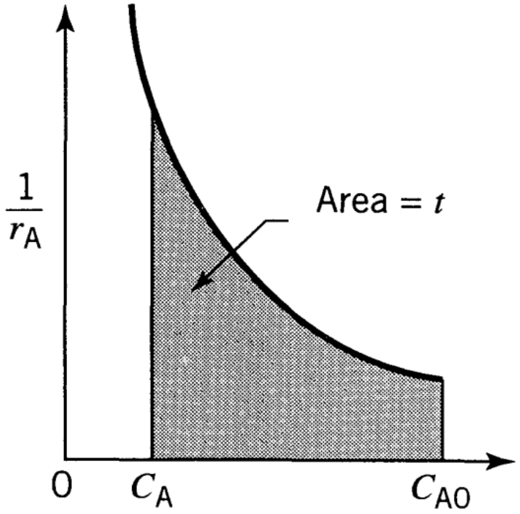
$$\frac{dN_A}{dt} = \frac{d[N_{A0}(1 - X_A)]}{dt} = -N_{A0}\frac{dX_A}{dt}$$

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

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

$$t = C_{A0}\int_0^{X_A}\frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_A}\frac{dC_A}{-r_A}$$





Space-Time and Space-Velocity

Space time

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

Space time is the time necessary to process one volume of reactor fluid at the entrance conditions.

$$\tau = \frac{1}{s} = \frac{C_{A0}V}{F_{A0}} = \frac{V}{v_0} = \frac{(\text{reactor volume})}{(\text{volumetric feed rate})}$$

Example: $v_0 = 0.01\ \text{m}^3/\text{s}$ and $V = 0.2\ \text{m}^3 \rightarrow \tau = 0.2\ \text{m}^3 / 0.01\ \text{m}^3/\text{s} = 20\ \text{s}$

It would take 20 s for the fluid at the entrance to move to the exit.

Typical space time for different reactors:

Batch : 15 min – 20 h (few kg/day – 100,000 tons/year ≈ 280 tons/day)

CSTR : 10 min – 4 h (10 to 3 x 10^6 tons/yr)

Tubular: 0.5s – 1h (50 to 5 x 10^6 tons/yr)

Space-velocity:

$$s = \frac{1}{\tau} = \begin{pmatrix} \text{number of reactor volumes of} \\ \text{feed at specified conditions which} \\ \text{can be treated in unit time} \end{pmatrix} = [\text{time}^{-1}]$$

$$SV = \frac{v_0}{V} = \frac{1}{\tau}$$

instead of using volumetric flow rate at the entrance, you use liquid – hourly & gas – hourly space velocities (LHSV, GHSV).

v_0 (for LHSV) is that of a liquid feed rate at 60°F or 75°F.

v_0 (for GHSV) is that of the one that measured at STP.

$$LHSV = \frac{v_0\big|_{liq}}{V} \qquad GHSV = \frac{v_0\big|_{STP}}{V}$$

Continuous Stirred Tank Reactor (CSTR)

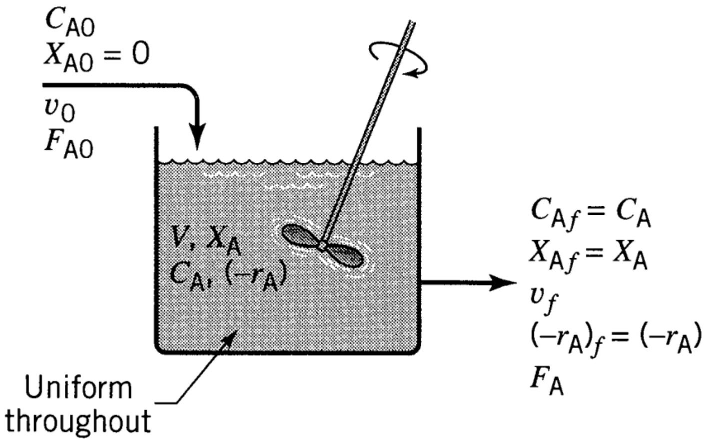
$$F_{\mathrm{A0}}X_{\mathrm{A}} = (-r_{\mathrm{A}})V$$

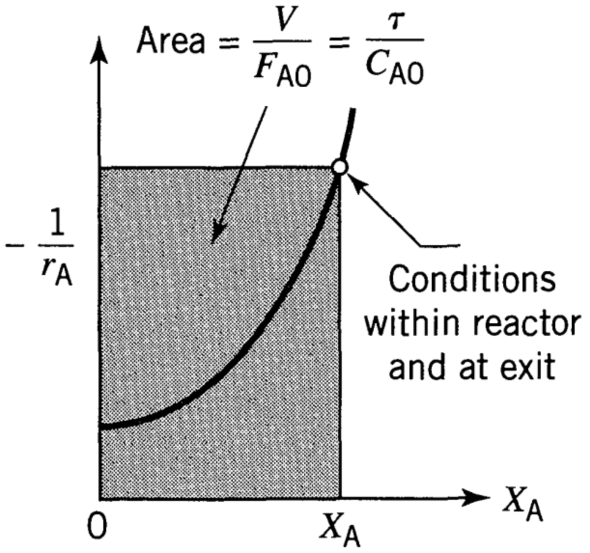
$$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{VC_{\mathrm{A0}}}{F_{\mathrm{A0}}} = \frac{C_{\mathrm{A0}}X_{\mathrm{A}}}{-r_{\mathrm{A}}}$$

$$\frac{V}{F_{\mathrm{A0}}} = \frac{\tau}{C_{\mathrm{A0}}} = \frac{\Delta X_{\mathrm{A}}}{-r_{\mathrm{A}}} = \frac{X_{\mathrm{A}}}{-r_{\mathrm{A}}}$$

$$\frac{V}{F_{\mathrm{A0}}} = \frac{\Delta X_{\mathrm{A}}}{(-r_{\mathrm{A}})_f}$$

$$\frac{V}{F_{\mathrm{A0}}} = \frac{X_{\mathrm{A}}}{-r_{\mathrm{A}}} = \frac{C_{\mathrm{A0}} - C_{\mathrm{A}}}{C_{\mathrm{A0}}(-r_{\mathrm{A}})}$$

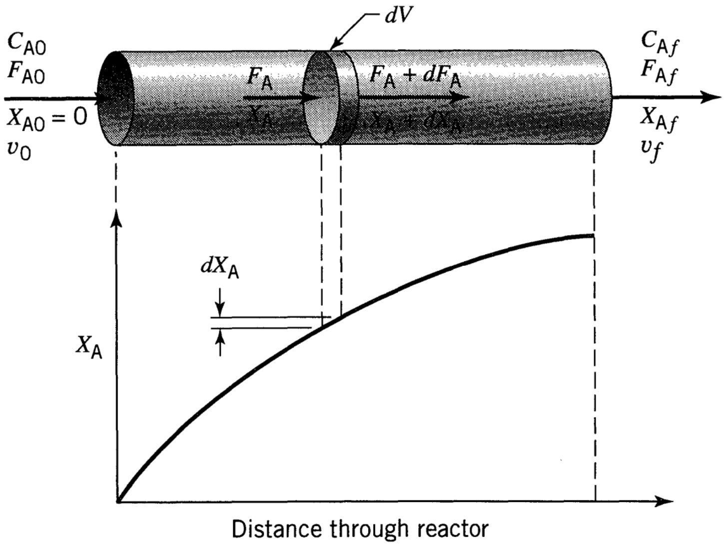


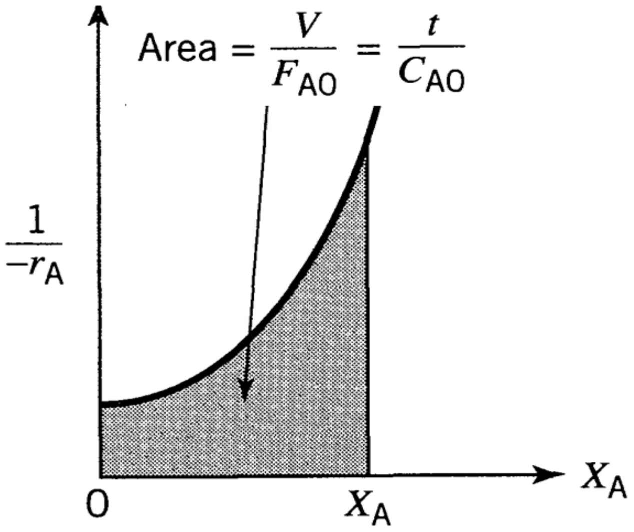


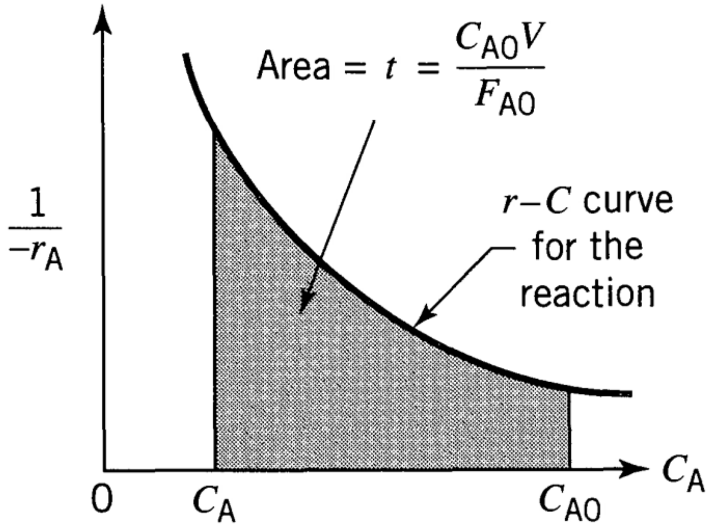
Plug Flow Reactor (PFR)

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

$$\tau = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$







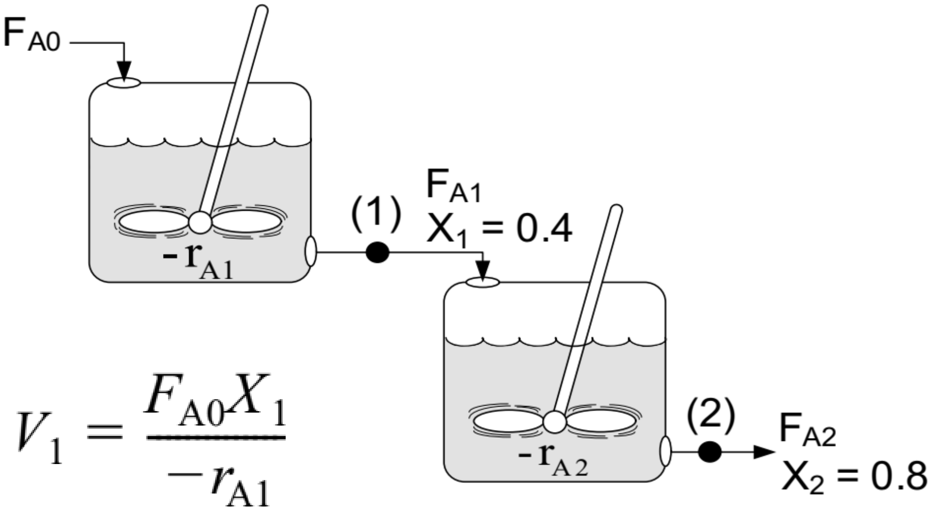
Holding Time and Space Time for Flow Reactors

$$\tau = \begin{pmatrix} \text{time needed to} \\ \text{treat one reactor} \\ \text{volume of feed} \end{pmatrix} = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}}, \quad [\text{hr}]$$

$$\bar{t} = \begin{pmatrix} \text{mean residence time} \\ \text{of flowing material} \\ \text{in the reactor} \end{pmatrix} = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)}, \quad [\text{hr}]$$

Reactors in Series

1. CSTRs in Series



In – Out + Generation = 0

Reactor 1: $F_{A0} - F_{A1} + r_{A1}V_1 = 0$

$$V_1 = \frac{F_{A0}X_1}{-r_{A1}}$$

In – Out + Generation = 0

Reactor 2: $F_{A1} - F_{A2} + r_{A2}V_2 = 0$

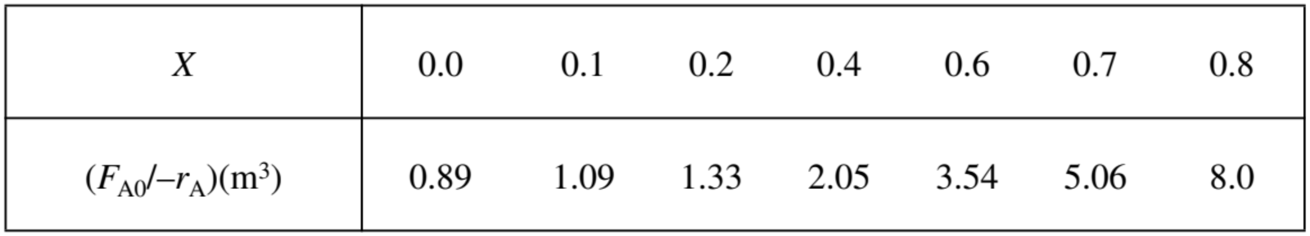
$$F_{A2} = F_{A0} - F_{A0}X_2$$

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{(F_{A0} - F_{A0}X_1) - (F_{A0} - F_{A0}X_2)}{-r_{A2}}$$

$$V_2 = \frac{F_{A0}}{-r_{A2}}(X_2 - X_1)$$

Example 6.1 CSTRs in series

For the two CSTRs in series, 40% conversion is achieved in the first reactor. What is the volume of each of the two reactors necessary to achieve 80% overall conversion of the entering species A?



X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$(F_{A0}/-r_A)(m^3)$	0.89	1.09	1.33	2.05	3.54	5.06	8.0

Solution

For Reactor 1, we observe from Table that when $X = 0.4$, then

$$\left(\frac{F_{A0}}{-r_{A1}}\right)_{X=0.4} = 2.05 \text{ m}^3$$

$$V_1 = \left(\frac{F_{A0}}{-r_{A1}}\right)_{X_1} X_1 = \left(\frac{F_{A0}}{-r_{A1}}\right)_{0.4} X_1 = (2.05)(0.4) = 0.82 \text{ m}^3 = 820 \text{ dm}^3$$

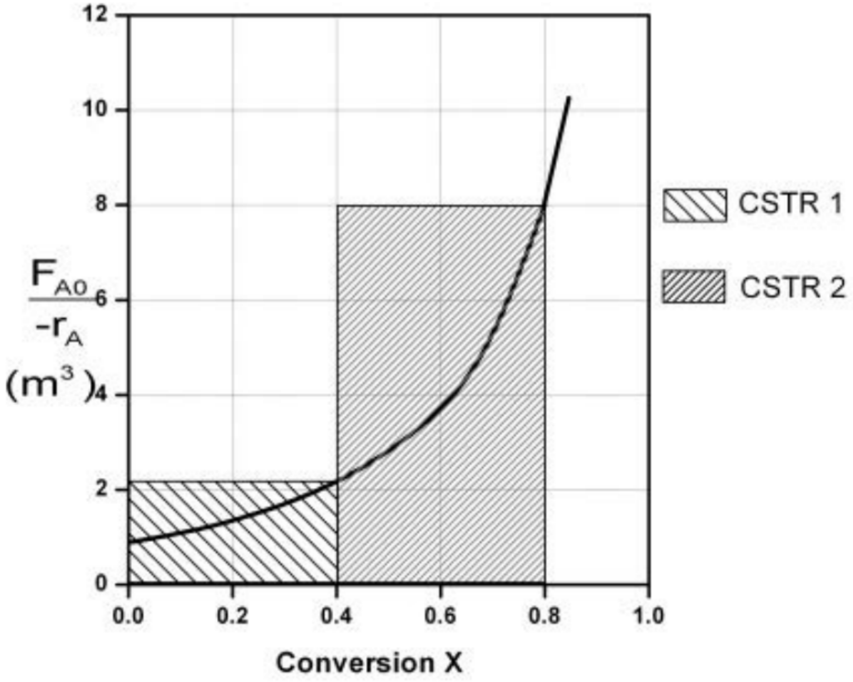
X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$(F_{A0}/-r_A)(\text{m}^3)$	0.89	1.09	1.33	2.05	3.54	5.06	8.0

For Reactor 2, when $X_2 = 0.8$, then $\left(\frac{F_{A0}}{-r_A}\right)_{X=0.8} = 8.0\ \text{m}^3$

$$V_2 = \left(\frac{F_{A0}}{-r_{A2}}\right)(X_2 - X_1)$$

$$V_2 = (8.0\ \text{m}^3)(0.8 - 0.4) = 3.2\ \text{m}^3 = 3200\ \text{dm}^3$$

$$V_2 = 3200\ \text{dm}^3\ \text{(liters)}$$

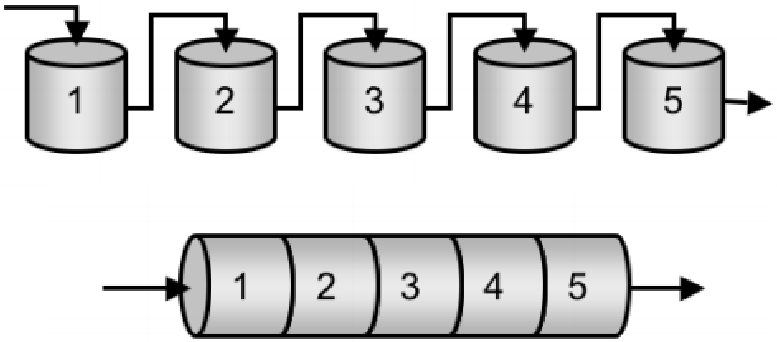


$$V = V_1 + V_2 = 0.82\ \text{m}^3 + 3.2\ \text{m}^3 = 4.02\ \text{m}^3 = 4020\ \text{dm}^3$$

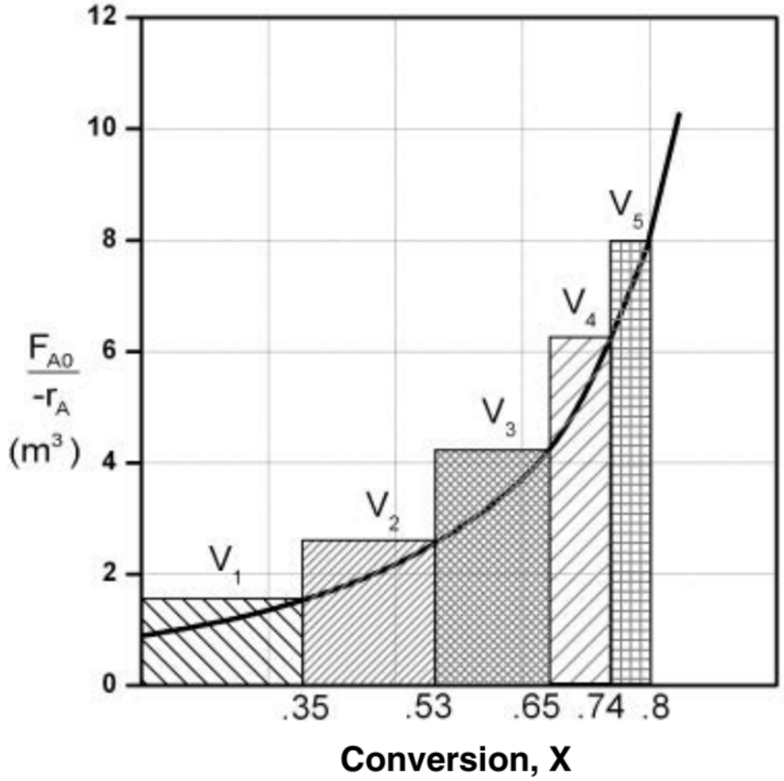
By comparison, the volume necessary to achieve 80% conversion in **one** CSTR is

$$V = \left(\frac{F_{\text{A0}}}{-r_{\text{A1}}}\right)X = (8.0)(0.8) = 6.4\ \text{m}^3 = 6400\ \text{dm}^3$$

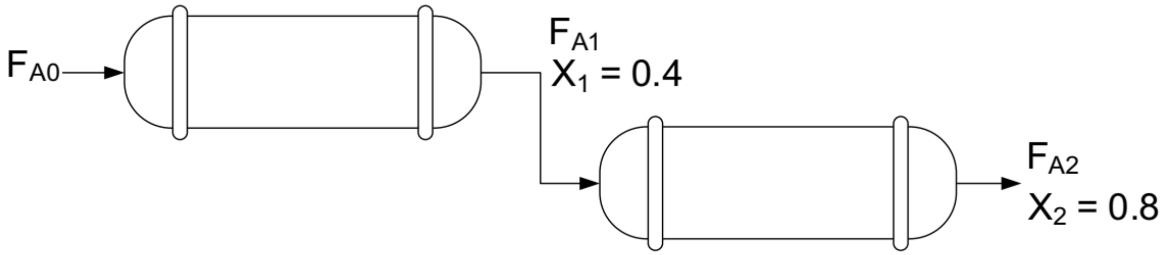
Approximating a PFR by a Large Number of CSTRs in Series



A one PFR can be modeled by a large number of CSTRs

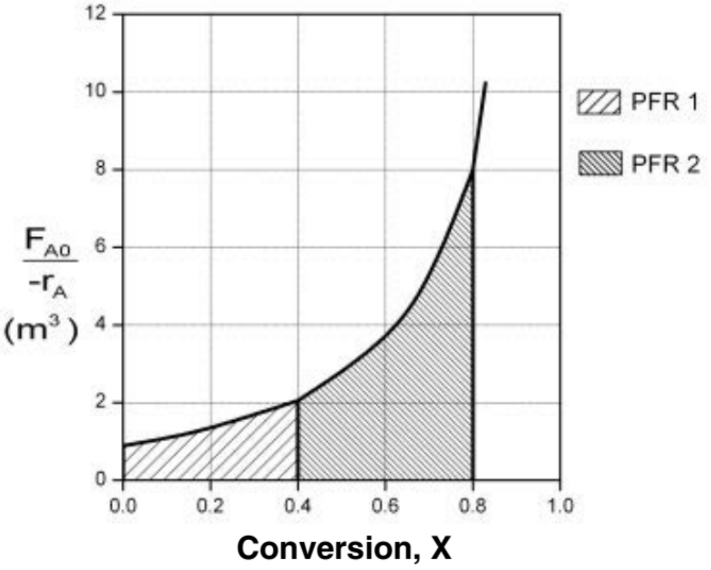


2. PFR in Series

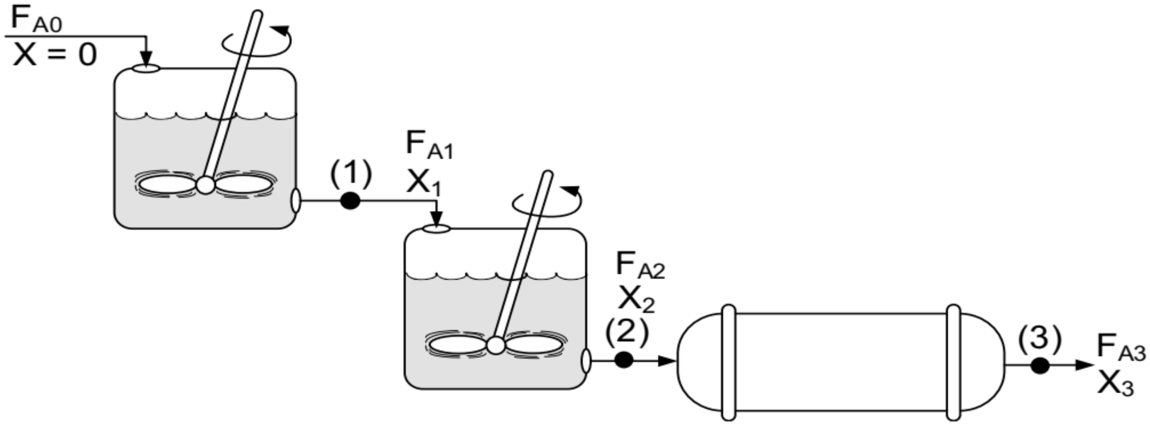


$$\int_0^{X_2} F_{A0}\frac{dX}{-r_A} \equiv \int_0^{X_1} F_{A0}\frac{dX}{-r_A} + \int_{X_1}^{X_2} F_{A0}\frac{dX}{-r_A}$$

A one PFR has a similar conversion as large number of small PFRs, as well as the total sizes of the small PFRs equals that of one large PFR



Combinations of CSTRs and PFRs in Series



Reactor 1:

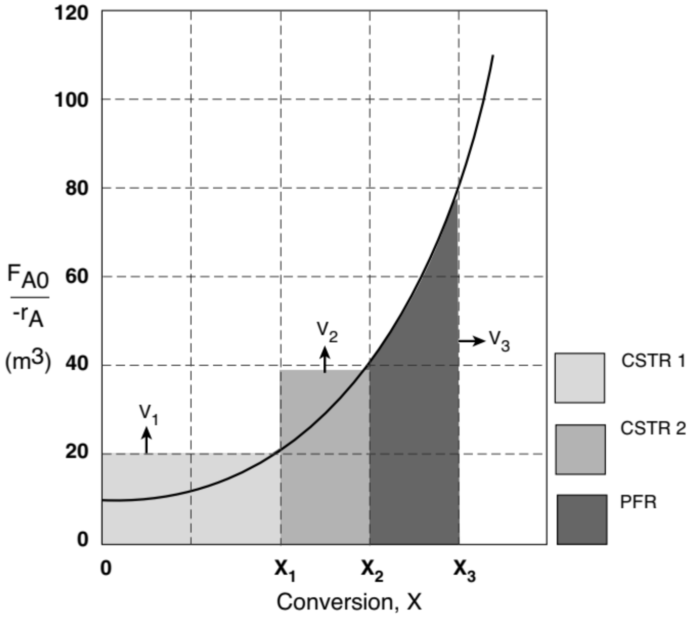
$$V_1 = \frac{F_{A0} X_1}{-r_{A1}}$$

Reactor 2:

$$V_2 = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}}$$

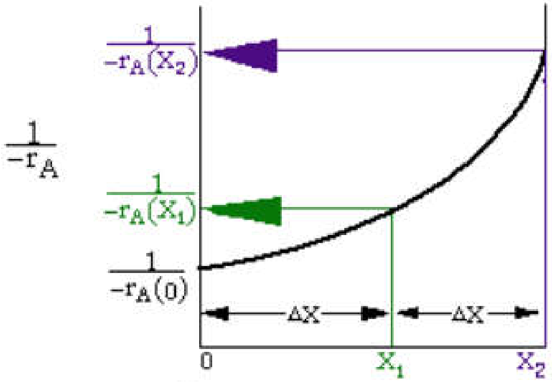
Reactor 3:

$$V_3 = \int_{X_2}^{X_3} \frac{F_{A0}}{-r_A} dX$$



Numerical Evaluation of Intergrals

The integral to calculate the PFR volume can be evaluated using a method such as Simpson's One-Third Rule.



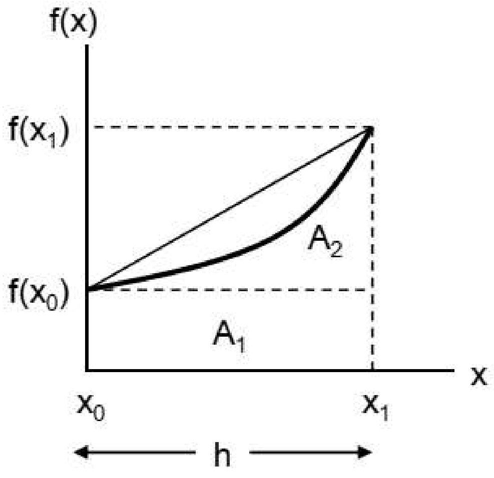
PFR: $V = F_{A0}\int_0^X \frac{dX}{-r_A} = F_{A0}\frac{\Delta X}{3}\left[\frac{1}{-r_{A(X=0)}} + \frac{4}{-r_{A(X_1)}} + \frac{1}{-r_{A(X_2)}}\right]$

NOTE: The intervals (ΔX) shown in the sketch are not drawn to scale. They should be equal.

Simpson's One-Third Rule is one of the most common numerical methods. It uses three data points. One numerical methods for evaluating integrals are:

1. Trapezoidal Rule (uses two data points)
2. Simpson's Three-Eighth's Rule (uses four data points)

Trapezoidal Rule



$$\int_{x_0}^{x_1} f(x)\cdot dx = \frac{1}{h}[f(x_0)+f(x_1)]$$

$$A_1 = f(x_0)\cdot h$$

$$A_2 = \frac{[f(x_1)-f(x_0)]\cdot h}{2}$$

$$A = A_1 + A_2$$

$$= h\cdot\left[f(x_0)+\frac{f(x_1)}{2}-\frac{f(x_0)}{2}\right]$$

$$= \frac{h}{2}\cdot[f(x_0)+f(x_1)]$$

Five Point Quadrature formula:

$$\int_{x_0}^{x_4} f(x)\cdot dx = \frac{h}{3}\cdot(f_0+4f_1+2f_2+4f_3+f_4) \quad where \quad h=\frac{x_4-x_0}{4}$$

$$\int_{x_0}^{x_N} f(x)\cdot dx = \frac{3h}{8}\cdot(f_0+3f_1+3f_2+2f_3+3f_4+3f_5+2f_6.....) \Longrightarrow$$

For N+1 points, where N is an integer.

Example: Consider the liquid phase reaction;

$$\mathbf{A \rightarrow Products}$$

which is to take place in a PFR. The following data was obtained in a batch reactor.

X	0	0.4	0.8
$-r_A$(mol/dm^{3}s)	0.01	0.008	0.002

If the molar feed of A to the PFR is 2 mol/s, what PFR volume is necessary to achieve 80 % conversion under identical conditions as those under which the batch data was obtained?

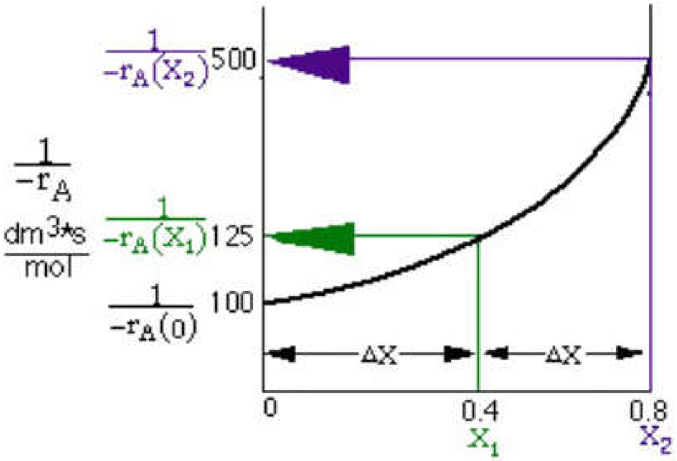
F_{A0} = 2 mol/s, fed to a plug flow reactor

$$PFR \therefore V = F_{A0}\int_{0}^{X}\frac{1}{-r_A}dX$$

Thus one needs ($1/-r_A$) as a function of X.

X	0	0.4	0.8
$-r_A\left(\text{mol/dm}^3\cdot \text{s}\right)$	0.101	0.008	0.002
$\Downarrow$			
$\frac{1}{-r_A}\left(\frac{\text{dm}^3\cdot \text{s}}{\text{mol}}\right)$	100	125	500

Construct a Levenspiel Plot $\frac{1}{-r_A}$ vs. X



For Simpson’s three point formula we have:

$$PFR : V = F_{A0}\int_0^X \frac{dX}{-r_A} = F_{A0}\cdot\frac{\Delta X}{3}\left[\frac{1}{-r_A(X=0)}+\frac{4}{-r_A(X_1)}+\frac{1}{-r_A(X_2)}\right]$$

$$PFR : V = F_{A0}\int_0^{0.8} \frac{dX}{-r_A} = 2\frac{mol}{s}\cdot\left\{\frac{0.4}{3}[100+4\cdot(125)+500]\frac{dm^3 s}{mol}\right\} = 293dm^3$$

To reach 80 % conversion, your PFR must be 293.3 dm^3.

Sizing in PFR

Example: Determine the volume in PFR to achieve a 80 % conversion.

$$For\ \ PFR: F_{A0} \cdot \frac{dX}{dV} = -r_A$$

$$\text{Re}\, arranging: V = F_{A0} \cdot \int_0^{0.8} \frac{dX}{-r_A} = \int_0^{0.8} \frac{F_{A0}}{-r_A} \cdot dX$$

Let's numerically evaluate the integral with trapezoidal rule

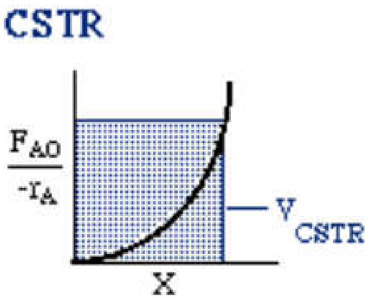
$$\int_0^{0.8} \frac{F_{A0}}{-r_A} \cdot dX \quad \Rightarrow \quad f(X) = \left.\frac{F_{A0}}{-r_A}\right|_{X=0} = 0.89$$

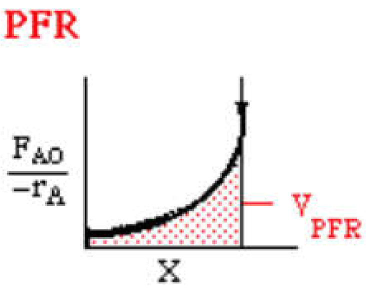
$$f(X) = \left.\frac{F_{A0}}{-r_A}\right|_{X=0.8} = 8.0$$

$$V = \frac{0.8}{2} \cdot (0.89 + 8.0) = 8.89 \cdot 0.4 = 3.556 m^3$$

With five point quadrature V = 2.165 m^3

Comparing CSTR & PFR Sizing



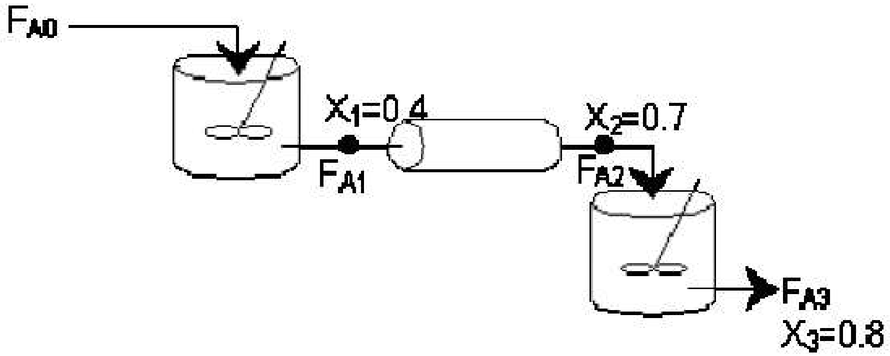


$V_{CSTR} > V_{PFR}$ for the same conversion and rxn conditions.

The reason is that CSTR always operates at lowest rxn rate. PFR starts at a high rate, then gradually decreases to the exit rate.

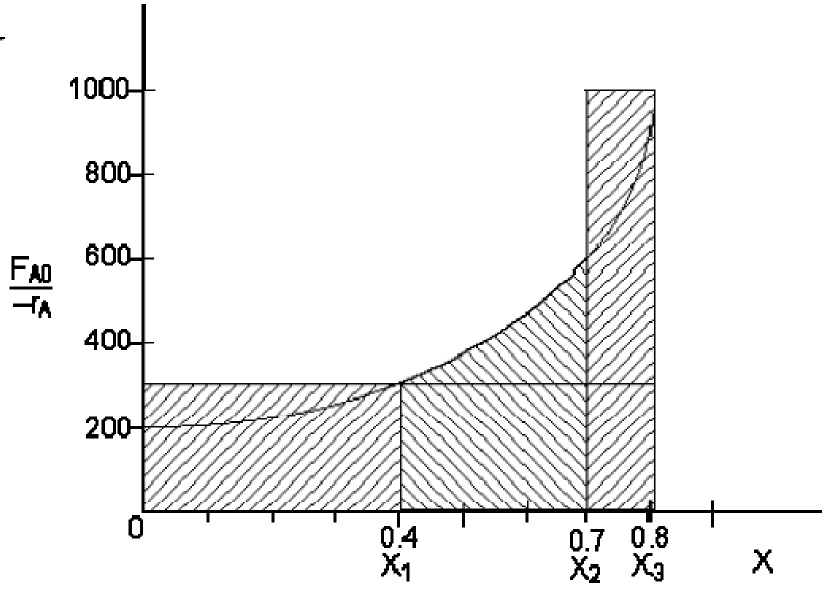
Reactors in Series: CSTR – PFR – CSTR

Using the data in the table, calculate the reactor volumes V_1, V_2 and V_3 for the CSTR/PFR/CSTR reactors in series sequence along with the corresponding conversion.



X	0	0.2	0.4	0.6	0.8
$-r_A\left(\frac{\text{mol}}{\text{dm}^3 \bullet \text{s}}\right)$	0.010	0.0091	0.008	0.005	0.002
$(1/-r_A)\left(\frac{\text{dm}^3 \bullet \text{s}}{\text{mol}}\right)$	100	110	125	200	500
$F_{A0}/-r_A\ (\text{dm}^3)$	200	220	250	400	1000

Use the plot of $\left(\frac{F_{A0}}{-r_A}\right)$ *vs. X*



(a) The CSTR design equation for Reactor 1 is:

$$V_1 = \left(\frac{F_{A0} \cdot X}{-r_{A1}}\right)$$

at $X = X_1 = 0.4$ the $(F_{A0} / -r_{A1}) = 300\ \text{dm}^3$

$V_1 = (300\ \text{dm}^3)(0.4) = 120\ \text{dm}^3$

The volume of the first CSTR is 120 dm^3

(b) Reactor 2: PFR The differential form of the PFR design is

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

Rearranging and intergrating with limits

when V = 0 $\quad X = X_1 = 0.4$

when $V = V_2 \quad X = X_2 = 0.7$

$$V = \int_{X_1}^{X_2} \left(\frac{F_{A0}}{-r_A} \right) \cdot dX = \int_{0.4}^{0.7} \left(\frac{F_{A0}}{-r_A} \right) \cdot dX$$

Choose three point quadrature formula with

$$\Delta X = \frac{X_2 - X_1}{2} = \frac{0.7 - 0.4}{2} = 0.15$$

$$V_2 = \frac{\Delta X}{3}\left[\frac{F_{A0}}{-r_A(0.4)} + \frac{4 \cdot F_{A0}}{-r_A(0.55)} + \frac{F_{A0}}{-r_A(0.7)}\right]$$

Interpreting for ($F_{A0}/-r_A$) at X = 0.55 we obtain

$$\left(\frac{F_{A0}}{-r_A}\right)_{X=0.55} = 370 dm^3$$

$$V_2 = \frac{0.15}{3}\left[300 dm^3 + 4 \cdot (370 dm^3) + 600 dm^3\right] = 119 dm^3$$

The volume of the PFR is V_2 = 119 dm^3

(c) Reactor 3: CSTR

Balance

$$in - out + generation$$

$$F_{A2} - F_{A3} + r_{A3} \cdot V_3 = 0$$

$$\boxed{V_3 = \frac{F_{A2} - F_{A3}}{-r_{A3}}}$$

$$F_{A2} = F_{A0} \cdot (1 - X_2)$$

$$F_{A3} = F_{A0} \cdot (1 - X_3)$$

$$V_3 = \frac{F_{A0}}{-r_{A3}} \cdot (X_3 - X_2)$$

$$V_3 = 600 dm^3 \cdot (0.7 - 0.4) = 180 dm^3$$

The volume of last CSTR is 180 dm^3

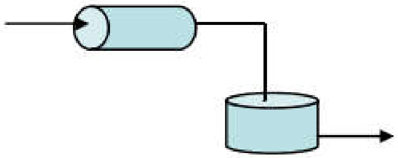
Summary:

CSTR $X_1 = 0.4$ $V_1 = 120\ \text{dm}^3$
PFR $X_2 = 0.7$ $V_2 = 119\ \text{dm}^3$
CSTR $X_3 = 0.8$ $V_3 = 180\ \text{dm}^3$

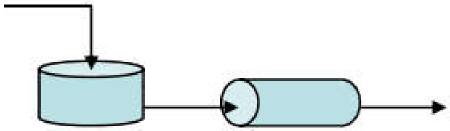
Total volume = 120 + 119 + 180 = 419 dm^3

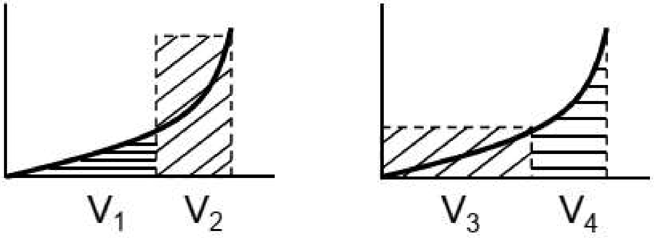
Reactor Sequencing

Is there any differences between having a CSTR – PFR system & PFR – CSTR system? Which arrangement is best?



or

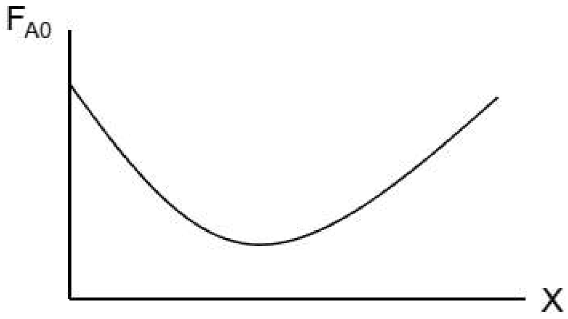




The volumes are different!

$V_1 + V_2 =? V_3 + V_4$

For isothermal rxns



Adiabatic rxns

The choice of reactors depend on ;

the Levenspiel plots

relative reactor sizes.

Isothermal parallel CSTRs and PFR

Performance of Isothermal parallel CSTRs

In designing a CSTR reactor in parallel, the inlet molar flowrates of feed will be divided equally to the number of reactors that are connected in parallel. Also, the exit conversion for each reactor is similar to that for all reactors. I addition, the rate of reaction is the same for all reactors.

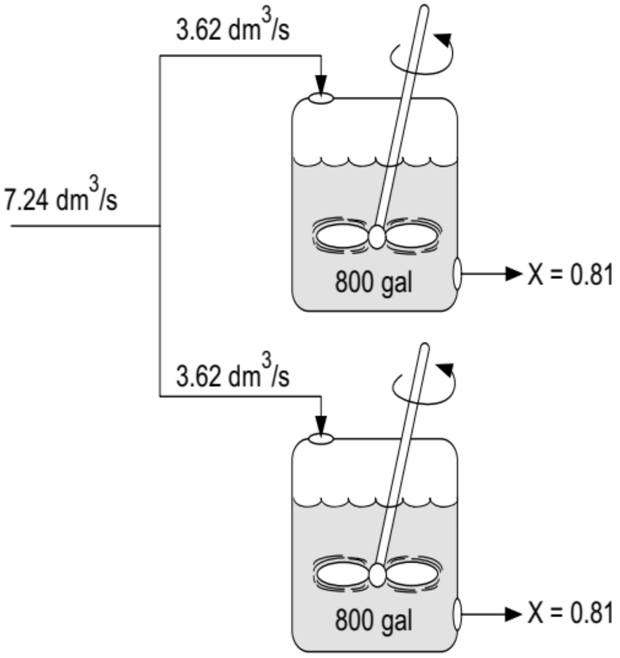


Figure E5-2.2 CSTRs in parallel.

$$X_1 = X_2 = X_3 = \ldots = X_n$$

$$r_{A_1} = r_{A_2} = r_{A_3} = \ldots = r_{A_n}$$

and $$V_i = \frac{F_{Ao,i}\, X_i}{-r_{A,i}}$$

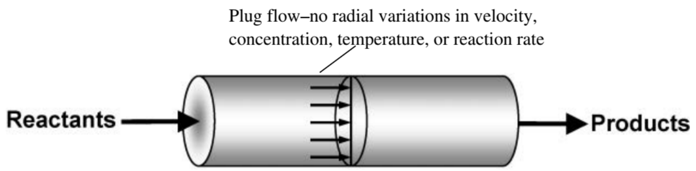
Substitute for $V_i = \frac{V}{n}$ and $F_{Ao\,i} = \frac{F_{Ao}}{n}$

$$V_i = \frac{F_{Ao,i}\,X_i}{-r_{A,i}} \quad \Longleftrightarrow \quad \frac{V}{n} = \frac{F_{Ao}}{n}\frac{X}{-r_A} \quad \text{or} \quad V = F_{Ao}\frac{X}{-r_A}$$

In conclusion

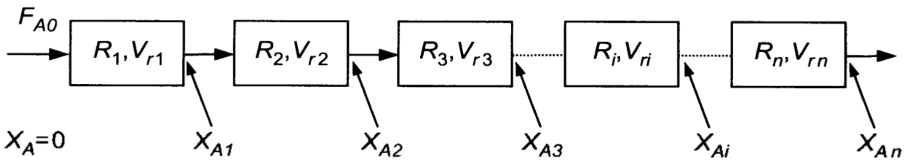
For a system of CSTRs that are connected in parallel, the conversion from one reactor is the same as the overall conversion from all reactors.

Performance of PFRs in series



The *differential form* of the PFR design equation where no catalyst is placed inside the reactor:

$$F_{A0}\frac{dX}{dV} = -r_A$$



Consider n plug flow reactors in series. For the i^{th} reactor, its volume V_{ri} is obtained as

$$\frac{V_{ri}}{F_{A0}} = \int_{X_{A(i-1)}}^{X_{Ai}} \left(\frac{1}{-r_A}\right) \mathrm{d}X_A$$

where X_{Ai} is the conversion of A in the stream leaving reactor i

The combined volume of all the reactors in the group V_r (total) is given by

$$V_r(\text{total}) = \sum^{n} V_{rn} = F_{A0}\left\{\int_0^{X_A1} \frac{\mathrm{d}X_A}{-r_A} + \ldots + \int_{X_{A(i-1)}}^{X_{Ai}} \frac{\mathrm{d}X_A}{-r_A} + \ldots + \int_{X_{A(n-1)}}^{X_{An}} \frac{\mathrm{d}X_A}{-r_A}\right\} = F_{A0}\int_0^{X_{An}} \frac{\mathrm{d}X_A}{-r_A}$$

In conclusion

So *n* PFRs in series give the same performance as a single PFR of the same total volume.

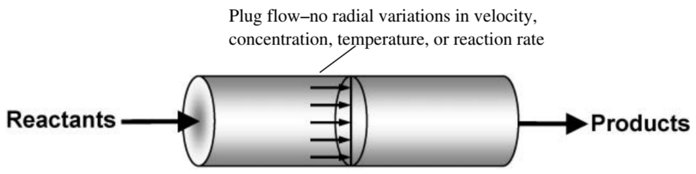
Performance of PFRs in parallel

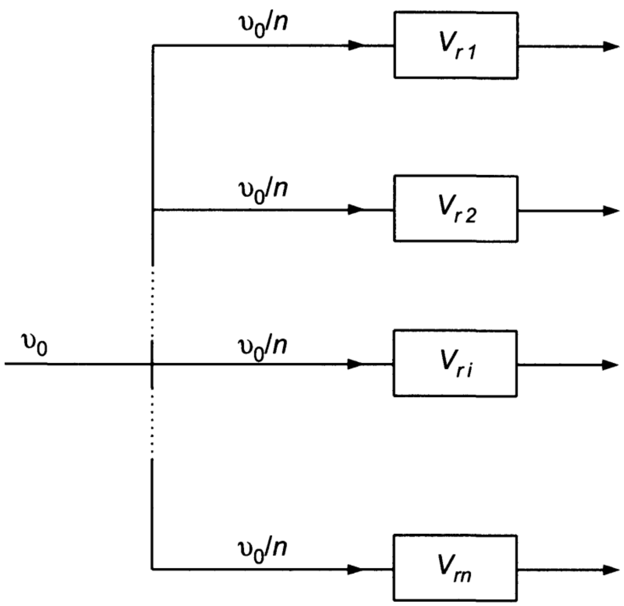
If $V_{r1} = V_{r2} = \ldots = V_r$

If the flow is split equally between each reactor

Then the conversion for each reactor will be the same.

Only the inlet flowrate will be split. Hence, the outlet product rate is decreased too. Multiple reactors in series are used if the feed flowrate is high and more reactors are needed to do the job.





Again, for the gas-phase reactions in a catalytic reactor, for example, the second order reaction:

$$-r'_A = kC_A^2$$

This rate is written in term of conversion by substituting the expression for concentration to get:

$$-r'_A = k\left[\frac{C_{A0}(1-X)}{1+\varepsilon X}\frac{P}{P_0}\frac{T_0}{T}\right]^2$$

Combining this equation with the design equation and assume isothermal condition, the independent variable for volume is replaced with mass of catalyst to get

$$F_{A0}\frac{dX}{dW} = k\left[\frac{C_{A0}(1-X)}{1+\varepsilon X}\right]^2\left(\frac{P}{P_0}\right)^2$$

Or, in term of volumetric flowrate by dividing by F_{A0} (i.e., $v_0 C_{A0}$) to yields

$$\frac{dX}{dW} = \frac{kC_{A0}}{v_0}\left(\frac{1-X}{1+\varepsilon X}\right)^2\left(\frac{P}{P_0}\right)^2$$

$$\frac{dX}{dW} = F_1(X, P)$$

This design equation is a function of conversion and pressure, and needs a coupling equation that should have a dependent variables of X and P.

Ergun Equation is used here

$$\frac{dP}{dW} = -\frac{\beta_0}{A_c(1-\phi)\rho_c}\frac{P_0}{P}\left(\frac{T}{T_0}\right)\frac{F_T}{F_{T0}}$$

Or by substituting $\frac{F_T}{F_{T0}} = 1 + \varepsilon X$ to get

$$\frac{dp}{dW} = -\frac{\alpha}{2p}(1+\varepsilon X)\frac{T}{T_0}$$

Where $\alpha = \frac{2\beta_0}{A_c\rho_c(1-\phi)P_0}$ and

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right] \quad \left(\text{e.g.,} \frac{\text{kPa}}{\text{m}}, \frac{\text{atm}}{\text{ft}}\right)$$

Notation of Ergun’s equation

P = pressure, lb_f/ft^2 or (kPa)

$$\phi = \text{porosity} = \frac{\text{volume of void}}{\text{total bed volume}} = \text{void fraction}$$

$$1 - \phi = \frac{\text{volume of solid}}{\text{total bed volume}}$$

$g_c = 32.174\ \text{lb}_m \cdot \text{ft/s}^2 \cdot \text{lb}_f$ (conversion factor)

$= 4.17 \times 10^8\ \text{lb}_m \cdot \text{ft/h}^2 \cdot \text{lb}_f$

(Recall that for the metric system $g_c = 1.0$)

D_P = diameter of particle in the bed, ft or (m)

μ = viscosity of gas passing through the bed, $\text{lb}_m/\text{ft} \cdot \text{h}$ or $(\text{kg/m} \cdot \text{s})$

z = length down the packed bed of pipe, ft or (m)

u = superficial velocity = volumetric flow rate ÷ cross-sectional area of pipe, ft/h or (m/s)

ρ = gas density, lb_m/ft^3 or (kg/m^3)

$G = \rho u$ = superficial mass velocity, $(\text{lb}_m/\text{ft}^2 \cdot \text{h})$ or $(\text{kg/m}^2 \cdot \text{s})$

Ergun equation is a function of conversion, temperature and pressure. However, for isothermal condition, this equation reduces to

$$\frac{dp}{dW} = F_2(X, p)$$

Which can be solved simultaneously with the design equation

$$\frac{dX}{dW} = F_1(X, p)$$

To get a conversion and pressure profile as a function of weigh of catalyst inside one reactor tube. The above equations can be solved analytically by having some assumptions to simplify these equations, or numerically for more complicated case.

Analytical Solution

To do the analytical solution, the following assumptions should be made

1. Compare the value of 1 with εX, shows that $\varepsilon = y_{Ao}\delta$ which is a fraction of δ. Multiplying a fraction of ε with a fraction X yields a smaller values comparing to 1. Hence the values of εX is assumed to be zero
2. For isothermal condition, there is no effect of temperature across the reactor volume

Then Ergun equation reduces to
$$\frac{dp}{dW} = -\frac{\alpha}{2p}$$

Integrating with $p = 1$ ($P = P_0$) at $W = 0$ yields

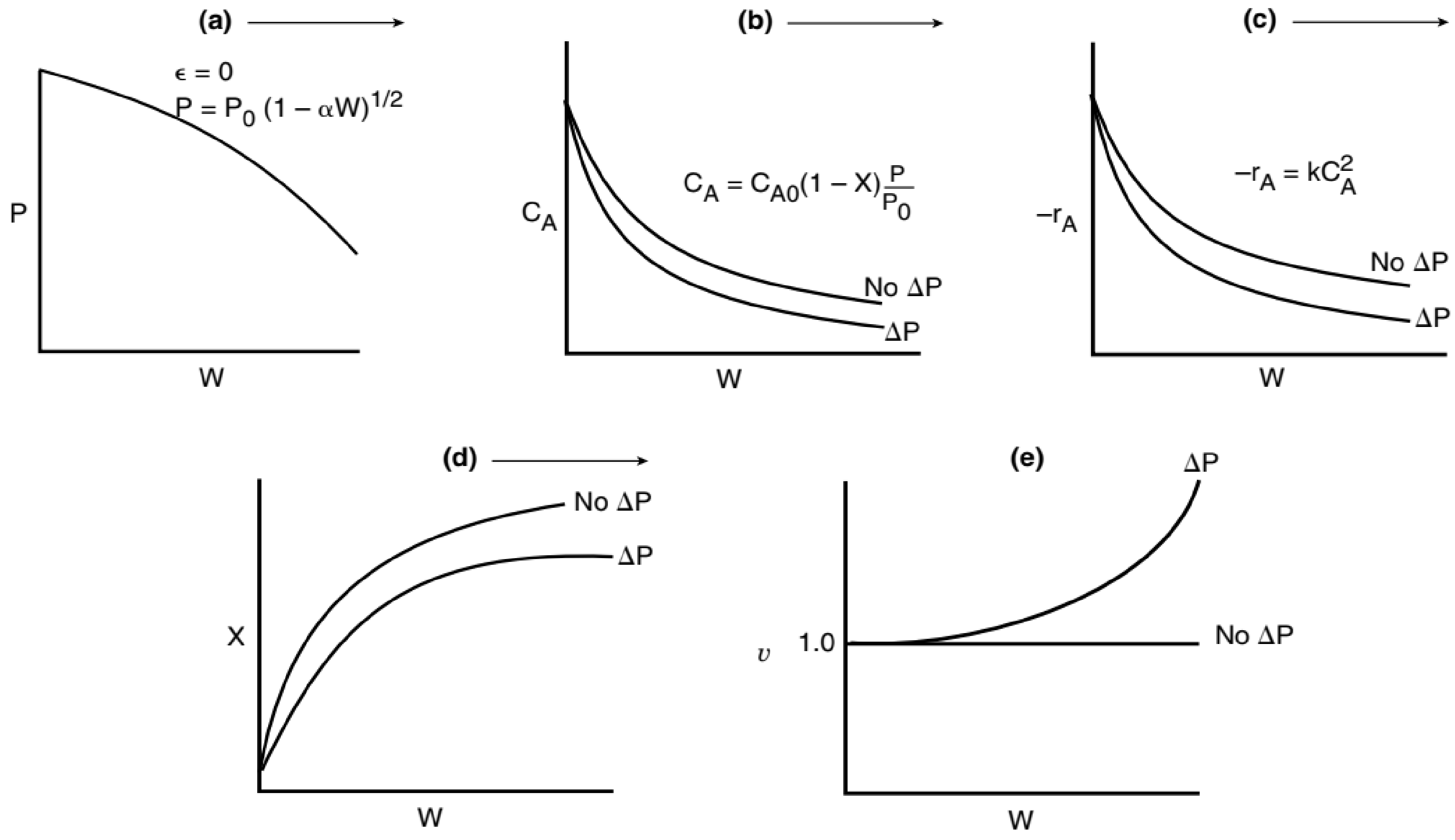
$$p^2 = (1 - \alpha W)$$

$$p = \frac{P}{P_0} = (1 - \alpha W)^{1/2}$$

$$p = \frac{P}{P_0} = \left(1 - \frac{2\beta_0 z}{P_0}\right)^{1/2}$$

$$\boxed{\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c P_0}} \quad (\text{kg}^{-1} \text{ or } \text{lb}_\text{m}^{-1})$$

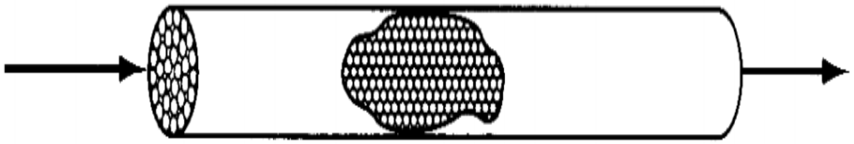
Variation of conversion, concentration, pressure and rate of reaction as a function of weight of catalyst



Topic 8

Pressure drop in reactors

Pressure drop in reactors



For gas-phase reactions, pressure drop can affect the concentration of the species in the rector and hence the conversion according

$$\mathrm{A} + \frac{b}{a}\,\mathrm{B} \longrightarrow \frac{c}{a}\,\mathrm{C} + \frac{d}{a}\,\mathrm{D}$$

Isothermal
To/T = 1

$$\begin{array}{l} F_{\mathrm{A}0}\dfrac{dX}{dV} = -r_{\mathrm{A}} \\[2ex] F_{\mathrm{A}0}\dfrac{dX}{dW} = -r'_{A} \end{array} \Longleftrightarrow -r_{\mathrm{A}} = k_{\mathrm{A}} C_{\mathrm{A}}^{\alpha} C_{\mathrm{B}}^{\beta} \Longleftrightarrow C_i = C_{\mathrm{A}0}\left(\frac{\Theta_i + \nu_i X}{1 + \varepsilon X}\right)\frac{P}{P_0}\cancel{\frac{T_0}{T}}$$

where $\Theta_i = \dfrac{F_{i0}}{F_{\mathrm{A}0}}$, $\varepsilon = y_{\mathrm{A}0}\delta$, and ν_{i} is the stoichiometric coefficient

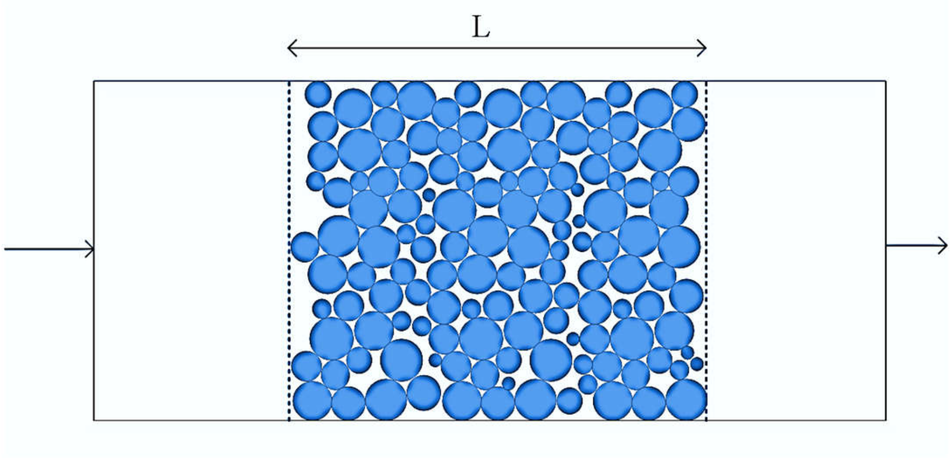
The pressure drop is affected by the following:

- Type of packing
- Type of species in reactor (viscous or not)
- Diameter and length of the reactor

Theoretical Basis of Fluid Flow through Packed Beds

For a flow through a bed:

The volume rate of flow is directly proportional to the pressure drop and inversely proportional to the thickness of the bed



Darcy's law ⇨ $$u = K\frac{(-\Delta P)}{l}$$

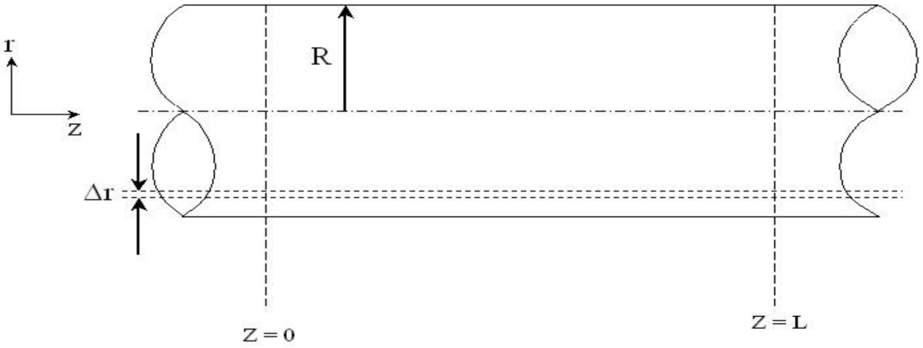
The resistance to flow arises mainly from viscous drag

$$u = B\frac{(-\Delta P)}{\mu l}$$

B is termed the permeability coefficient for the bed

The momentum balance

rate momentum IN – rate of momentum OUT + sum of forces acting on the system = accumulation



1. Rate of momentum in across cylindrical surface = $(2\pi\ r\ L)\ \tau_{rz}|_{r}$
2. Rate of momentum out across cylindrical surface = $(2\pi\ r\ L)\ \tau_{rz}|_{r+\Delta r}$
3. Rate of momentum in across annular surface at $z = 0$ is

   $(2\pi\ r\ \Delta r\ u_z)(\rho\ u_z)|_{z=0}$
4. Rate of momentum out across annular surface at $z = L$ is

   $(2\pi\ r\ \Delta r\ u_z)(\rho\ u_z)|_{z=L}$
5. Pressure force acting on system = $(2\pi\ r\ \Delta r)(P_0 - P_L)$

Where P_0 and P_L is the fluid pressure at $z = 0$ and at $z = L$, respectively.

The general momentum balance equation

$$(2\pi\, rL)\left(\tau_{rz}\big|_{r} - \tau_{rz}\big|_{r+\Delta r}\right) + (2\pi\, r\Delta r u_z)\,(\rho u_z)\big|_{z=0} - (2\pi\, r\Delta r u_z)\,(\rho u_z)\big|_{z=L} + (2\pi\, r\Delta r)\,(P_0 - P_L) = 0$$

⇨ $$\frac{d}{dr}(r\tau_{rz}) = \frac{(P_0 - P_L)}{L} r$$

$$\tau_{rz} = \frac{(P_0 - P_L)}{2L} r + \frac{C_1}{r}$$

the boundary condition at r = 0, $\tau_{rz} = 0$ ⇨ $$\tau_{rz} = \frac{(P_0 - P_L)}{2L} r$$

the shear stress $$\tau_{rz} = -\mu \frac{du_z}{dr}$$

Substitute the shear stress in momentum equation

$$\frac{du_z}{dr} = \frac{(P_0 - P_L)}{2\mu L} r$$

Integrate the above equation ⇨ $u_z = \frac{(P_0 - P_L)}{4\mu L} r^2 + C_2$

B. C. at r = R, $u_z = 0$ ⇨ $C_2 = -\frac{(P_0 - P_L)}{4\mu L} R^2$

$$u_z = \frac{(P_0 - P_L)}{4\mu L} R^2 \left(1 - \left(\frac{r}{R} \right)^2 \right)$$

The average velocity

$$u = \frac{\int_0^{2\pi}\int_0^{R} r\, u_z\, dr\ \ d\theta}{\int_0^{2\pi}\int_0^{R} r\ dr\ \ d\theta} \quad \Rightarrow \quad u = \frac{\Delta p\, d_t^2}{32\, \mu\, L}$$

Rearranging equation

$$\frac{\Delta p}{L} = \frac{32\, \mu\, u}{d_t^2}$$

Hagen-Poiseuille equation

Considering a unit volume packed bed, the volumes occupied by the voids and the solid particles are ε and (1-ε) respectively

Let S is the surface area per unit volume of the solid material in the bed. Thus the total surface area (SB) in a packed bed of unit volume is (1 - ε) S

$$SB = (1 - \varepsilon)\, S$$

For random packing, this is equal to four times the volume occupied by the fluid divided by the surface area of particles in contact with the fluid.

The equivalent diameter is

$$d_e = \frac{4\varepsilon}{(1-\varepsilon)S}$$

The velocity of the fluid becomes

$$u_1 = \frac{\Delta P}{32\,\mu\,L}\left(\frac{16\,\varepsilon^2}{(1-\varepsilon)^2 S^2}\right)$$

The average velocity through the pore channels (u_1) is defined as the superficial velocity (u) divided by the porosity of the bed

$$u = \frac{\Delta P}{2\,\mu\,L}\left(\frac{\varepsilon^3}{(1-\varepsilon)^2 S^2}\right)$$

Ergun equation

$$\boxed{\frac{dP}{dz} = -\frac{G}{\rho g_c D_P}\left(\frac{1-\phi}{\phi^3}\right)\left[\overbrace{\frac{150(1-\phi)\mu}{D_P}}^{\text{Term 1}} + \overbrace{1.75G}^{\text{Term 2}}\right]}$$

Term 1 is dominant for laminar flow, and **Term 2** is dominant for turbulent flow

P = pressure, lb_f/ft^2 or (kPa)

$\phi = \text{porosity} = \dfrac{\text{volume of void}}{\text{total bed volume}} = \text{void fraction}$

z = length down the packed bed of pipe, ft or (m)

u = superficial velocity = volumetric flow rate ÷ cross-sectional area of pipe, ft/h or (m/s)

$G = \rho u$ = superficial mass velocity, $(\text{lb}_m/\text{ft}^2 \cdot \text{h})$ or $(\text{kg/m}^2 \cdot \text{s})$

μ = viscosity of gas passing through the bed, $\text{lb}_m/\text{ft} \cdot \text{h}$ or $(\text{kg/m} \cdot \text{s})$

D_P = diameter of particle in the bed, ft or (m)

$g_c = 32.174\ \text{lb}_m \cdot \text{ft/s}^2 \cdot \text{lb}_f$ (conversion factor)

$= 4.17 \times 10^8\ \text{lb}_m \cdot \text{ft/h}^2 \cdot \text{lb}_f$

(Recall that for the metric system $g_c = 1.0$)

$1 - \phi = \dfrac{\text{volume of solid}}{\text{total bed volume}}$

ρ = gas density, lb_m/ft^3 or (kg/m^3)

PBR is operated at steady state, the mass flow rate at any point down the reactor, $\dot{m}$ (kg/s), is equal to the entering mass flow rate, $\dot{m}_o$ (i.e., equation of continuity)

$$\dot{m}_0 = \dot{m} \quad \Rightarrow \quad \rho_0 v_0 = \rho v$$

$$v = v_0 \frac{P_0}{P}\left(\frac{T}{T_0}\right)\frac{F_\mathrm{T}}{F_\mathrm{T0}} \quad \Rightarrow \quad \rho = \rho_0 \frac{v_0}{v} = \rho_0 \frac{P}{P_0}\left(\frac{T_0}{T}\right)\frac{F_\mathrm{T0}}{F_\mathrm{T}}$$

Combining Equations

$$\boxed{\frac{dP}{dz} = -\frac{G}{\rho g_c D_\mathrm{P}}\left(\frac{1-\phi}{\phi^3}\right)\left[\overbrace{\frac{150(1-\phi)\mu}{D_\mathrm{P}}}^{\text{Term 1}} + \overbrace{1.75G}^{\text{Term 2}}\right]}$$

$$\Rightarrow \quad \frac{dP}{dz} = -\underbrace{\frac{G(1-\phi)}{\rho_0 g_c D_\mathrm{P}\phi^3}\left[\frac{150(1-\phi)\mu}{D_\mathrm{P}} + 1.75G\right]}_{\beta_0}\frac{P_0}{P}\left(\frac{T}{T_0}\right)\frac{F_\mathrm{T}}{F_\mathrm{T0}}$$

$$\frac{dP}{dz} = - \underbrace{\frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right]}_{\beta_0} \frac{P_0}{P}\left(\frac{T}{T_0}\right)\frac{F_T}{F_{T0}}$$

Simplifying yields

$$\boxed{\frac{dP}{dz} = -\beta_0 \frac{P_0}{P}\left(\frac{T}{T_0}\right)\frac{F_T}{F_{T0}}}$$

$$\boxed{\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right] \quad \left(\text{e.g.,}\ \frac{\text{kPa}}{\text{m}},\ \frac{\text{atm}}{\text{ft}}\right)}$$

The catalyst weight
$$\underbrace{W}_{\begin{bmatrix}\text{Weight of}\\ \text{catalyst}\end{bmatrix}} = \underbrace{(1-\phi)A_c z}_{\begin{bmatrix}\text{Volume of}\\ \text{solids}\end{bmatrix}} \times \underbrace{\rho_c}_{\begin{bmatrix}\text{Density of}\\ \text{solid catalyst}\end{bmatrix}}$$

The *bulk density* $\rho_b = \rho_c\,(1-\phi)$

$$\frac{dP}{dW} = -\frac{\beta_0}{A_c(1-\phi)\rho_c}\,\frac{P_0}{P}\left(\frac{T}{T_0}\right)\frac{F_{\mathrm{T}}}{F_{\mathrm{T0}}}$$

Further simplification yields
$$\frac{dP}{dW} = -\frac{\alpha}{2}\,\frac{T}{T_0}\,\frac{P_0}{P/P_0}\left(\frac{F_{\mathrm{T}}}{F_{\mathrm{T0}}}\right)$$

Let $p = (P / P_0)$.

$$\Rightarrow \quad \boxed{\frac{dp}{dW} = -\frac{\alpha}{2p}\frac{T}{T_0}\frac{F_{\mathrm{T}}}{F_{\mathrm{T0}}}} \quad \Leftrightarrow \quad \boxed{\alpha = \frac{2\beta_0}{A_c \rho_c (1-\phi) P_0}}$$

Example 8.1 Design of an isothermal PFR with pressure drop

IN PFR, The gas phase reaction:

$2A \longrightarrow B \qquad -r'_A = kC_A^2$ **2^{nd} order reaction rate**

The design equation for an isothermal ideal gas phase reaction with ΔP is

$$F_{A0}\frac{dX_A}{dW} = -r'_A$$

This equation requires to substitute the concentration in the rate expression by

$$C_A = \frac{C_{A0}(1-X_A)}{1+\varepsilon X_A}\left(\frac{P}{P_0}\right)$$

To yield

$$\frac{dX_A}{dW} = \frac{k\left(C_{A0}{}^2\right)}{F_{A0}}\frac{(1-X_A)^2}{(1+\varepsilon X_A)^2}\left(\frac{P}{P_0}\right)^2$$

This equation has two dependent variables (X_A and P) and one independent variable (W). Therefore another coupling equation that contains these dependent variables in the right hand side and rate of change of pressure in left hand side should be included to obtain these variables as a function of weight of catalyst. Ergun Equation is used to relates P to W as

$$\frac{dP}{dW} = -\frac{\alpha}{2}\left(\frac{T}{T_0}\right)\left(\frac{P_0}{(P/P_0)}\right)(1+\varepsilon X_A)$$

As differential form of pressure drop in PBR:

This equation can be simplified to: $$\frac{dy}{dW} = -\frac{\alpha}{2y}(1+\varepsilon X_A)\left(\frac{T}{T_0}\right)$$

$$y = \frac{P}{P_0} \qquad \varepsilon = \frac{N_{Tf} - N_{T0}}{N_{T0}} = \delta y_{A0} \qquad \alpha = \frac{2\beta_0}{A_c \rho_c (1-\phi) P_0}$$

$$(1-\phi)\text{: fraction of solid in bed} = \frac{\text{volume of solid}}{\text{total bed volume}}$$

A_C: cross-sectional area

ρ_C: particle density

β: constant for each reactor, calculated using a complex equation that depends on properties of bed (gas density, particle size, gas viscosity, void volume in bed, etc)

α: constant dependant on the packing in the bed

Simultaneously solve dX_A/dW and dP/dW (or dy/dW) using Polymath or analytically after simplification as shown in the next slide

Analytical Solutions to P/P_0

Sometimes P/P_0 can be calculated analytically. When T is constant and $\varepsilon = 0$:

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\underset{1}{\cancel{\left(\frac{T}{T_0}\right)}}\underbrace{\left(1+\overset{0}{\cancel{\varepsilon}}X_A\right)}_{1} \qquad \rightarrow \frac{dy}{dW} = -\frac{\alpha}{2y}$$

Evaluate

To pressure change

$$\rightarrow 2ydy = -\alpha dW \qquad \rightarrow \int_{\frac{P}{P_0}=1}^{\frac{P}{P_0}=y} 2ydy = -\alpha\int_0^W dW \qquad \rightarrow y^2\Big]_1^{P/P_0} = -\alpha W$$

From no pressure change

$$\rightarrow \left(\frac{P}{P_0}\right)^2 - 1 = -\alpha W \qquad \rightarrow \boxed{\frac{P}{P_0} = \sqrt{1-\alpha W}}$$

Only for isothermal rxn where ε=0

Pressure Drop Example

This gas phase reaction is carried out isothermally in a PBR. Relate the catalyst weight to X_A

GAS PHASE: $2A \longrightarrow B$ $-r'_A = kC_A^2$

2nd order reaction rate

$$F_{A0}\frac{dX_A}{dW} = -r'_A$$

$$C_A = \frac{C_{A0} - C_{A0}X_A}{1+\underset{0}{\cancel{\varepsilon}}X_A}\left(\frac{P}{P_0}\right)\underset{1}{\cancel{\left(\frac{T_0}{T}\right)}} \quad \Rightarrow \quad \to C_A = C_{A0}(1-X_A)\left(\frac{P}{P_0}\right)$$

$$\varepsilon = \frac{N_{Tf} - N_{T0}}{N_{T0}} = \frac{1-1}{1} = 0$$

ε = 0 and isothermal, so: $\frac{P}{P_0} = \sqrt{1-\alpha W}$ $\xrightarrow{\text{Plug into } C_A}$ $C_A = C_{A0} - C_{A0} X_A \sqrt{1-\alpha W}$

Plug into PBR design equation:

$$F_{A0}\frac{dX_A}{dW} = kC_A{}^2 \rightarrow F_{A0}\frac{dX_A}{dW} = k\left(C_{A0}(1-X_A)\sqrt{1-\alpha W}\right)^2$$

Simplify, integrate, and solve for X_A in terms of W or W in terms of X_A:

$$\rightarrow F_{A0}\frac{dX_A}{dW} = kC_{A0}{}^2(1-X_A)^2(1-\alpha W)$$

$$\rightarrow \frac{F_{A0}}{kC_{A0}{}^2}\int_0^{X_A}\frac{dX_A}{(1-X_A)^2} = \int_0^W (1-\alpha W)dW$$

$$\rightarrow \frac{F_{A0}}{kC_{A0}^{2}} \int_{0}^{X_A} \frac{dX_A}{(1-X_A)^2} = \int_{0}^{W} (1-\alpha W)\,dW$$

Solve for X_A

$$\rightarrow \left(\frac{X_A}{1-X_A}\right) = W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)$$

$$\rightarrow X_A = W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right) - W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)X_A$$

$$\rightarrow X_A + W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)X_A = W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)$$

$$\boxed{\rightarrow X_A = \frac{\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)}{1+\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)}}$$

$$\boxed{\rightarrow W = \frac{1-\sqrt{1-\left(\frac{2\upsilon_0\alpha}{kC_{A0}}\right)\left(\frac{X_A}{1-X_A}\right)}}{\alpha}}$$

Example 8.2 Calculating Pressure Drop in a Packed Bed

Plot the pressure drop in a 60-ft length of 1½-inch schedule 40 pipe packed with catalyst pellets ¼ inch in diameter. There is 104.4 lb_m/h of gas passing through the bed. The temperature is constant along the length of pipe at 260°C. The void fraction is 45% and the properties of the gas are similar to those of air at this temperature. The entering pressure is 10 atm.

Solution

1½-inch schedule 40 pipe ⇨ $A_c = 0.01414 \text{ ft}^2$

$$\frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0}\right)^{1/2} \qquad \beta_0 = \frac{G(1-\phi)}{g_c \rho_0 D_p \phi^3}\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right]$$

$G = \dfrac{\dot{m}}{A_c}$ ⇨ $G = \dfrac{104.4 \text{ lb}_m/\text{h}}{0.01414 \text{ ft}^2} = 7383.3 \dfrac{\text{lb}_m}{\text{h} \cdot \text{ft}^2}$

For air at 260°C and 10 atm ⇨

$$\mu = 0.0673\ \text{lb}_\text{m}/\text{ft}\cdot\text{h}$$

$$\rho_0 = 0.413\ \text{lb}_\text{m}/\text{ft}^3$$

$$D_p = 1/4\ \text{in.} = 0.0208\ \text{ft},\quad \phi = 0.45\ \text{and}$$

$$g_c = 4.17 \times 10^8\ \frac{\text{lb}_\text{m}\cdot\text{ft}}{\text{lb}_\text{f}\cdot\text{h}^2}$$

$$v_0 = \frac{\dot{m}}{\rho_0} = \frac{104.4\ \text{lb}_\text{m}/\text{h}}{0.413\ \text{lb}_\text{m}/\text{ft}^3} = 252.8\ \text{ft}^3/\text{h}\ \ (7.16\ \text{m}^3/\text{h})$$

$$\beta_0 = \frac{G(1-\phi)}{g_c\rho_0 D_p\phi^3}\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right]$$

$$\beta_0 = \left[\frac{7383.3\ \text{lb}_\text{m}/\text{ft}^2\cdot\text{h}(1-0.45)}{(4.17\times 10^8\ \text{lb}_\text{m}\cdot\text{ft}/\text{lb}_\text{f}\cdot\text{h}^2)(0.413\ \text{lb}_\text{m}/\text{ft}^3)(0.0208\ \text{ft})(0.45)^3}\right] \times \left[\frac{150(1-0.45)(0.0673\ \text{lb}_\text{m}/\text{ft}\cdot\text{h})}{0.0208\ \text{ft}} + 1.75(7383.3)\ \frac{\text{lb}_\text{m}}{\text{ft}^2\cdot\text{h}}\right]$$

$$\beta_0 = 0.01244\ \frac{\mathrm{lb_f \cdot h}}{\mathrm{ft \cdot lb_m}}\left[\overbrace{266.9}^{\text{Term 1}} + \overbrace{12{,}920.8}^{\text{Term 2}}\right]\frac{\mathrm{lb_m}}{\mathrm{ft^2 \cdot h}} = 164.1\ \frac{\mathrm{lb_f}}{\mathrm{ft^3}}$$

$$\beta_0 = 164.1\ \frac{\mathrm{lb_f}}{\mathrm{ft^3}} \times \frac{1\ \mathrm{ft^2}}{144\ \mathrm{in.^2}} \times \frac{1\ \mathrm{atm}}{14.7\ \mathrm{lb_f/in.^2}}$$

$$\boxed{\frac{1\ \mathrm{atm}}{\mathrm{ft}} = 333\frac{\mathrm{kPa}}{\mathrm{m}}}$$

$$\boxed{\beta_0 = 0.0775\ \frac{\mathrm{atm}}{\mathrm{ft}} = 25.8\ \frac{\mathrm{kPa}}{\mathrm{m}}}$$

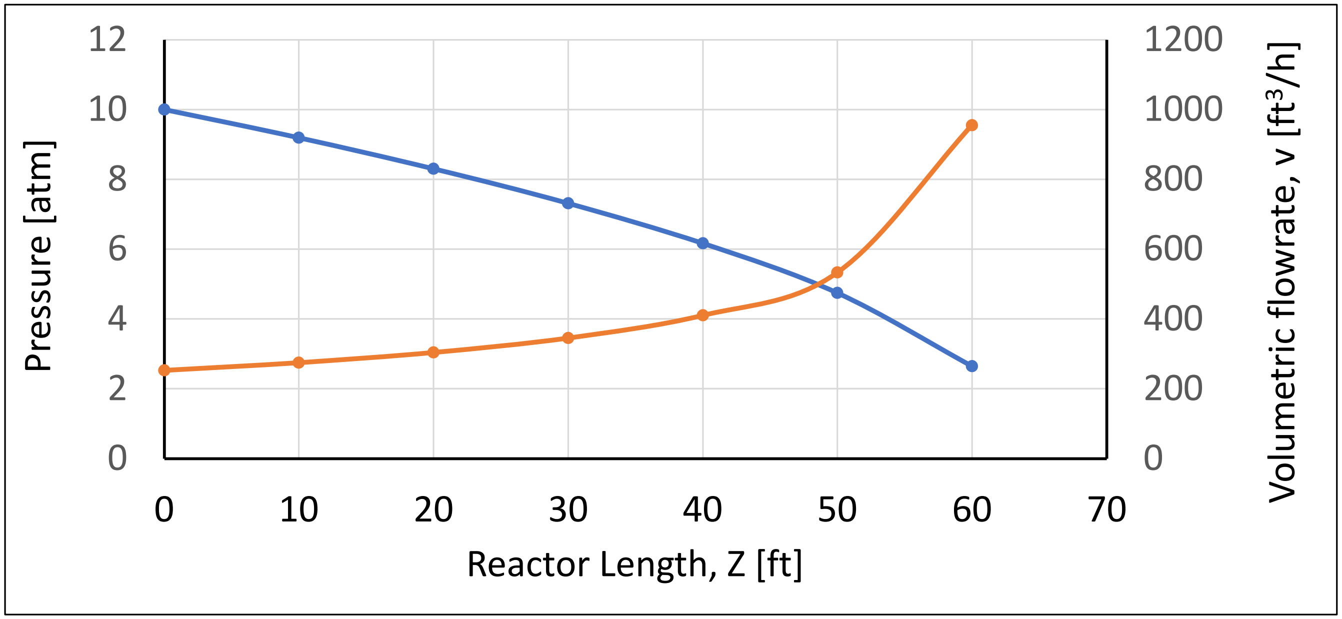
$$\frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0}\right)^{1/2}$$

$$p = \frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0}\right)^{1/2} = \left(1 - \frac{\overbrace{2 \times 0.0775}^{0.155}\ \mathrm{atm/ft} \times 60\ \mathrm{ft}}{10\ \mathrm{atm}}\right)^{1/2} = 0.265$$

$P = 0.265P_0 = 2.65 \text{ atm} \ \ (268 \ \text{kPa})$ ⇨ $\Delta P = P_0 - P = 10 - 2.65 = 7.35 \text{ atm} \ \ (744 \ \text{kPa})$

for the case $\varepsilon = 0$ and $T = T_0$ ⇨ $v = v_0 \dfrac{P_0}{P}$

z (ft)	0	10	20	30	40	50	60
p/po	1.00	0.92	0.83	0.73	0.62	0.47	0.26
p	10.00	9.19	8.31	7.31	6.16	4.74	2.65
v (ft3/h)	252.80	275.01	304.34	345.62	410.10	532.95	955.49

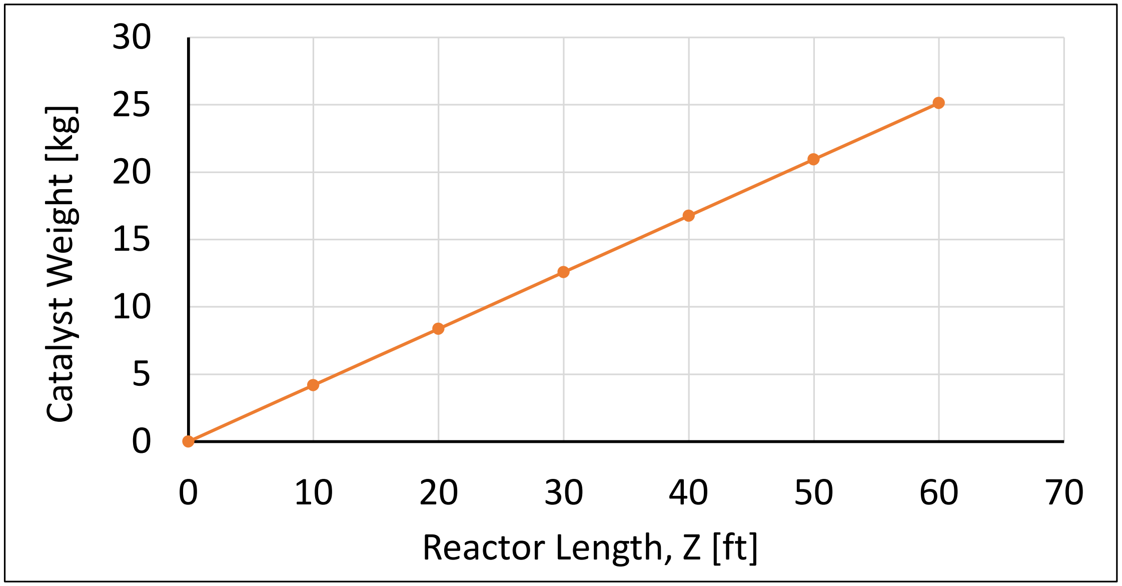


For $\rho_c = 120\ \text{lb}_\text{m}/\text{ft}^3$

$$\alpha = \frac{2\beta_0}{\rho_c(1-\phi)A_cP_0} = \frac{2(0.0775)\text{atm/ft}}{120\ \text{lb}_\text{m}/\text{ft}^3(1-0.45)(0.01414\text{ft}^2)10\,\text{atm}}$$

$$\boxed{\alpha = 0.0165\ \text{lb}_\text{m}^{-1} = 0.037\ \text{kg}^{-1}}$$

$$\boxed{p = \frac{P}{P_0} = (1-\alpha W)^{1/2}}$$



Topic 9. Multiple Reactions

In this class we will study the types of multiple reactions and provide the algorithm that being used for determination the rate and flowrates of the exit species from different types of reactors:

Types of multiple reactions

Multiple reactions are classified into four different types:

1. Parallel reactions
2. Series reactions
3. Independent reactions
4. Complex reactions

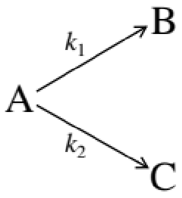
For these reaction, in design we will use *molar flow rates* and *concentrations* and we will not use conversion!

Consequently for each of these reactions there is one or more products is/are needed and the yield from the process will be obtained. Therefore we will study

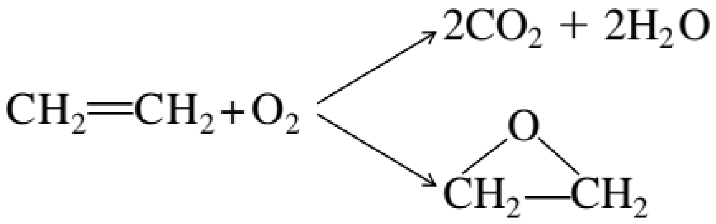
1. Selectivity of reaction
2. Yield from the reactor and process

1. Parallel Reactions (competing reactions)

Parallel reactions are reactions where the reactant is consumed by two different reaction pathways to form different products such as *A* and *C* according:



For example, in order to produce ethylene oxide from ethylene, an oxidation reaction takes place between ethylene and oxygen. The stoichiometric ratio between ethylene and oxygen is the factor to either produce ethylene oxide or to have complete burn of ethylene to carbon dioxide and water. Therefore, a parallel reaction takes place here, one leads toa a desired product (ethylene oxide) and the other leads to undesired product CO2.



2. Series Reactions (consecutive reactions)

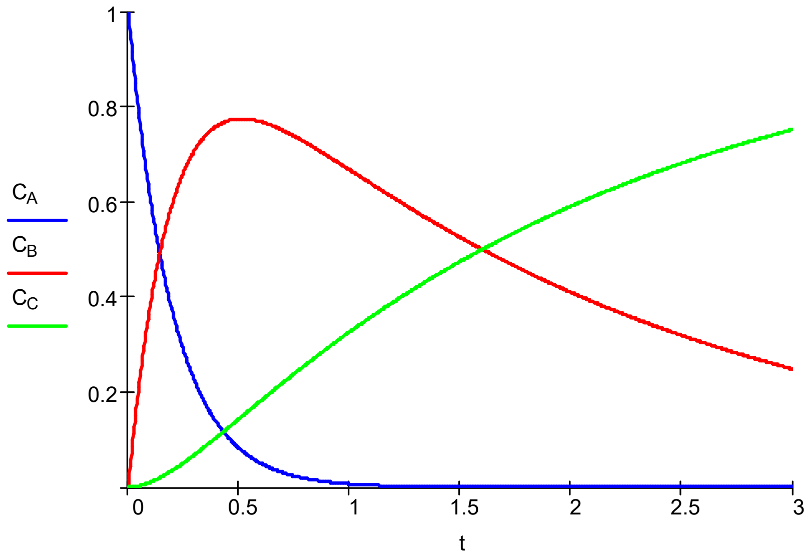
This type of multiple reactions happened when a reactions produces a product such as *B* and this product (either unstable or affected by other factors or species) is further converted to another product such as *C* according:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

An example is the oxidation of methanol, where the desired formaldehyde is readily degraded to carbon dioxide

CH3OH → HCHO → CO2

Here the desired product is the formaldehyde, B (HCHO) and it is desired the amount of this product as maximum as possible as shown in the figure



3. Independent Parallel Reactions

These reactions occur in reactor at the same time but neither the products nor the reactants react with each other as:

$$\mathrm{A} \longrightarrow \mathrm{B+C}$$
$$\mathrm{D} \longrightarrow \mathrm{E+F}$$

An example is the cracking of crude oil to form gasoline, where two of the many reactions occurring are

$$\mathrm{C_{15}H_{32}} \longrightarrow \mathrm{C_{12}C_{26}+C_3H_6}$$
$$\mathrm{C_8H_{18}} \longrightarrow \mathrm{C_6H_{14}+C_2H_4}$$

Here more than one material reacts on the surface of catalyst at the same time. Suppose we need to produce C_6H_{14} from C_8H_{18}, unfortunately, other reaction such as the first one takes place on the surface of the catalyst. Why don't we need that, because this first reaction consumes the active surface of the catalyst and hence reduces the yield of the second reaction.

4. Complex Reactions

These reactions are combination of series and independent parallel reactions as:

$$\begin{aligned} A+B &\longrightarrow C+D \\ A+C &\longrightarrow E \\ E &\longrightarrow G \end{aligned}$$

An example is a combination of parallel and series reactions is the formation of butadiene from ethanol:

$$\begin{aligned} C_2H_5OH &\longrightarrow C_2H_4+H_2O \\ C_2H_5OH &\longrightarrow CH_3CHO+H_2 \\ C_2H_4+CH_3CHO &\longrightarrow C_4H_6+H_2O \end{aligned}$$

Here ethanol is reacted in two parallel reactions to produce either ethylene (C_2H_4) or acetaldehyde CH_3CHO where both products further reacted to produce butadiene C_4H_6 and water.

Desired and Undesired Reactions

Regardless what type of reaction is (parallel, series, independent or complex, there is one reaction is needed while other reactions are not needed. The needed one lead to a desired reaction while the other reactions produces unwanted products as shown in the reactions

$$\begin{aligned} \mathrm{A} &\xrightarrow{k_{\mathrm{D}}} \mathrm{D} \\ \mathrm{A} &\xrightarrow{k_{\mathrm{U}}} \mathrm{U} \end{aligned}$$

or

$$\mathrm{A} \xrightarrow{k_{\mathrm{D}}} \mathrm{D} \xrightarrow{k_{\mathrm{U}}} \mathrm{U}$$

Therefore, it is needed to maximize the desired product and minimize the underside product.

The selectivity of these reaction give indication what is the ratio between the rates of these reactions, the extent of these reactions or the number of moles of these reactions according

Selectivity of reactions

$$A \xrightarrow{k_D} D \xrightarrow{k_U} U$$

Instantaneous selectivity

$$S_{D/U} = \frac{r_D}{r_U} = \frac{\text{rate of formation of D}}{\text{rate of formation of U}}$$

Overall selectivity

$$\tilde{S}_{D/U} = \frac{F_D}{F_U} = \frac{\text{Exit molar flow rate of desired product}}{\text{Exit molar flow rate of undesired product}}$$

Special case, for reactions occur in batch reactor, the overall selectivity is defined as

$$\tilde{S}_{D/U} = \frac{N_D}{N_U}$$

Yield of reactions

$$A \xrightarrow{k_D} D \xrightarrow{k_U} U$$

Similarly, the yield is defined as the ratio of the reaction rate of a given product to the reaction rate of the key reactant A (*Instantaneous yield based on reaction rates*) as

Instantaneous yield based on reaction rates

$$Y_D = \frac{r_D}{-r_A}$$

The *overall yield*, $\tilde{Y}_D$, is based on mole or molar flow rates and defined as the ratio of moles of product formed at the end of the reaction to the number of moles of the key reactant, A

Overall yield based on moles

For a batch system

$$\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A}$$

For flow system

$$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A}$$

Summary: Selectivity and Yield

$A \rightarrow D$ (*desired*)

$A \rightarrow U$ (*undesired*)

	Instantaneous	**Overall**
Selectivity	$S_{DU} = \frac{r_D}{r_U}$	$\tilde{S}_{DU} = \frac{F_D}{F_U}$
Yield	$Y_D = \frac{r_D}{-r_A}$	$\tilde{Y}_D = \frac{F_D}{F_{Ao} - F_A}$

The *overall* selectivity, $\tilde{S}$, and yields, $\tilde{Y}$, are important in determining profits.

The instantaneous selectivity give insights in choosing reactors and reaction schemes that will help maximize the profit.

For CSTRs: the overall selectivity and instantaneous selectivity are the same (identical)
: the overall yield and instantaneous yield are also the same (identical)

How to maximize the selectivity

Consider the following parallel reactions:

$$(1)\quad A \xrightarrow{k_D} D \qquad \text{(Desired)}$$

$$(2)\quad A \xrightarrow{k_U} U \qquad \text{(Undesired)}$$

Rate laws for formation of desired and undesired products, and rate of disappearance of A

$$r_D = k_D C_A^{\alpha_1}$$

$$r_U = k_U C_A^{\alpha_2}$$

$$-r_A = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$$

Instantaneous selectivity

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1-\alpha_2}$$

Instantaneous yield

$$Y_D = \frac{r_D}{-r_A} = \frac{k_D C_A^{\propto 1}}{k_D C_A^{\propto 1} + k_U C_A^{\propto 2}}$$

How to Maximizing the Desired Product for One Reactant?

$$(1)\quad A \xrightarrow{k_D} D \qquad \text{(Desired)}$$

$$(2)\quad A \xrightarrow{k_U} U \qquad \text{(Undesired)}$$

Instantaneous selectivity

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

Case 1: $\alpha_1 > \alpha_2$

$$\alpha_1 - \alpha_2 = a$$

$$a > 0$$

$$\Rightarrow \quad S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^a$$

To increase selectivity, Make C_A as large as possible by using a PFR or batch reactor. In a perfectly mixed CSTR, the concentration of reactant within the reactor is always at its lowest value and therefore the CSTR should not be chosen.

Case 2: $\alpha_2 > \alpha_1$

$$\Rightarrow \quad S_{D/U} = \frac{r_D}{r_U} = \frac{k_D C_A^{\alpha_1}}{k_U C_A^{\alpha_2}} = \frac{k_D}{k_U C_A^{\alpha_2 - \alpha_1}} = \frac{k_D}{k_U C_A^b}$$

$$b = \alpha_2 - \alpha_1$$

For the ratio to be high, the concentration of A should be as low as possible.

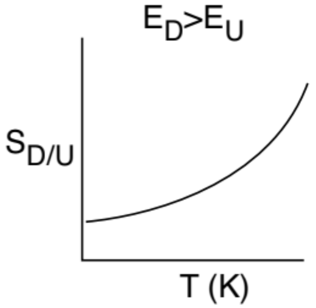
Use a CSTR and dilute the feed stream

What is the Effect of temperature on selectivity ?

$$S_{\mathrm{D/U}} \sim \frac{k_{\mathrm{D}}}{k_{\mathrm{U}}} = \frac{A_{\mathrm{D}}}{A_{\mathrm{U}}} e^{-[(E_{\mathrm{D}}-E_{\mathrm{U}})/RT]}$$

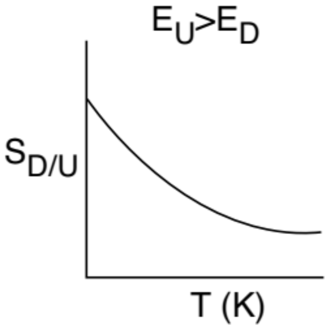
Case 3: $E_{\mathrm{D}} > E_{\mathrm{U}}$

The specific reaction rate of the desired reaction (and therefore the overall rate) increases more rapidly with increasing temperature



Case 4: $E_{\mathrm{U}} > E_{\mathrm{D}}$

The reaction should be carried out at a low temperature



EXAMPLE 9.1

The following reactions are observed when an olefin is epoxidized with oxygen:

$$\text{alkene} + O_2 \Longrightarrow \text{epoxide}$$

$$\text{epoxide} + O_2 \Longrightarrow CO_2 + H_2O$$

$$\text{alkene} + O_2 \Longrightarrow CO_2 + H_2O$$

Calculate the maximum epoxide selectivity assuming an excess of dioxygen.

Solution

The reaction network is assumed to be:

$$\begin{tikzcd}
\text{A} + \text{O} \arrow[r, "k_1"] \arrow[d, "k_3"'] & \text{EP} + \text{O} \arrow[r, "k_2"] & \text{CD} \\
\text{CD} & &
\end{tikzcd}$$

A: alkene
O: oxygen
(*desired*) **EP: epoxide**
(*undesired*) **CD: carbon dioxide**

The rate expressions for this network are:

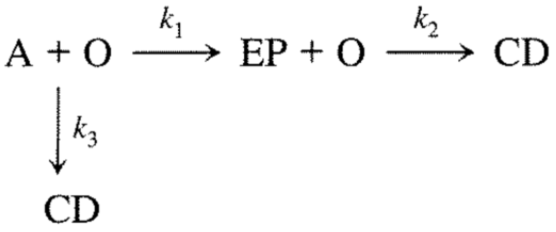
$$-r_A = k_1 C_A C_O + k_3 C_A C_O$$

$$r_{EB} = k_1 C_A C_O - k_2 C_{EB} C_O$$

$$r_{CD} = k_2 C_{EP} C_O + k_3 C_A C_O$$

Instantaneous Selectivity

$$\mathrm{S_{DU}} = \frac{\mathrm{r_D}}{\mathrm{r_U}}$$



$$S_{D/U} = \frac{r_{EB}}{r_{CD}} = \frac{k_1 C_A C_O - k_2 C_{EB} C_O}{k_2 C_{EP} C_O + k_3 C_A C_O}$$

$$-r_A = k_1 C_A C_O + k_3 C_A C_O$$

$$r_{EB} = k_1 C_A C_O - k_2 C_{EB} C_O$$

$$r_{CD} = k_2 C_{EP} C_O + k_3 C_A C_O$$

Instantaneous Yield

$$\mathrm{Y_D} = \frac{\mathrm{r_D}}{-\mathrm{r_A}}$$

$$Y_D = \frac{r_{EB}}{-r_A} = \frac{k_1 C_A C_O - k_2 C_{EB} C_O}{k_1 C_A C_O + k_3 C_A C_O}$$

In all cases above the concentration of oxygen can be omitted as it is in excess.

EXAMPLE 9.2

Maximizing the Selectivity for the Famous Trambouze Reactions

Reactant A decomposes by three simultaneous reactions to form three products, one that is desired, B, and two that are undesired, X and Y. These gas-phase reactions, along with the appropriate rate laws, are called the *Trambouze reactions* (*AIChE J., 5*, 384).

1) $\mathrm{A} \xrightarrow{k_1} \mathrm{X} \qquad -r_{1\mathrm{A}} = r_{\mathrm{X}} = k_1 = 0.0001 \dfrac{\mathrm{mol}}{\mathrm{dm}^3 \cdot \mathrm{s}}$

2) $\mathrm{A} \xrightarrow{k_2} \mathrm{B} \qquad -r_{2\mathrm{A}} = r_{\mathrm{B}} = k_2 C_{\mathrm{A}} = (0.0015\ s^{-1}) C_{\mathrm{A}}$

3) $\mathrm{A} \xrightarrow{k_3} \mathrm{Y} \qquad -r_{3\mathrm{A}} = r_{\mathrm{Y}} = k_3 C_{\mathrm{A}}^2 = \left(0.008 \dfrac{\mathrm{dm}^3}{\mathrm{mol} \cdot \mathrm{s}}\right) C_{\mathrm{A}}^2$

The specific reaction rates are given at 300 K and the activation energies for reactions (1), (2), and (3) are $E1$ = 10,000 kcal/mole, $E2$ = 15,000 kcal/mole, and $E3$ = 20,000 kcal/mole.

How, and under what conditions (e.g., reactor type(s), temperature, concentrations), should the reaction be carried out to maximize the selectivity of species B for an entering concentration of species A of 0.4 M and a volumetric flow rate of 2.0 dm^3/s?

Solution

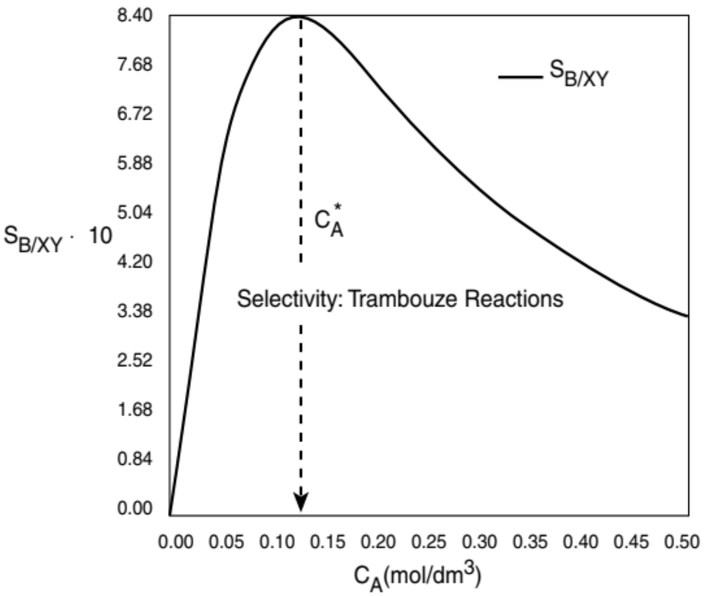
Instantaneous Selectivity

$$s_i = \frac{r_i}{\sum r_j}, \quad j = 1, \cdots, \text{all products of interest}$$

The instantaneous selectivity of species B with respect to species X and Y is

$$S_{B/XY} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2}$$

When we plot $S_{B/XY}$ vs. C_A, we see that there is a maximum



To find the maximum, C_A^*, we differentiate $S_{B/XY}$ with respect to C_A, set the derivative to zero, and solve for C_A^*. That is

$$\frac{dS_{B/XY}}{dC_A} = 0 = \frac{k_2[k_1 + k_3 C_A^{*2}] - k_2 C_A^*[2k_3 C_A^*]}{[k_1 + k_3 C_A^{*2}]^2} \quad \Longrightarrow \quad C_A^* = \sqrt{\frac{k_1}{k_3}} = \sqrt{\frac{0.0001(\text{ mol/dm}^3 \cdot \text{s})}{0.008\ (\text{dm}^3/\text{mol} \cdot \text{s})}} = 0.112 \text{ mol/dm}^3$$

Therefore, to maximize the selectivity $S_{B/XY}$, we want to carry out our reaction in such a manner that the CSTR concentration of A is always at C_A^*. The corresponding selectivity at C_A^* is

$$S_{B/XY} = \frac{k_2 C_A^*}{k_1 + k_3 C_A^{*2}} = \frac{k_2 \sqrt{\frac{k_1}{k_3}}}{k_1 + k_1} = \frac{k_2}{2\sqrt{k_1 k_3}} = \frac{0.0015}{2[(0.0001)(0.008)]^{1/2}}$$

$$\boxed{S_{B/XY} = 0.84}$$

Maximize the selectivity with respect to temperature

From previous part we had $S_{\mathrm{B/XY}} = \frac{r_\mathrm{B}}{r_\mathrm{X}+r_\mathrm{Y}} = \frac{k_2 C_\mathrm{A}}{k_1 + k_3 C_\mathrm{A}^2}$ and $C_\mathrm{A}^* = \sqrt{\frac{k_1}{k_3}}$

Substitute the second term in the first one

$$S_{\mathrm{B/XY}} = \frac{k_2 C_\mathrm{A}^*}{k_1 + k_3 C_\mathrm{A}^{*2}} = \frac{k_2\sqrt{\frac{k_1}{k_3}}}{k_1 + k_1} = \frac{k_2}{2\sqrt{k_1 k_3}}$$

or

$$S_{\mathrm{B/XY}} = \frac{A_2}{2\sqrt{A_1 A_3}} \exp\left[\frac{\frac{E_1+E_3}{2} - E_2}{RT}\right]$$

Case 1: If $\frac{E_1+E_3}{2} < E_2$ $\left\{\right.$ Run at as high a temperature as possible with existing equipment and watch out for other side reactions that might occur at higher temperatures

Case 2: If $\frac{E_1+E_3}{2} > E_2$ $\left\{\right.$ Run at low temperatures but not so low that a significant conversion is not achieved

For the activation energies given in this example

$$\frac{E_1+E_3}{2}-E_2=\frac{10,000+20,000}{2}-15,000 \ = 0$$

So the selectivity for this combination of activation energies is independent of temperature!

What is the conversion of A in the CSTR?

$$\boxed{X^* = \frac{C_{A0}-C_A^*}{C_{A0}} = \frac{0.4-0.112}{0.4} = 0.72}$$

Topic 10. Multiple Reactions
Reactor selection and Design

In this class we will study the types of reactors needed to run multiple reactions and their design:

Reactor Selection and Operating Conditions

Reactor Selection will be based on:

1. Safety
2. Selectivity
3. Yield
4. Temperature control
5. Cost

Consider two simultaneous reactions

$$A+B \xrightarrow{k_1} D \qquad r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$

$$A+B \xrightarrow{k_2} U \qquad r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

The instantaneous selectivity is to be maximized

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1-\alpha_2} C_B^{\beta_1-\beta_2}$$

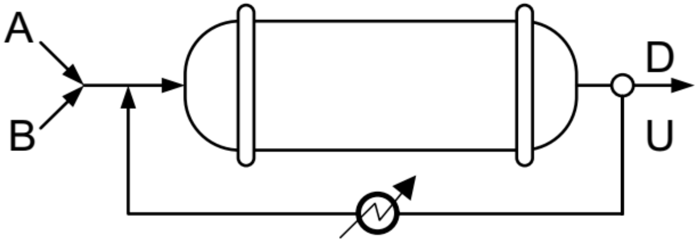
Case 1: If the reactions are highly exothermic

$$\mathrm{A+B} \xrightarrow{k_1} \mathrm{D}$$

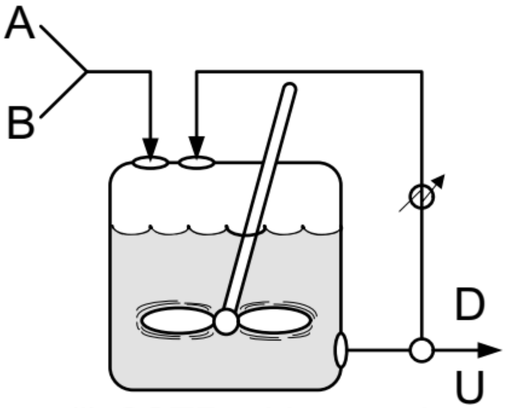
$$\mathrm{A+B} \xrightarrow{k_2} \mathrm{U}$$

$$S_{\mathrm{D/U}} = \frac{r_{\mathrm{D}}}{r_{\mathrm{U}}} = \frac{k_1}{k_2}\, C_{\mathrm{A}}^{\alpha_1-\alpha_2} C_{\mathrm{B}}^{\beta_1-\beta_2}$$

- First choice is to used reactors with recycle stream
- If the Desired is exothermic and the Undesired is endothermic use recycle stream
- If the Desired is endothermic and Undesired is exothermic



(i) Tubular reactor with recycle



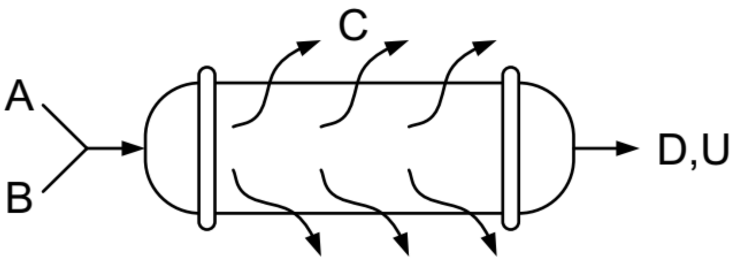
(j) CSTR with recycle

Case 2: For reversible reactions with thermodynamically limited

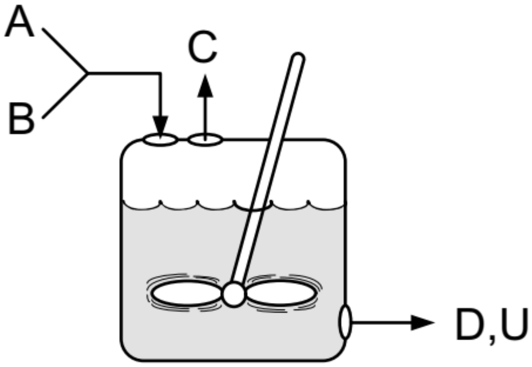
$$A + B \rightleftharpoons C + D$$

If the equilibrium lies far to the left (reactant side):

- Use membrane reactor for limited gas-phase reactions
- Use reactive distillation reactor for liquid-phase reactions when one of the products has a higher volatility (e.g., C) than the other species in the reactor.



(k) Membrane reactor



(l) Reactive distillation

Example 10.1 Choice of Reactor and Conditions to Minimize Unwanted Products

Given the following parallel reactions. Find all possibilities of configuration and pathways to increase the selectivity of the desired product.

$$A + B \longrightarrow D: \qquad r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$

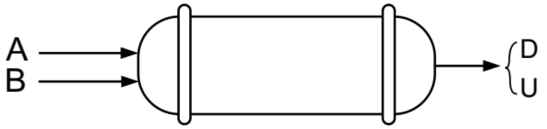
$$A + B \longrightarrow U: \qquad r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

Solution

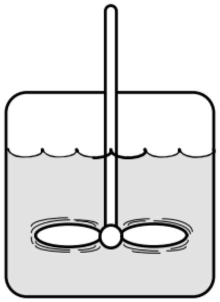
Case 1: $\alpha_1 > \alpha_2$, $\beta_1 > \beta_2$. Let $a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2} \quad \Rightarrow \quad S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{a} C_B^{b}$$

To maximize the ratio $\frac{r_D}{r_U}$, maintain the concentrations of both A and B as high as possible:
Use: A tubular reactor, A batch reactor, or High pressures (if gas phase), and reduce inerts



(b) Tubular reactor



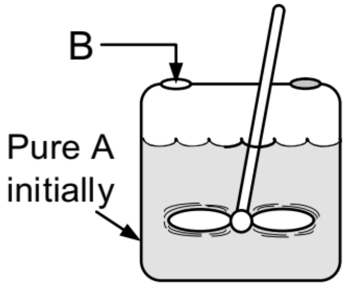
(c) Batch

Case 2: $\alpha_1 > \alpha_2$, $\beta_1 < \beta_2$. Let $a = \alpha_1 - \alpha_2$ and $b = \beta_2 - \beta_1$

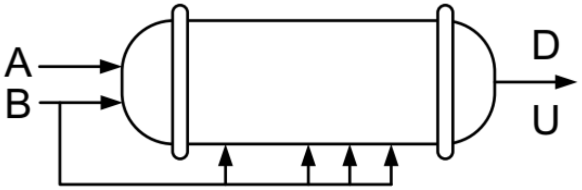
$$S_{\mathrm{D/U}} = \frac{r_{\mathrm{D}}}{r_{\mathrm{U}}} = \frac{k_1}{k_2} C_{\mathrm{A}}^{\alpha_1-\alpha_2} C_{\mathrm{B}}^{\beta_1-\beta_2} \quad \Rightarrow \quad S_{\mathrm{D/U}} = \frac{r_{\mathrm{D}}}{r_{\mathrm{U}}} = \frac{k_1 C_{\mathrm{A}}^{a}}{k_2 C_{\mathrm{B}}^{b}}$$

To maximize the ratio $\frac{r_D}{r_U}$, the concentration of A should be high and the concentration of B is low, Use:

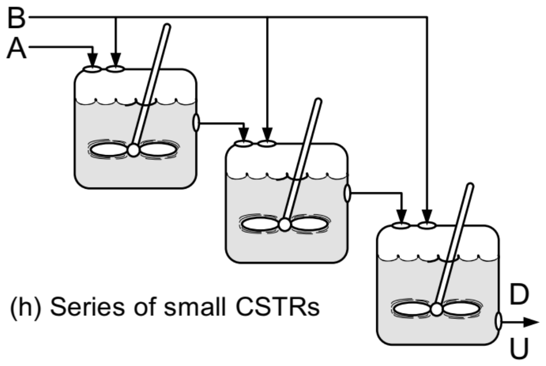
- A semi-batch reactor in which B is fed slowly into a large amount of A
- A membrane reactor or a tubular reactor with side streams of B continually fed to the reactor
- A series of small CSTRs with A fed only to the first reactor and small amounts of B fed to each reactor. In this way, B is mostly consumed before the CSTR exit stream flows into the next reactor



(d) Semibatch



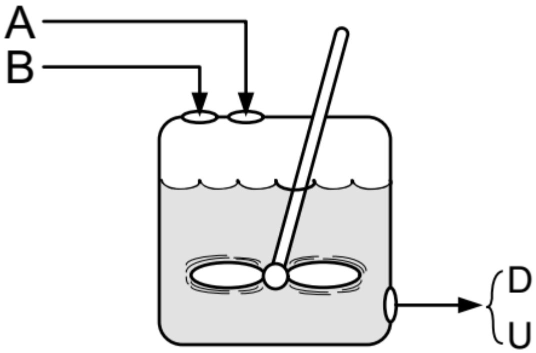
(f) A membrane reactor or a tubular reactor with side streams



(h) Series of small CSTRs

Case 3: $\alpha_1 < \alpha_2$, $\beta_1 < \beta_2$. Let $a = \alpha_2 - \alpha_1$ and $b = \beta_2 - \beta_1$

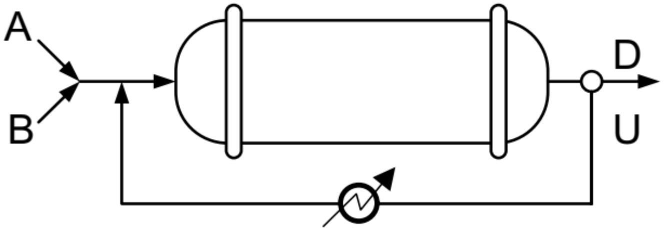
$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2} \quad \Rightarrow \quad S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2 C_A^a C_B^b}$$



(a) CSTR

The reaction should be carried out at low concentrations of A and of B. Use:

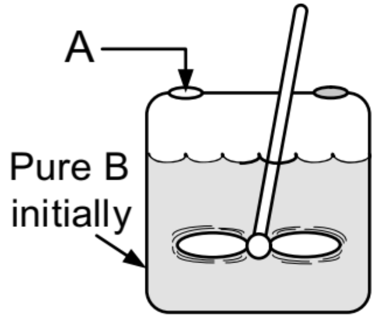
- A CSTR
- A tubular reactor in which there is a large recycle ratio
- A feed diluted with inerts.
- Low pressure (if gas phase).



(i) Tubular reactor with recycle

Case 4: $\alpha_1 < \alpha_2$, $\beta_1 > \beta_2$. Let $a = \alpha_2 - \alpha_1$ and $b = \beta_1 - \beta_2$

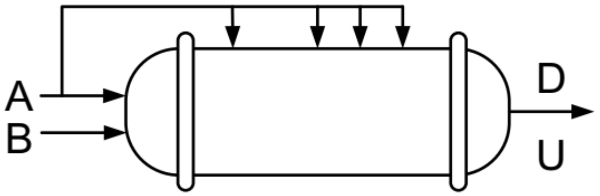
$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2} \Rightarrow S_{D/U} = \frac{r_D}{r_U} = \frac{k_1 C_B^b}{k_2 C_A^a}$$



(e) Semibatch

To maximize the selectivity, run the reaction at high concentrations of B and low concentrations of A. Use

- A semi-batch reactor with A slowly fed to a large amount of B
- A membrane reactor or a tubular reactor with side streams of A
- A series of small CSTRs with fresh A fed to each reactor.



(g) A membrane reactor or a tubular reactor with side streams

Design of a batch reactor for a series of reactions

The bellow elementary liquid-phase series reaction is carried out in a batch reactor.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The reaction is heated very rapidly to the reaction temperature, where it is held at this temperature until the time it is quenched.

a) Plot and analyze the concentrations of species A, B, and C as a function of time.
b) Calculate the time to quench the reaction when the concentration of B will be a maximum.
c) What are the overall selectivity and yields at this quench time?

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(1) Reaction 1 $A \xrightarrow{k_1} B$ $-r_{1A} = k_1 C_A$

(2) Reaction 2 $B \xrightarrow{k_2} C$ $-r_{2B} = k_2 C_B$

1. **Mole Balances:**

2A. **Mole Balance on A:** $\dfrac{dN_A}{dt} = r_A V$

$r_{1A} = -k_1 C_A$ $\dfrac{dC_A}{dt} = r_A$ ⇨ $\dfrac{dC_A}{dt} = -k_1 C_A$

Integrating with the initial condition $C_A = C_{A0}$ at t = 0

$ln \dfrac{C_A}{C_{A0}} = -k_1 t$ ⇨ $C_A = C_{A0} e^{-k_1 t}$

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

(1) Reaction 1 $\mathrm{A} \xrightarrow{k_1} \mathrm{B}$ $-r_{1\mathrm{A}} = k_1 C_{\mathrm{A}}$

(2) Reaction 2 $\mathrm{B} \xrightarrow{k_2} \mathrm{C}$ $-r_{2\mathrm{B}} = k_2 C_{\mathrm{B}}$

1. **Mole Balances:** **Mole Balance on B:** $\dfrac{dC_{\mathrm{B}}}{dt} = r_{\mathrm{B}}$

$$r_{1\mathrm{B}} = -r_{1\mathrm{A}} = k_1 C_{\mathrm{A}} \qquad r_{2\mathrm{B}} = -k_2 C_{\mathrm{B}} \;\Rightarrow\; r_{\mathrm{B}} = r_{1\mathrm{B}} + r_{2\mathrm{B}} \;\Rightarrow\; r_{\mathrm{B}} = k_1 C_{\mathrm{A}} - k_2 C_{\mathrm{B}}$$

$$\frac{dC_{\mathrm{B}}}{dt} = k_1 C_{\mathrm{A}} - k_2 C_{\mathrm{B}}$$

Rearranging and substituting for $C_{\mathrm{A}} = C_{\mathrm{A}0} e^{-k_1 t}$ $\Rightarrow$ $\dfrac{dC_{\mathrm{B}}}{dt} + k_2 C_{\mathrm{B}} = k_1 C_{\mathrm{A}0} e^{-k_1 t}$

Using the integrating factor gives $\dfrac{d\left(C_{\mathrm{B}} e^{k_2 t}\right)}{dt} = k_1 C_{\mathrm{A}0} e^{(k_2 - k_1)t}$

At time t = 0, $C_{\mathrm{B}} = 0$. $C_{\mathrm{B}} = k_1 C_{\mathrm{A}0} \left[\dfrac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} \right]$

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(1) Reaction 1 $\quad A \xrightarrow{k_1} B \quad -r_{1A} = k_1 C_A$

(2) Reaction 2 $\quad B \xrightarrow{k_2} C \quad -r_{2B} = k_2 C_B$

1. **Mole Balances:** **Mole Balance on C:** $\frac{dC_C}{dt} = r_C$

$$r_C = -r_{2B} = k_2 C_B$$ ⇨ $$\frac{dC_C}{dt} = k_2 C_B$$

Substituting for C_B $\quad C_B = k_1 C_{A0}\left[\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1}\right]$

$$\frac{dC_C}{dt} = \frac{k_1 k_2 C_{A0}}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

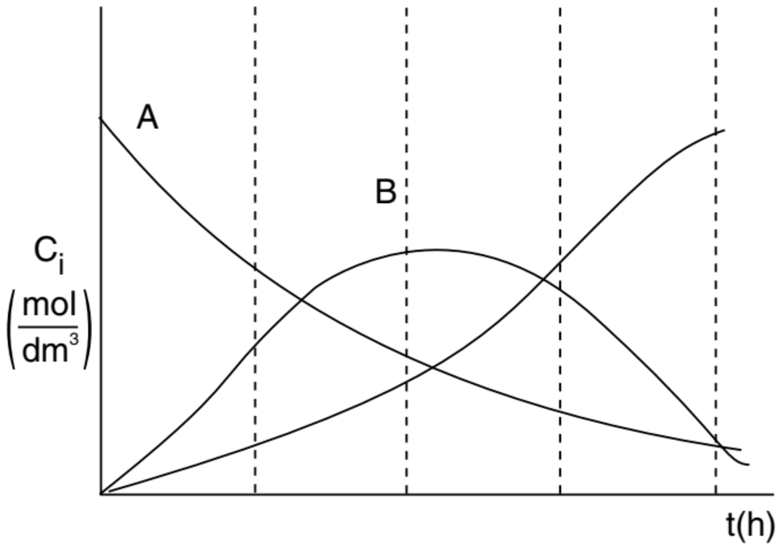
integrating with $C_C = 0$ at $t = 0$

⇨ $$C_C = \frac{C_{A0}}{k_2 - k_1}\left[k_2\left[1 - e^{-k_1 t}\right] - k_1\left[1 - e^{-k_2 t}\right]\right]$$

$$C_A = C_{A0} e^{-k_1 t}$$

$$C_B = k_1 C_{A0} \left[\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} \right]$$

$$C_C = \frac{C_{A0}}{k_2 - k_1} \left[k_2 \left[1 - e^{-k_1 t} \right] - k_1 \left[1 - e^{-k_2 t} \right] \right]$$



Optimum Yield

$$\frac{dC_B}{dt} = 0 = \frac{k_1 C_{A0}}{k_2 - k_1} \left[-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \right]$$

$$\boxed{t_{max} = \frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1}}$$

$$\boxed{C_A = C_{A0} \left[\frac{k_1}{k_2} \right]^{\frac{k_1}{k_2 - k_1}}}$$

$$\boxed{C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[\left(\frac{k_1}{k_2} \right)^{\frac{k_1}{k_2 - k_1}} - \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}} \right]}$$

Evaluate: Substituting for $C_{A0} = 2$ mol/dm^3, $k_1 = 0.5\text{h}^{-1}$, and $k_2 = 0.2\text{h}^{-1}$ the concentrations as a function of time are

$$C_A = 2\,\text{mol/dm}^3\left(e^{-0.5t}\right)$$

$$C_B = \frac{2\left(\text{mol/dm}^3\right)}{(0.2-0.5)}(0.5)\left[e^{-0.5t} - e^{-0.2t}\right]$$

$$C_B = 3.33\left(\text{mol/dm}^3\right)\left[e^{-0.2t} - e^{-0.5t}\right]$$

$$C_C = 2\,\text{mol/dm}^3 - 2\left(\text{mol/dm}^3\right)e^{-0.5t} - 3.33\,\text{mol/dm}^3\left[e^{-0.2t} - e^{-0.5t}\right]$$

$$t_{max} = \frac{1}{0.2-0.5}\ln\frac{0.2}{0.5} = \frac{1}{0.3}\ln\frac{0.5}{0.2} \qquad \boxed{t_{max} = 3.05\text{ h}}$$

The time to quench the reaction is at 3.05 h.

At t_{max} = 3.05 h, the concentrations of A, B, and C are

$$C_A = 2\frac{\text{mol}}{\text{dm}^3}\left[\left(\frac{0.5}{0.2}\right)^{\left(\frac{(0.5)}{0.2-0.5}\right)}\right] = 0.44\frac{\text{mol}}{\text{dm}^3}$$

$$C_B = 2\frac{\text{mol}}{\text{dm}^3}\frac{(0.5)}{(0.2-0.5)}\left[\left(\frac{0.5}{0.2}\right)^{\left(\frac{0.5}{0.2-0.5}\right)} - \left(\frac{0.5}{0.2}\right)^{\left(\frac{0.2}{0.2-0.5}\right)}\right]$$

$$C_B = 1.07\frac{\text{mol}}{\text{dm}^3}$$

The concentration of C at the time we quench the reaction is

$$C_C = C_{A0} - C_A - C_B = 2 - 0.44 - 1.07 = 0.49 \text{ mol/dm}^3$$

The overall selectivity and yield at the reaction quench time.

The selectivity is $$\tilde{S}_{B/C} = \frac{C_B}{C_C} = \frac{1.07}{0.49} = 2.2$$

The yield is $$\tilde{Y}_B = \frac{C_B}{C_{A0} - C_A} = \frac{1.07}{2.0 - 0.44} = 0.69$$

Design of a plug flow reactor (PFR) for a series of reactions

The bellow elementary liquid-phase series reaction is carried out in a batch reactor.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

The reaction is heated very rapidly to the reaction temperature, where it is held at this temperature until the time it is quenched.

a) Plot and analyze the concentrations of species A, B, and C as a function of time.
b) Calculate the time to quench the reaction when the concentration of B will be a maximum.
c) What are the overall selectivity and yields at this quench time?

For species A: $\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$

Design equation: $\frac{dF_A}{dW} = r_A'$ Rate of disappearance of A: $-r_A' = k_1 C_A$

$$F_A = C_A v_0$$

Combine design with rate and stoichiometry equations: $v_0 \frac{dC_A}{dW} = -k_1 C_A$

The space time related to mass of packing: $\tau' = \frac{W}{v_0} = \frac{\rho_b V}{v_0} = \rho_b \tau$

Integrating with $C_A = C_{A0}$ at $W = 0$ $\boxed{C_A = C_{A0} e^{-k_1 \tau'}}$

For species B:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

$$\boxed{C_A = C_{A0} e^{-k_1 \tau'}}$$

Design equation: $\frac{dF_B}{dW} = r'_{Bnet}$

Rate of B: $r'_{Bnet} = k_1 C_A - k_2 C_B$

$$F_B = C_B v_0$$

Combine design with rate and stoichiometry equations: $v_0 \frac{dC_B}{dW} = k_1 C_A - k_2 C_B$

Substituting for C_A, dividing v_0 into W: $\frac{dC_B}{d\tau'} + k_2 C_B = k_1 C_{A0} e^{-k_1 \tau'}$

Integrating

$$\boxed{C_B = k_1 C_{A0} \frac{e^{-k_1 \tau'} - e^{-k_2 \tau'}}{k_2 - k_1}}$$

For species B:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\boxed{C_A = C_{A0} e^{-k_1 \tau'}}$$

Maximizing B lead derivation of C_B w.r.t τ':

$$\boxed{C_B = k_1 C_{A0} \frac{e^{-k_1 \tau'} - e^{-k_2 \tau'}}{k_2 - k_1}}$$

$$\frac{dC_B}{d\tau'} = 0 \quad \Rightarrow \quad \tau'_{opt} = \frac{1}{k_1 - k_2} \mathit{In} \frac{k_1}{k_2}$$

$$W_{opt} = \frac{v_0}{k_1 - k_2} \mathit{In} \frac{k_1}{k_2}$$

$$X_{opt} = \frac{C_{A0} - C_A}{C_{A0}} = 1 - e^{-k_1 \tau'_{opt}}$$

$$X_{opt} = 1 - \exp\left[- \mathit{In} \left(\frac{k_1}{k_2} \right)^{k_1/(k_1 - k_2)} \right] = 1 - \left(\frac{k_1}{k_2} \right)^{k_1/(k_2 - k_1)}$$

For species C:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\boxed{C_A = C_{A0} e^{-k_1 \tau'}}$$

$$\frac{dC_C}{d\tau'} = r_C' = k_2 C_B = \frac{k_1 k_2 C_{A0}}{k_2 - k_1}[e^{-k_1 \tau'} - e^{-k_2 \tau'}]$$

$$\boxed{C_B = k_1 C_{A0} \frac{e^{-k_1 \tau'} - e^{-k_2 \tau'}}{k_2 - k_1}}$$

$$C_C = \frac{C_{A0}}{k_2 - k_1}[k_2[1 - e^{-k_1 \tau'}] - k_1[1 - e^{-k_2 \tau'}]] \quad \Leftrightarrow \quad C_C = C_{A0} - C_A - C_B$$

Design of an isothermal, isobaric plug flow reactor (PFR) for a general multiple reactions

Consider the following parallel reactions:

$$\text{Reaction 1:} \quad \mathrm{A} \xrightarrow{k_1} \mathrm{B} \qquad -r_{1\mathrm{A}} = k_{1\mathrm{A}} C_{\mathrm{A}}$$

$$\text{Reaction 2:} \quad 2\mathrm{A} \xrightarrow{k_2} \mathrm{C} \qquad -r_{2\mathrm{A}} = k_{2\mathrm{A}} C_{\mathrm{A}}^2$$

Mole balances:

$$\frac{dF_{\mathrm{A}}}{dV} = r_{\mathrm{A}} \qquad r_{\mathrm{A}} = r_{1\mathrm{A}} + r_{2\mathrm{A}} = -k_{1\mathrm{A}} C_{\mathrm{A}} - k_{2\mathrm{A}} C_{\mathrm{A}}^2$$

$$\frac{dF_{\mathrm{B}}}{dV} = r_{\mathrm{B}} \qquad r_{\mathrm{B}} = r_{1\mathrm{B}} = k_{1\mathrm{A}} C_{\mathrm{A}}$$

$$\frac{dF_{\mathrm{C}}}{dV} = r_{\mathrm{C}} \qquad r_{\mathrm{C}} = r_{2\mathrm{C}} = \frac{1}{2} k_{2\mathrm{A}} C_{\mathrm{A}}^2$$

Reaction 1: $\mathrm{A} \xrightarrow{k_1} \mathrm{B}$

Reaction 2: $2\mathrm{A} \xrightarrow{k_2} \mathrm{C}$

Rate laws $r_{1\mathrm{A}} = -k_{1\mathrm{A}} C_\mathrm{A}$ $r_{2\mathrm{A}} = -k_{2\mathrm{A}} C_\mathrm{A}^2$

Relative rates

$$\frac{r_{1\mathrm{A}}}{-1} = \frac{r_{1\mathrm{B}}}{1}; \qquad r_{1\mathrm{B}} = -r_{1\mathrm{A}} = k_{1\mathrm{A}} C_\mathrm{A}$$

$$\frac{r_{2\mathrm{A}}}{-2} = \frac{r_{2\mathrm{C}}}{1}; \qquad r_{2\mathrm{C}} = -\frac{1}{2}\ r_{2\mathrm{A}} = \frac{k_{2\mathrm{A}}}{2} C_\mathrm{A}^2$$

Net rates

$$r_\mathrm{A} = r_{1\mathrm{A}} + r_{2\mathrm{A}} = -k_{1\mathrm{A}} C_\mathrm{A} - k_{2\mathrm{A}} C_\mathrm{A}^2$$

$$r_\mathrm{B} = r_{1\mathrm{B}} = k_{1\mathrm{A}} C_\mathrm{A}$$

$$r_\mathrm{C} = r_{2\mathrm{C}} = \frac{1}{2} k_{2\mathrm{A}} C_\mathrm{A}^2$$

Stoichiometry

$$C_j = C_{T0}\left(\frac{F_j}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right) \quad \Longleftrightarrow \quad C_j = \frac{C_{A0}(\Theta_j + \nu_j X)}{1+\varepsilon X}\left(\frac{P}{P_0}\right)\frac{T_0}{T}$$

TABLE 4-3 CONCENTRATIONS IN A VARIABLE-VOLUME GAS FLOW SYSTEM

$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v}$	$= \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0}$	$= C_{A0}\left(\frac{1-X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)$
$C_B = \frac{F_B}{v} = \frac{F_{A0}[\Theta_B - (b/a)X]}{v}$	$= \frac{F_{A0}[\Theta_B - (b/a)X]}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0}$	$= C_{A0}\left(\frac{\Theta_B - (b/a)X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)$
$C_C = \frac{F_C}{v} = \frac{F_{A0}[\Theta_C + (c/a)X]}{v}$	$= \frac{F_{A0}[\Theta_C + (c/a)X]}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0}$	$= C_{A0}\left(\frac{\Theta_C + (c/a)X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)$
$C_D = \frac{F_D}{v} = \frac{F_{A0}[\Theta_D + (d/a)X]}{v}$	$= \frac{F_{A0}[\Theta_D + (d/a)X]}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0}$	$= C_{A0}\left(\frac{\Theta_D + (d/a)X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)$
$C_I = \frac{F_I}{v} = \frac{F_{A0}\Theta_I}{v}$	$= \frac{F_{A0}\Theta_I}{v_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0}$	$= \frac{C_{A0}\Theta_I}{1+\varepsilon X}\left(\frac{T_0}{T}\right)\frac{P}{P_0}$

Isothermal and isobaric condition

$$C_j = C_{T0}\left(\frac{F_j}{F_T}\right)$$

$$C_A = C_{T0}\left(\frac{F_A}{F_T}\right) \qquad C_B = C_{T0}\left(\frac{F_B}{F_T}\right) \qquad C_C = C_{T0}\left(\frac{F_C}{F_T}\right)$$

$$F_T = F_A + F_B + F_C$$

There are 7 unknowns (F_A, F_B, F_C, C_A, C_B, C_C, F_T) with 7 equations that should be solved simultaneously to obtained the desired variables. Note: these equations can be reduced to 3 with 3 variables by implicitly inserting the concentration equations with the rate ones and substitute in the mole balance equations.

Example 10.2 Parallel Reactions in a PFR

For the bellow gas-phase reactions that occur in a PFR, Pure A is fed at a rate of 100 mol/s, a temperature of 150 °C, and a concentration of 0.1 mol/dm^3. Determine the molar flow rate profiles down the reactor if it is operated isothermally at 722 K and at 1 bar.

Additional information

$$\Delta H_{\mathrm{Rx1A}} = -20{,}000 \text{ J/(mol of A reacted in reaction 1)}$$

$$\Delta H_{\mathrm{Rx2A}} = -60{,}000 \text{ J/(mol of A reacted in reaction 2)}$$

$$k_{1\mathrm{A}} = 10 \exp\left[\frac{E_1}{R}\left(\frac{1}{300} - \frac{1}{T}\right)\right] \mathrm{s}^{-1}$$

$$E_1/R = 4000 \text{ K}$$

$$E_2/R = 9000 \text{ K}$$

$$k_{2\mathrm{A}} = 0.09 \exp\left[\frac{E_2}{R}\left(\frac{1}{300} - \frac{1}{T}\right)\right] \frac{\mathrm{dm}^3}{\mathrm{mol} \cdot \mathrm{s}}$$

Solution

$$\frac{dF_A}{dV} = -k_1 C_A - k_2 C_A^2 \qquad \frac{dF_B}{dV} = k_1 C_A \qquad \frac{dF_C}{dV} = \frac{1}{2} k_2 C_A^2$$

$$\frac{dF_A}{dV} = -k_1 C_A - k_2 C_A^2$$

$$\frac{dF_A}{dV} = -k_1 C_{T0} \frac{F_A}{F_T} - k_2 \left(C_{T0} \frac{F_A}{F_T} \right)^2$$

$$\frac{dF_B}{dV} = k_1 C_A$$

$$\frac{dF_B}{dV} = k_1 C_{T0} \frac{F_A}{F_T}$$

$$\frac{dF_C}{dV} = \frac{1}{2} k_2 C_A^2$$

$$\frac{dF_C}{dV} = \frac{1}{2} k_2 \left(C_{T0} \frac{F_A}{F_T} \right)^2$$

$$F_T = F_A + F_B + F_C$$

There are 4 unknowns (F_A, F_B, F_C, F_T) with 4 equations that should be solved simultaneously to obtained the desired variables. POLYMATH, MATHEMATICA, MATLAB, Numerical Techniques, etc.. can do the job.

Isothermal Reactor design (Molar flow approach)

This approach of reactor design is used when we do have more than one reaction that takes place in the reactor, or for membrane reactors or even at unsteady state operation. Therefore, it is not convenient to express the design in term of conversion. For example, if we have two reactions are takes place inside the reactor, so if we consider the approach of conversion; which conversion should we choose? The one that is for the first reaction or that is for the second one or both?

Therefore, the upcoming approach is helpful for these cases. The algorithm aside summarizes the topics being covered in this chapter.

Isothermal reactor design algorithm (Molar flowrate approach)

$$aA + bB \longrightarrow cC + dD$$

1. Mole balances:

CSTR	*PFR*	*PBR*
$V = \dfrac{F_{A0} - F_A}{-r_A}$	$\dfrac{dF_A}{dV} = r_A$	$\dfrac{dF_A}{dW} = r_A{}'$
$V = \dfrac{F_{B0} - F_B}{-r_B}$	$\dfrac{dF_B}{dV} = r_B$	$\dfrac{dF_B}{dW} = r_B{}'$
$V = \dfrac{F_{C0} - F_C}{-r_C}$	$\dfrac{dF_C}{dV} = r_C$	$\dfrac{dF_C}{dW} = r_C{}'$
$V = \dfrac{F_{D0} - F_D}{-r_D}$	$\dfrac{dF_D}{dV} = r_D$	$\dfrac{dF_D}{dW} = r_D{}'$

$$a\mathrm{A} + b\mathrm{B} \longrightarrow c\mathrm{C} + d\mathrm{D}$$

2. Rates:

Rate Law

$$-r_{\mathrm{A}}{}' = k_{\mathrm{A}} C_{\mathrm{A}}^{\alpha} C_{\mathrm{B}}^{\beta}$$

Relative Rates

$$\frac{r'_{\mathrm{A}}}{-a} = \frac{r'_{\mathrm{B}}}{-b} = \frac{r'_{\mathrm{C}}}{c} = \frac{r'_{\mathrm{D}}}{d}$$

then

$$r'_{\mathrm{B}} = \frac{b}{a}\, r'_{\mathrm{A}} \qquad r'_{\mathrm{C}} = -\frac{c}{a}\, r'_{\mathrm{A}} \qquad r'_{\mathrm{D}} = -\frac{d}{a}\, r'_{\mathrm{A}}$$

3. **Stoichiometry**:

Concentrations

$$C_{\mathrm{A}} = C_{\mathrm{T0}}\frac{F_{\mathrm{A}}}{F_{\mathrm{T}}}\frac{T_0}{T}\ p \qquad C_{\mathrm{B}} = C_{\mathrm{T0}}\frac{F_{\mathrm{B}}}{F_{\mathrm{T}}}\frac{T_0}{T}\ p$$

$$C_{\mathrm{C}} = C_{\mathrm{T0}}\frac{F_{\mathrm{C}}}{F_{\mathrm{T}}}\frac{T_0}{T}\ p \qquad C_{\mathrm{D}} = C_{\mathrm{T0}}\frac{F_{\mathrm{D}}}{F_{\mathrm{T}}}\frac{T_0}{T}\ p$$

$$\frac{dp}{dW} = \frac{-\alpha}{2p}\frac{F_{\mathrm{T}}}{F_{\mathrm{T0}}}\frac{T}{T_0}, \quad p = \frac{P}{P_0}$$

Total molar flow rate: $F_{\mathrm{T}} = F_{\mathrm{A}} + F_{\mathrm{B}} + F_{\mathrm{C}} + F_{\mathrm{D}} + F_{\mathrm{I}}$

4. **Combine:**

   Appropriate reactor mole balance on each species
   Rate law
   Concentration for each species
   Pressure-drop equation

5. **Evaluate:**

   1. Specify and enter parameter values: $k_A, C_{T0}, \alpha, \beta, T_0, a, b, c, d$
   2. Specify and enter entering molar flow rates: $F_{A0}, F_{B0}, F_{C0}, F_{D0}$, and final volume, V_{final}

6. **Use an ODE solver.**

   Many times we will let the ODE solver replace **Step 4, Combine**.

Design of Isothermal PFR Reactor having several gas phase reactions

Suppose we d have two parallel reactions take place in a PFR. Then the design of this reactor should be conducted as follows;

$$A + B \rightarrow C$$
$$E \rightarrow A + D$$

1. Writing the design equation for each species in reactor in term of molar flowrate for that targeted species.

For example, for the following reaction $\mathrm{A} + 2\mathrm{B} \rightleftarrows \mathrm{C}$

the design equations are: $\frac{dF_{\mathrm{A}}}{dV} = r_{\mathrm{A}}, \frac{dF_{\mathrm{B}}}{dV} = r_{\mathrm{B}}, \frac{dF_{\mathrm{C}}}{dV} = r_{\mathrm{C}}$

2. The second step is to obtain the rate of reaction for the limiting reactant. Suppose for the above example the key reactant is *A*, then for the equilibrium reaction

$$\mathrm{A} + 2\mathrm{B} \rightleftarrows \mathrm{C}$$

$$-r_{\mathrm{A}} = k_{\mathrm{A}}\left(C_{\mathrm{A}}C_{\mathrm{B}}^{2} - \frac{C_{\mathrm{C}}}{K_{\mathrm{C}}}\right)$$

$$\frac{dF_{\mathrm{A}}}{dV} = r_{\mathrm{A}}, \quad \frac{dF_{\mathrm{B}}}{dV} = r_{\mathrm{B}}, \quad \frac{dF_{\mathrm{C}}}{dV} = r_{\mathrm{C}}$$

$$-r_{\mathrm{A}} = k_{\mathrm{A}}\left(C_{\mathrm{A}}C_{\mathrm{B}}^{2} - \frac{C_{\mathrm{C}}}{K_{\mathrm{C}}}\right)$$

To substitute in the design equations aside, we need to relate the rate of reaction of each species to that of *A* as

$$\frac{r_A}{\nu_A} = \frac{r_B}{\nu_B} = \frac{r_C}{\nu_C} = \cdots = \frac{r_i}{\nu_i}$$

For our example, this relation becomes

$$\frac{r_A}{-1} = \frac{r_B}{-2} = \frac{r_C}{+1}$$

3. This leads to a relation between the rates of each species to be used in the design equation as

$$r_B = 2r_A, \ r_C = -r_A$$

4. Now, write the concentrations in terms of molar flow rates

- For gas phase reaction $C_i = C_{To} \frac{F_i}{F_T} \frac{T_o}{T} \frac{P}{P_o}$

  Whereas for species A, B and C

$$C_A = C_{To} \frac{F_A}{F_T} \frac{T_o}{T} \frac{P}{P_o} \qquad C_B = C_{To} \frac{F_B}{F_T} \frac{T_o}{T} \frac{P}{P_o} \qquad C_C = C_{To} \frac{F_C}{F_T} \frac{T_o}{T} \frac{P}{P_o}$$

$$A + 2B \rightleftharpoons C$$

$$\boxed{\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}}$$

$$\boxed{\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}}$$

$$C_i = C_{To} \frac{F_i}{F_T} \frac{T_o}{T} \frac{P}{P_o}$$

The total molar flow rates in the above equation is estimated as

$$F_T = F_A + F_B + F_C$$

Now substitute in the rate equation to get

$$-r_A = k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\right]$$

$$-r_B = 2\,k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\right]$$

$$r_C = k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\right]$$

$$A + 2B \rightleftharpoons C$$

$$\frac{dF_A}{dV} = r_A,\quad \frac{dF_B}{dV} = r_B,\quad \frac{dF_C}{dV} = r_C$$

$$\boxed{\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}}$$

$$\boxed{\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}}$$

$$C_i = C_{To}\frac{F_i}{F_T}\frac{T_o}{T}\frac{P}{P_o}$$

- Then, the rate of molar flow rate for each species

$$\frac{dF_A}{dV} = -k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\right]$$

$$\frac{dF_B}{dV} = -2k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\right]$$

$$\frac{dF_C}{dV} = k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\right]$$

$$F_T = F_A + F_B + F_C$$

$$A + 2B \rightleftarrows C$$

$$\frac{dF_A}{dV} = r_A,\quad \frac{dF_B}{dV} = r_B,\quad \frac{dF_C}{dV} = r_C$$

$$\boxed{\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}}$$

$$\boxed{\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}}$$

$$C_i = C_{To}\frac{F_i}{F_T}\frac{T_o}{T}\frac{P}{P_o}$$

These four design equations, having six dependent variables, F_A, F_B, F_C, F_T, T and P. Therefore, we need six equations to be solved simultaneously to get these variables. Here we have four equations, thus we need two more equations: the pressure equation (Ergun equation) and the heat equation.

$$\frac{dF_A}{dV} = -k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\right]$$

$$\frac{dF_B}{dV} = -2k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\right]$$

$$\frac{dF_C}{dV} = k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{T_o}{T}\frac{P}{P_o}\right)\right]$$

$$F_T = F_A + F_B + F_C$$

For isothermal condition (where we did not study the non-isothermal condition yet), Also for a plug flow reactor where there is no catalyst to have a pressure drop, we can neglect the term for pressure and the design equations become

$$\frac{dF_A}{dV} = -k_A\left[\left(C_{To}\frac{F_A}{F_T}\right)\left(C_{To}\frac{F_B}{F_T}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\right)\right]$$

$$\frac{dF_B}{dV} = -2k_A\left[\left(C_{To}\frac{F_A}{F_T}\right)\left(C_{To}\frac{F_B}{F_T}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\right)\right]$$

$$\frac{dF_C}{dV} = k_A\left[\left(C_{To}\frac{F_A}{F_T}\right)\left(C_{To}\frac{F_B}{F_T}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\right)\right]$$

$$F_T = F_A + F_B + F_C$$

These equations reduce to four dependent variables and can be solved simultaneously to obtain these variables. POLYMATH can do the job

For **packed bed catalytic reactor** where a pressure drop takes place in an isothermal reactor, the design equation will be written in term of weight of catalyst

$$\frac{dF_A}{dW} = -k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{P}{P_o}\right)\right]$$

$$\frac{dF_B}{dW} = -2k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{P}{P_o}\right)\right]$$

$$\frac{dF_C}{dW} = k_A\left[\left(C_{To}\frac{F_A}{F_T}\frac{P}{P_o}\right)\left(C_{To}\frac{F_B}{F_T}\frac{P}{P_o}\right)^2 - \frac{1}{K_C}\left(C_{To}\frac{F_C}{F_T}\frac{P}{P_o}\right)\right]$$

$$F_{\mathrm{T}} = F_{\mathrm{A}} + F_{\mathrm{B}} + F_{\mathrm{C}}$$

$$\frac{dp}{dW} = \frac{\beta_o}{A_c(1-\phi)\rho_c}\frac{p_o}{p}\frac{F_T}{F_{To}}$$

Example 11.1 Multiple Gas-Phase Reactions in a PBR

The following complex gas-phase elementary reactions take place isothermally in a PBR. The feed is equimolar in A and B with F_{A0}= 10 mol/min and the volumetric flow rate is 100 L/min. The catalyst weight is 1,000 kg, the pressure drop is $\alpha = 0.0019\ kg^{-1}$, and the total entering concentration is $C_{T0} = 0.2\ mol/L$.

$$(1) \qquad A + 2B \rightarrow C \qquad -r'_{1A} = k_{1A} C_A C_B^2$$

$$(2) \qquad 2A + 3C \rightarrow D \qquad -r'_{2C} = k_{2C} C_A^2 C_C^3$$

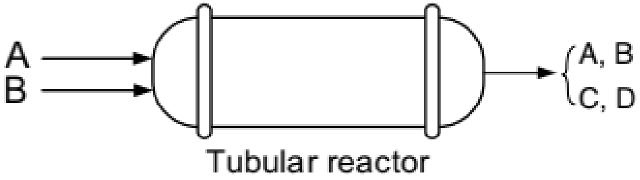
$$k_{1A} = 100\left(\frac{\text{dm}^9}{\text{mol}^2 \cdot \text{kg-cat} \cdot \text{min}}\right) \text{ and } k_{2C} = 1{,}500\left(\frac{\text{dm}^{15}}{\text{mol}^4 \cdot \text{kg-cat} \cdot \text{min}}\right)$$

Show how the values of F_A, F_B, F_C, F_D, y, and $S_{C/D}$ varies with catalyst weight, W

Solution

(1) $A + 2B \rightarrow C \qquad -r'_{1A} = k_{1A} C_A C_B^2$

(2) $2A + 3C \rightarrow D \qquad -r'_{2C} = k_{2C} C_A^2 C_C^3$



1. Mole Balances

(1) $$\frac{dF_A}{dW} = r'_A \qquad \left(F_{A0} = 10\,\frac{\text{mol}}{\text{min}}\right) \qquad W_f = 1{,}000\ \text{kg}$$

(2) $$\frac{dF_B}{dW} = r'_B \qquad \left(F_{B0} = 10\,\frac{\text{mol}}{\text{min}}\right)$$

(3) $$\frac{dF_C}{dW} = r'_C$$

(4) $$\frac{dF_D}{dW} = r'_D$$

2. Rates

(1)	$A + 2B \rightarrow C$	$-r'_{1A} = k_{1A}C_A C_B^2$
(2)	$2A + 3C \rightarrow D$	$-r'_{2C} = k_{2C}C_A^2 C_C^3$

Net Rates

(5) $r'_A = r'_{1A} + r'_{2A}$

(6) $r'_B = r'_{1B}$

(7) $r'_C = r'_{1C} + r'_{2C}$

(8) $r'_D = r'_{2D}$

Rate Laws

(9) $r'_{1A} = -k_{1A}C_A C_B^2$

(10) $r'_{2C} = -k_{2C}C_A^2 C_C^3$

Relative Rates

Reaction 1: $A + 2B \rightarrow C$ $\quad \frac{r'_{1A}}{-1} = \frac{r'_{1B}}{-2} = \frac{r'_{1C}}{1}$

(11) $r'_{1B} = 2\ r'_{1A}$

(12) $r'_{1C} = -r'_{1A}$

Reaction 2: $2A + 3C \rightarrow D$ $\quad \frac{r'_{2A}}{-2} = \frac{r'_{2C}}{-3} = \frac{r'_{2D}}{1}$

(13) $r'_{2A} = \frac{2}{3}r'_{2C}$

(14) $r'_{2D} = -\frac{1}{3}r'_{2C}$

The net rates of reaction for species A, B, C, and D are

$$\boxed{\begin{aligned} r'_A &= r'_{1A} + r'_{2A} = -k_{1A}C_A C_B^2 - \frac{2}{3}k_{2C}C_A^2 C_C^3 \\ r'_B &= r'_{1B} = -2k_{1A}C_A C_B^2 \\ r'_C &= r'_{1C} + r'_{2C} = k_{1A}C_A C_B^2 - k_{2C}C_A^2 C_C^3 \\ r'_D &= r'_{2D} = \frac{1}{3}k_{2C}C_A^2 C_C^3 \end{aligned}}$$

(1)	$A + 2B \rightarrow C$	$-r'_{1A} = k_{1A}C_A C_B^2$
(2)	$2A + 3C \rightarrow D$	$-r'_{2C} = k_{2C}C_A^2 C_C^3$

Selectivity

(Overall selectivity)

$$\tilde{S}_{C/D} = \frac{F_C}{F_D}$$

Note that: at $W = 0$, $F_D = 0$ causing $S_{C/D}$ to go to infinity. Therefore, this selectivity is set $S_{C/D} = 0$ at $W = 0$ and calculate its value at higher catalyst mass

3. Stoichiometry Isothermal $T = T_0$

(16) $C_{\mathrm{A}} = C_{\mathrm{T0}}\left(\frac{F_{\mathrm{A}}}{F_{\mathrm{T}}}\right)p$

(17) $C_{\mathrm{B}} = C_{\mathrm{T0}}\left(\frac{F_{\mathrm{B}}}{F_{\mathrm{T}}}\right)p$

(18) $C_{\mathrm{C}} = C_{\mathrm{T0}}\left(\frac{F_{\mathrm{C}}}{F_{\mathrm{T}}}\right)p$

(19) $C_{\mathrm{D}} = C_{\mathrm{T0}}\left(\frac{F_{\mathrm{D}}}{F_{\mathrm{T}}}\right)p$

(20) $\frac{dp}{dW} = -\frac{\alpha}{2p}\left(\frac{F_{\mathrm{T}}}{F_{\mathrm{T0}}}\right)$

(21) $F_{\mathrm{T}} = F_{\mathrm{A}} + F_{\mathrm{B}} + F_{\mathrm{C}} + F_{\mathrm{D}}$

4. Parameters

(22) $C_{\mathrm{T0}} = 0.2 \ \mathrm{mol/dm^3}$

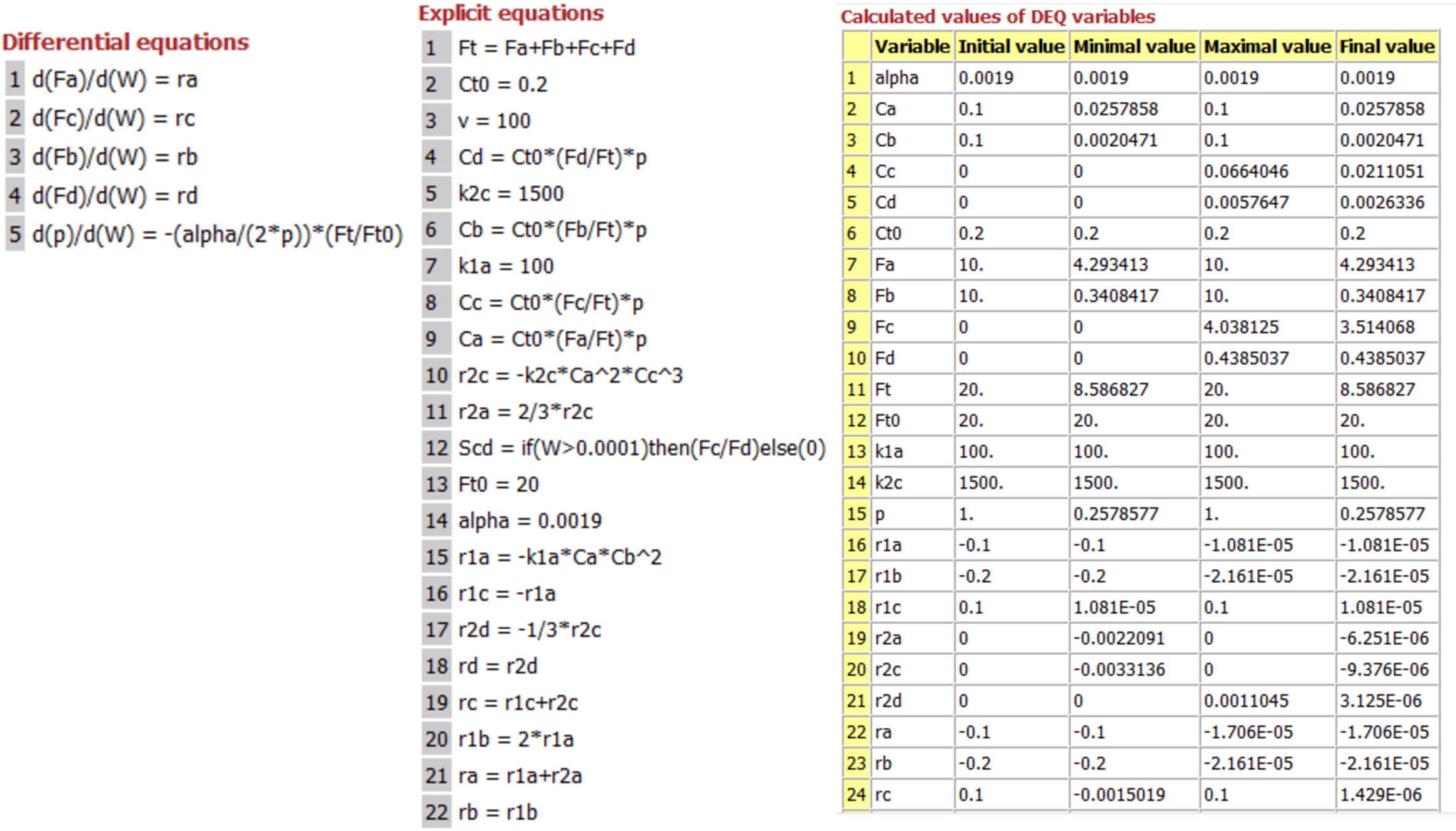
(23) $\alpha = 0.0019 \ \mathrm{kg}^{-1}$

(24) $v_0 = 100 \, \mathrm{dm^3/min}$

(25) $k_{1\mathrm{A}} = 100 \left(\mathrm{dm^3/mol}\right)^2 / \mathrm{min} / \mathrm{kg\text{-}cat}$

(26) $k_{2\mathrm{C}} = 1{,}500 \left(\mathrm{dm^{15}/mol^4}\right) / \mathrm{min} / \mathrm{kg\text{-}cat}$

(27) $F_{T0} = 20 \ \mathrm{mol/min}$



Differential equations

```
1 d(Fa)/d(W) = ra
2 d(Fc)/d(W) = rc
3 d(Fb)/d(W) = rb
4 d(Fd)/d(W) = rd
5 d(p)/d(W) = -(alpha/(2*p))*(Ft/Ft0)
```

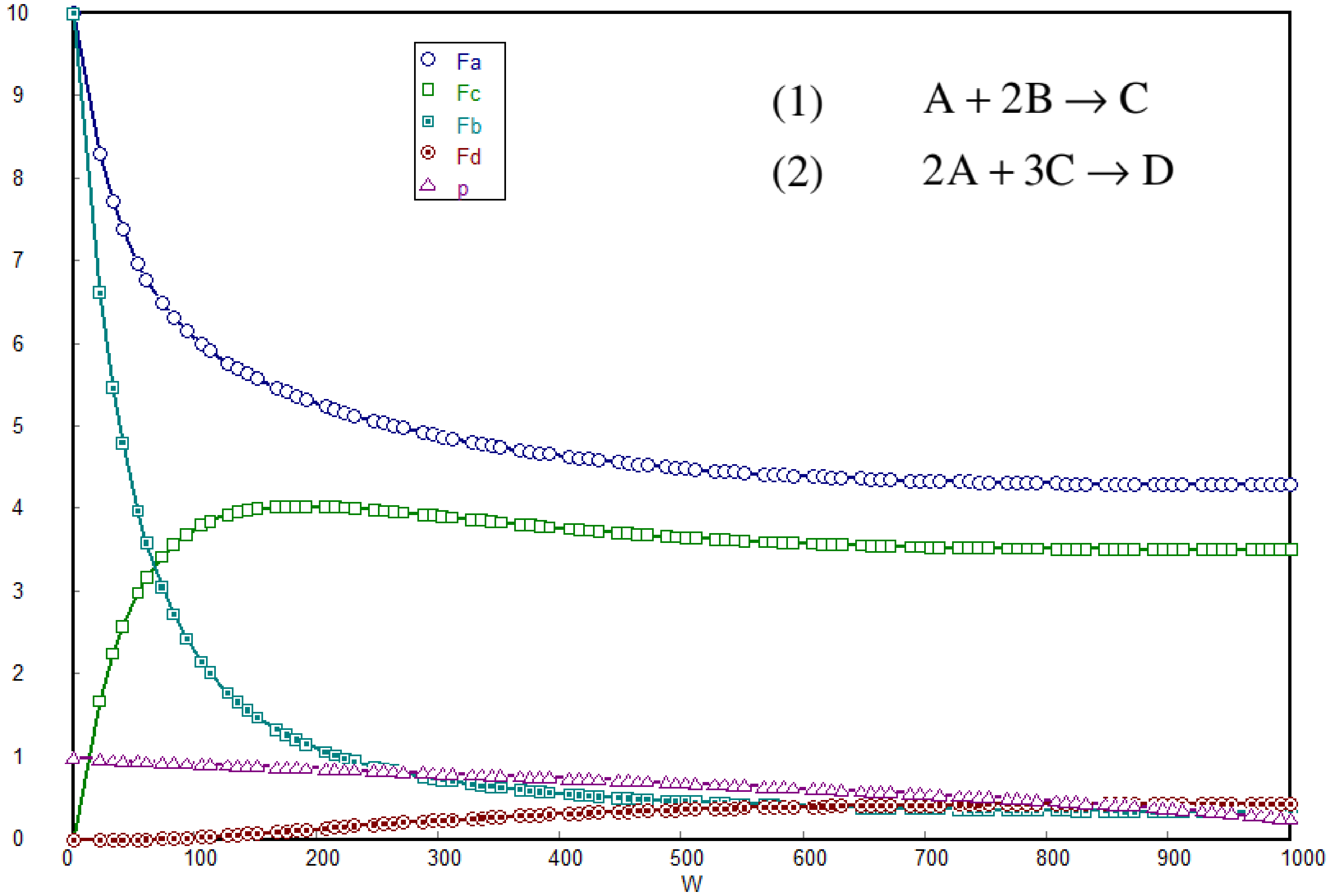
Explicit equations

```
1  Ft = Fa+Fb+Fc+Fd
2  Ct0 = 0.2
3  v = 100
4  Cd = Ct0*(Fd/Ft)*p
5  k2c = 1500
6  Cb = Ct0*(Fb/Ft)*p
7  k1a = 100
8  Cc = Ct0*(Fc/Ft)*p
9  Ca = Ct0*(Fa/Ft)*p
10 r2c = -k2c*Ca^2*Cc^3
11 r2a = 2/3*r2c
12 Scd = if(W>0.0001)then(Fc/Fd)else(0)
13 Ft0 = 20
14 alpha = 0.0019
15 r1a = -k1a*Ca*Cb^2
16 r1c = -r1a
17 r2d = -1/3*r2c
18 rd = r2d
19 rc = r1c+r2c
20 r1b = 2*r1a
21 ra = r1a+r2a
22 rb = r1b
```

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	alpha	0.0019	0.0019	0.0019	0.0019
2	Ca	0.1	0.0257858	0.1	0.0257858
3	Cb	0.1	0.0020471	0.1	0.0020471
4	Cc	0	0	0.0664046	0.0211051
5	Cd	0	0	0.0057647	0.0026336
6	Ct0	0.2	0.2	0.2	0.2
7	Fa	10.	4.293413	10.	4.293413
8	Fb	10.	0.3408417	10.	0.3408417
9	Fc	0	0	4.038125	3.514068
10	Fd	0	0	0.4385037	0.4385037
11	Ft	20.	8.586827	20.	8.586827
12	Ft0	20.	20.	20.	20.
13	k1a	100.	100.	100.	100.
14	k2c	1500.	1500.	1500.	1500.
15	p	1.	0.2578577	1.	0.2578577
16	r1a	-0.1	-0.1	-1.081E-05	-1.081E-05
17	r1b	-0.2	-0.2	-2.161E-05	-2.161E-05
18	r1c	0.1	1.081E-05	0.1	1.081E-05
19	r2a	0	-0.0022091	0	-6.251E-06
20	r2c	0	-0.0033136	0	-9.376E-06
21	r2d	0	0	0.0011045	3.125E-06
22	ra	-0.1	-0.1	-1.706E-05	-1.706E-05
23	rb	-0.2	-0.2	-2.161E-05	-2.161E-05
24	rc	0.1	-0.0015019	0.1	1.429E-06

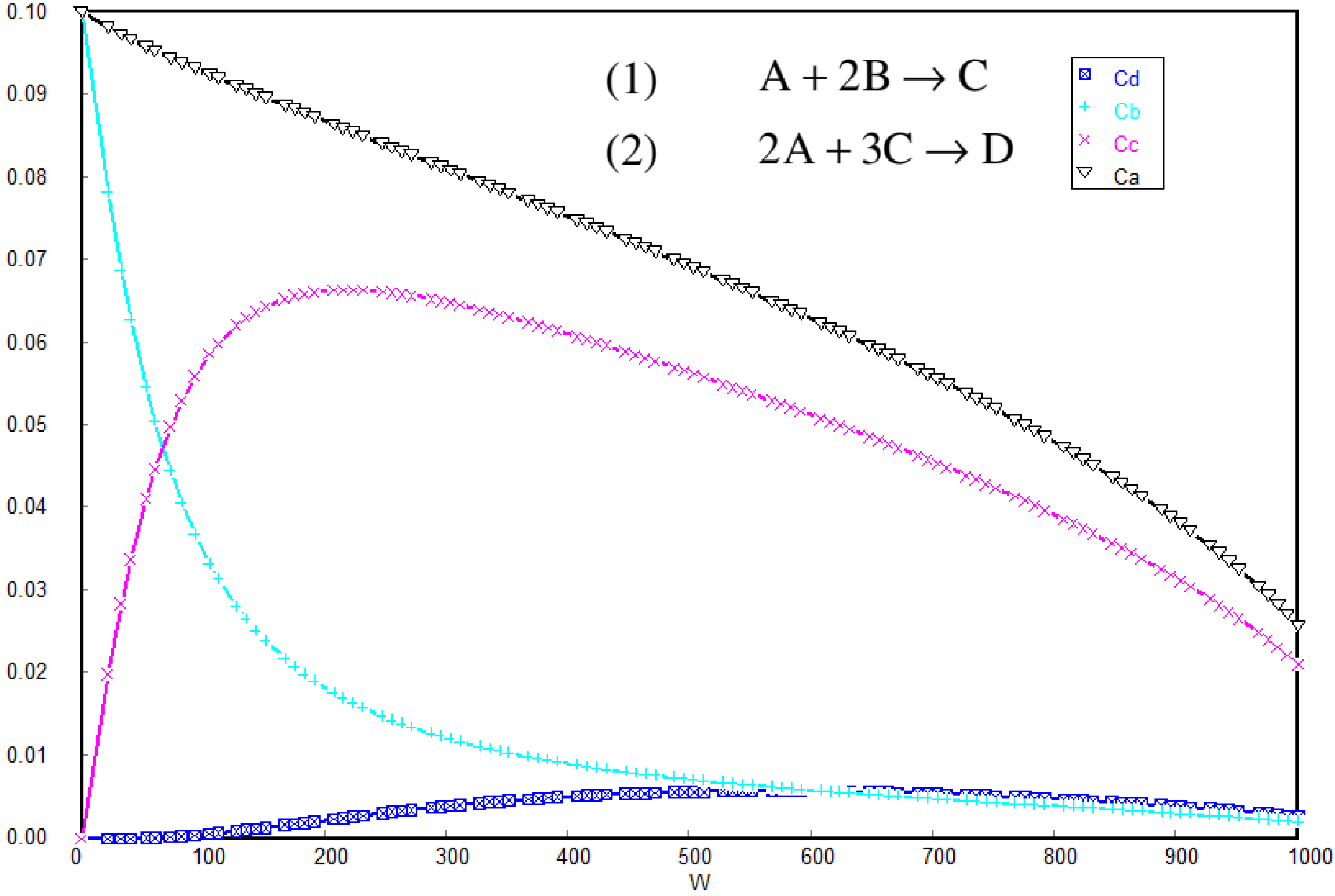
Variation of molar flowrates and pressure drop with weight of catalyst



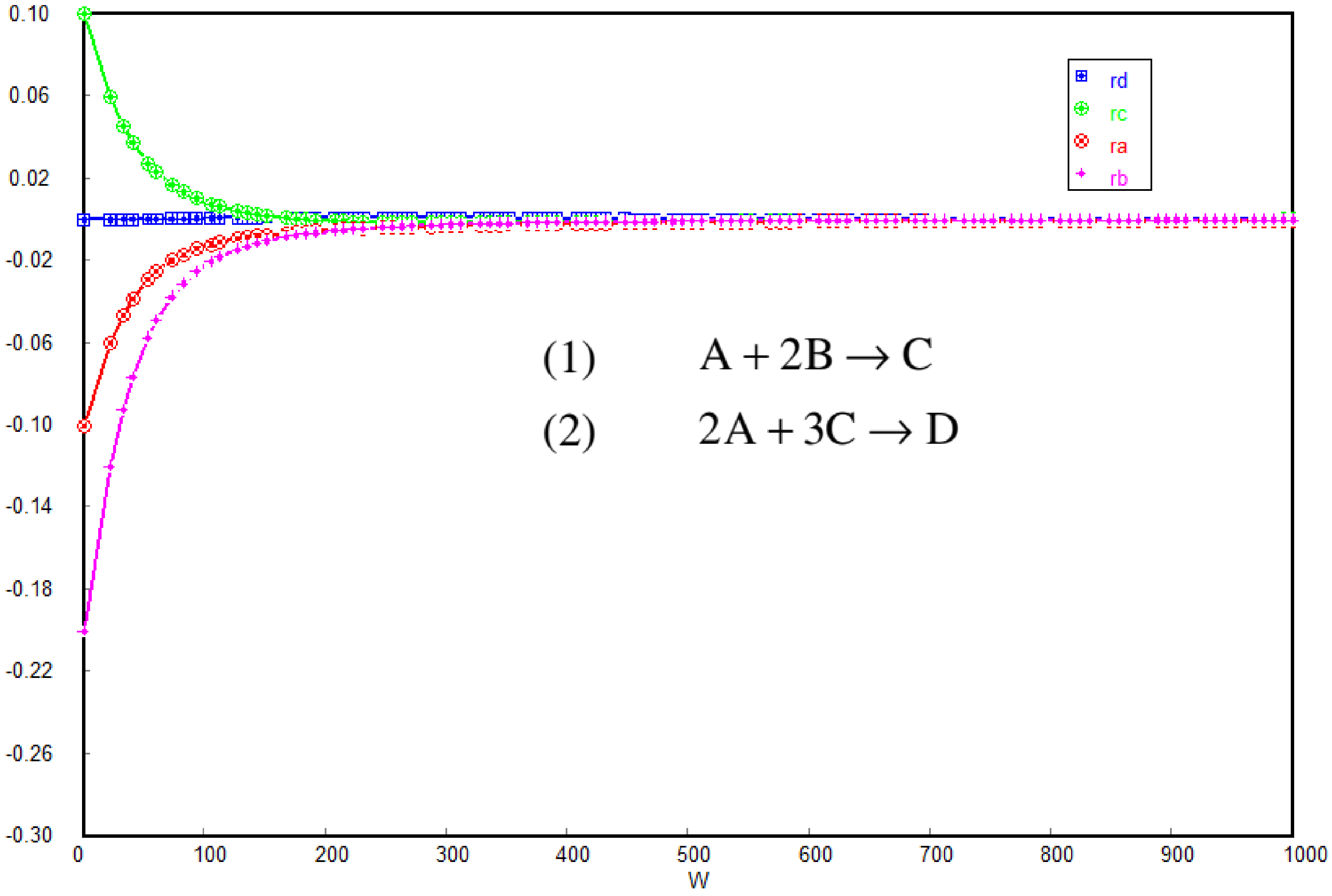
(1) $A + 2B \rightarrow C$

(2) $2A + 3C \rightarrow D$

Variation of concentrations with weight of catalyst



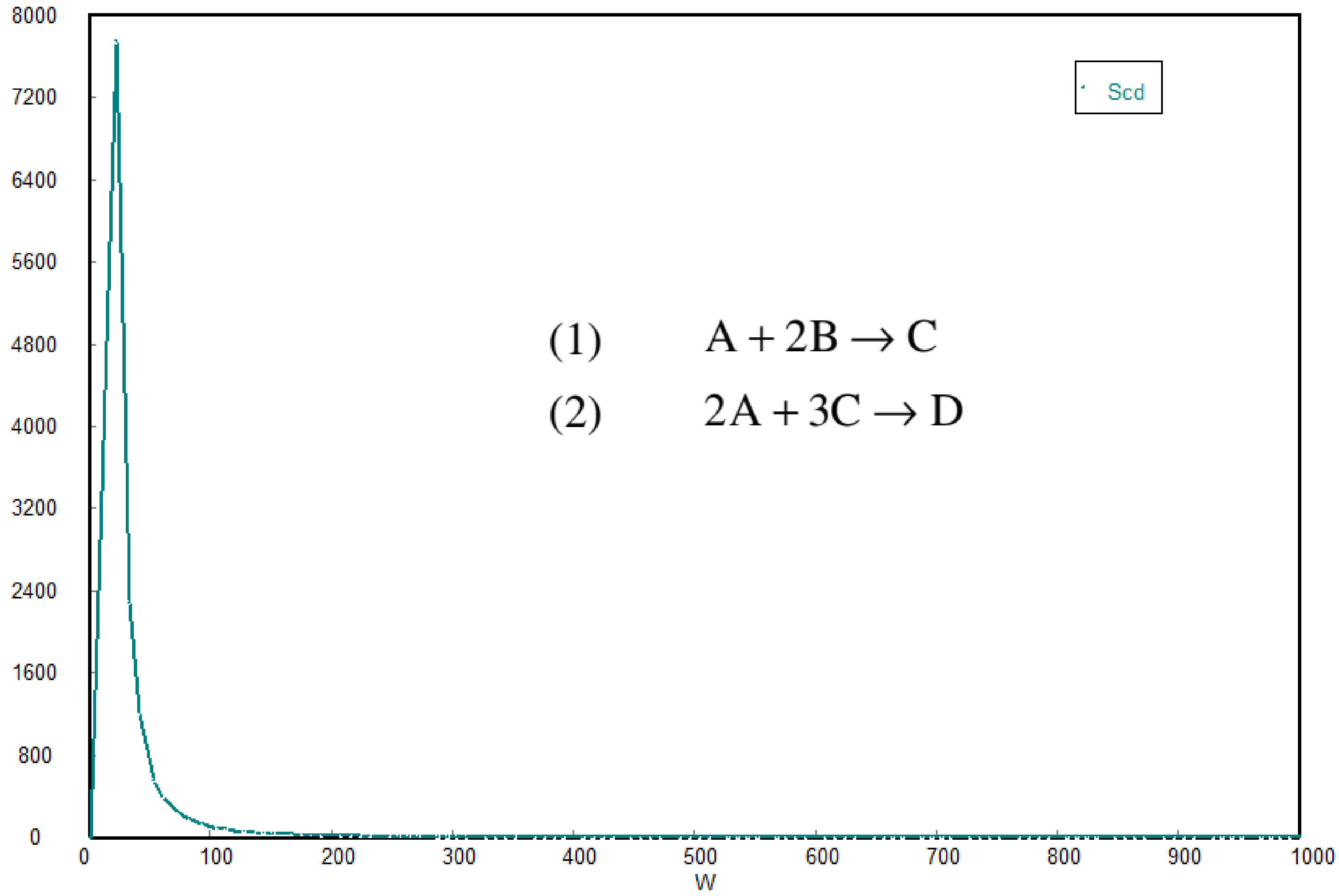
Variation of reaction rates with weight of catalyst



$$(1) \quad A + 2B \rightarrow C$$

$$(2) \quad 2A + 3C \rightarrow D$$

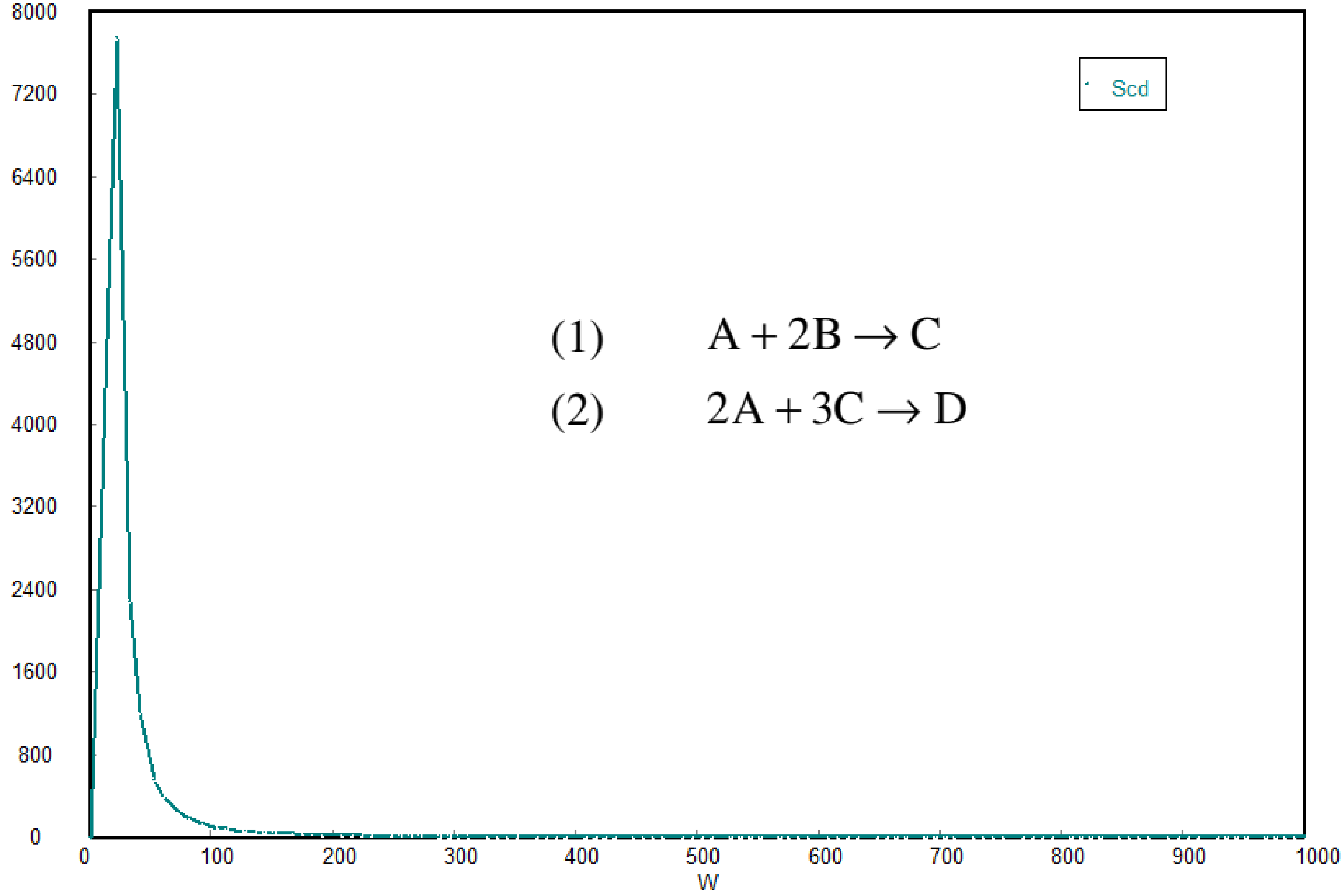
Variation of reaction selectivity with weight of catalyst



$$(1) \quad A + 2B \rightarrow C$$

$$(2) \quad 2A + 3C \rightarrow D$$

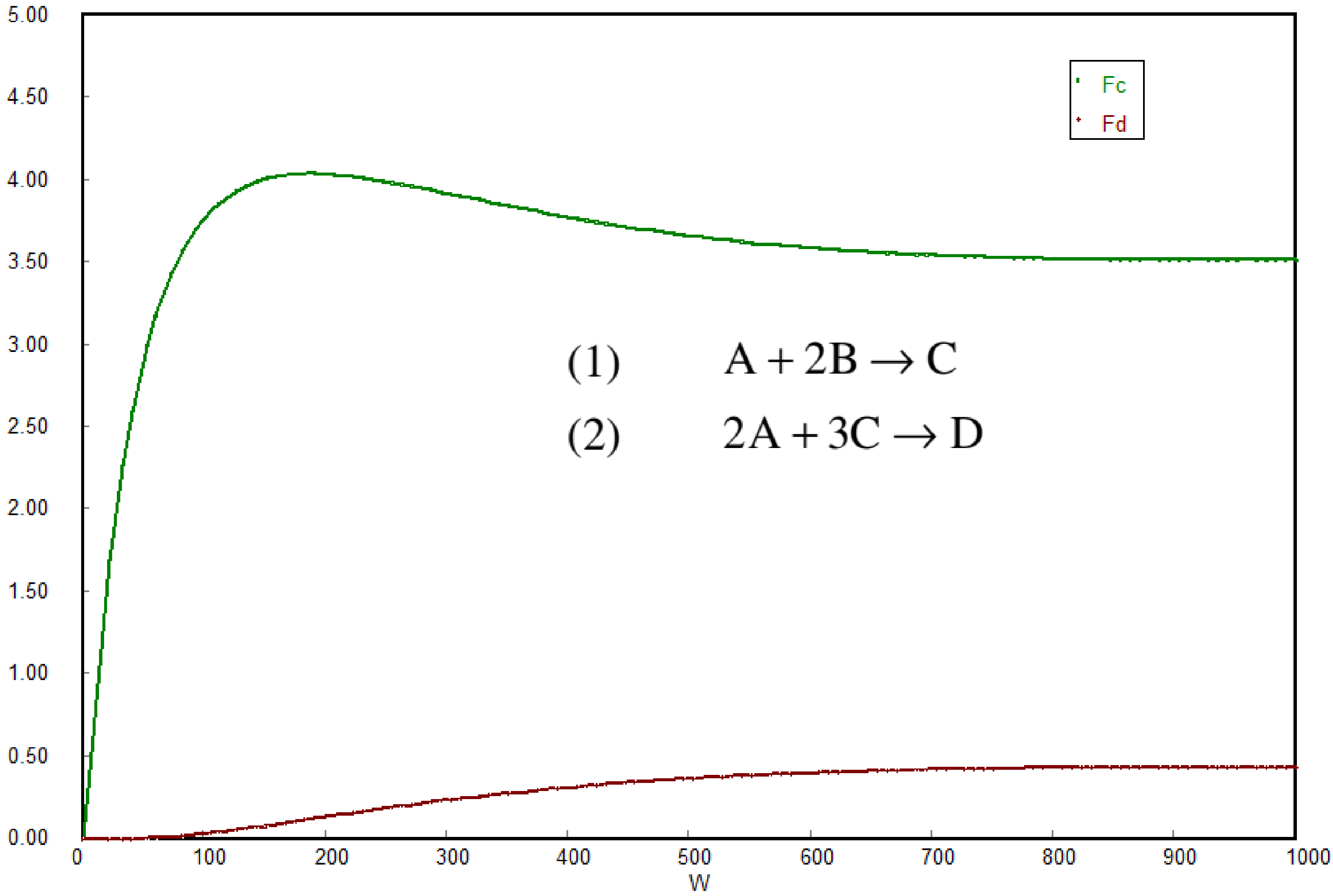
Variation of reaction selectivity with weight of catalyst



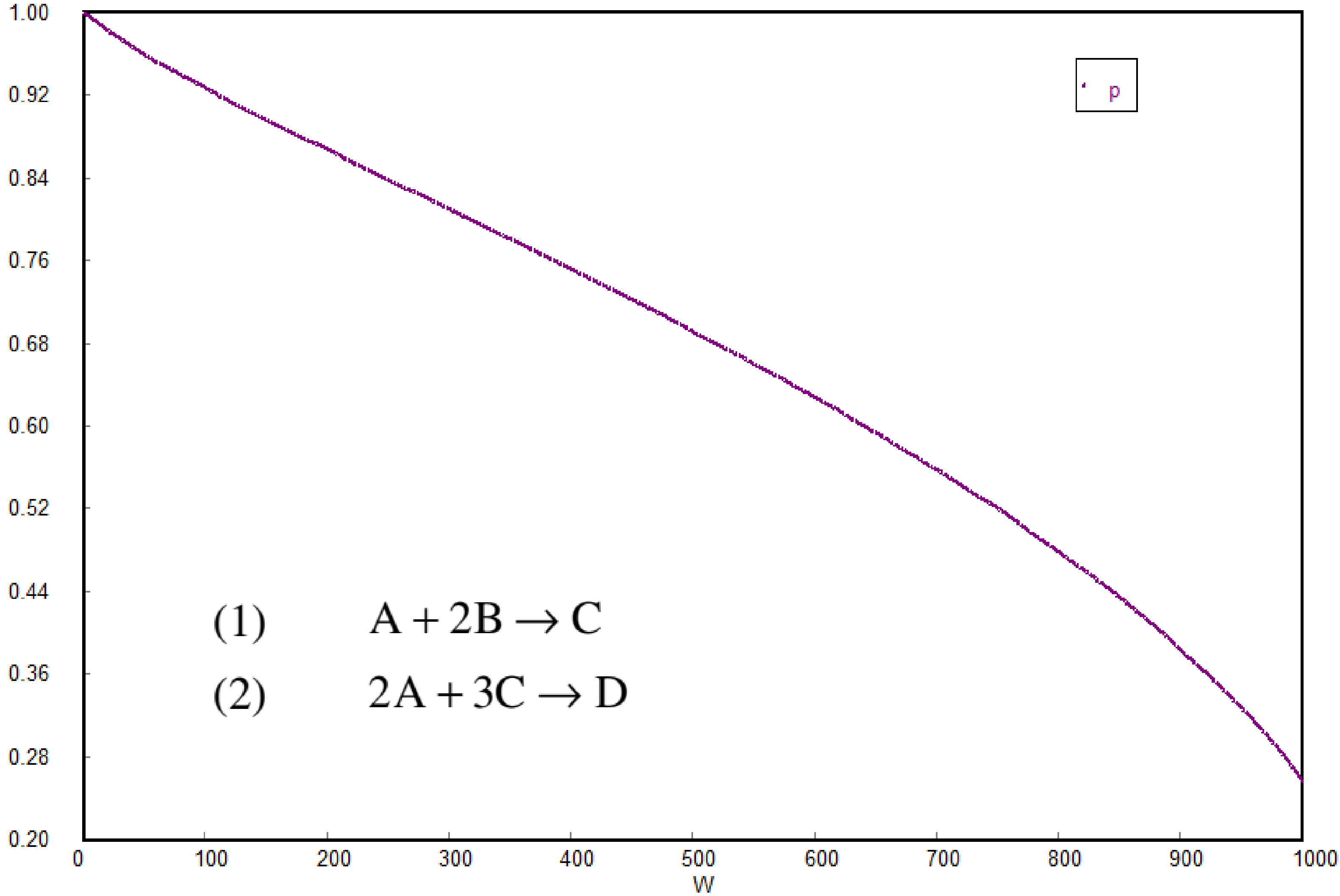
(1) $A + 2B \rightarrow C$

(2) $2A + 3C \rightarrow D$

Variation of flowrate of desired *C* and non-desired *D* with weight of catalyst



Variation pressure drop with weight of catalyst



$$(1) \qquad A + 2B \rightarrow C$$

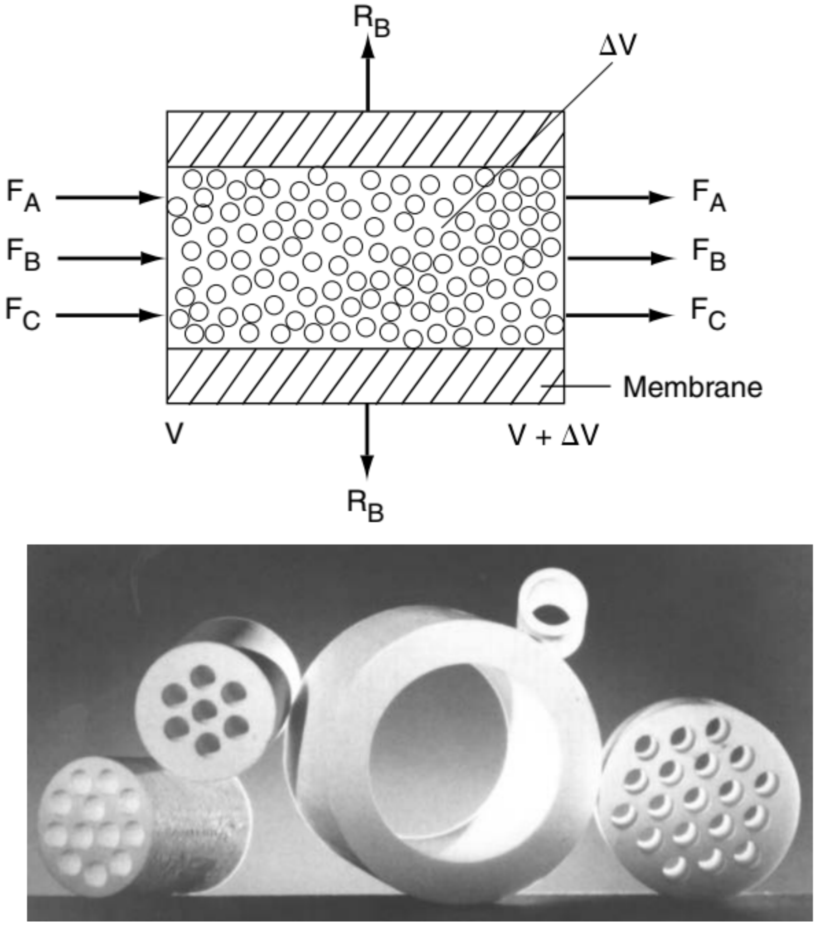
$$(2) \qquad 2A + 3C \rightarrow D$$

Isothermal membrane reactor design algorithm
(Molar flowrate approach)

The design of membrane reactor is different from the design of other reactors that is membrane reactor one or more species (mainly products) are withdrawn from the reactor by diffusion while moving from the inlet to exit of this reactor

For example, A is decomposing into B and C over a catalyst inside the membrane reactor while we need to get the product B out of the reactor once it forms. This will maximize the conversion by shifting the reaction toward more product B as shown

$$A \rightleftarrows 3B + C$$



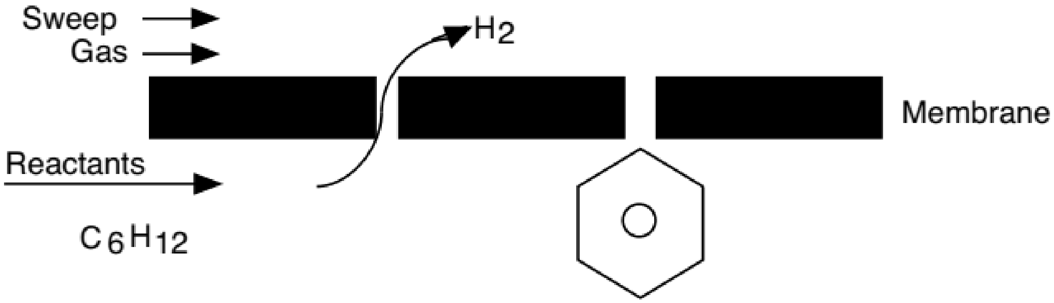
Membrane reactors; schematic for mole balance and photo of ceramic reactors

Design of Isothermal Membrane Reactor having catalyst

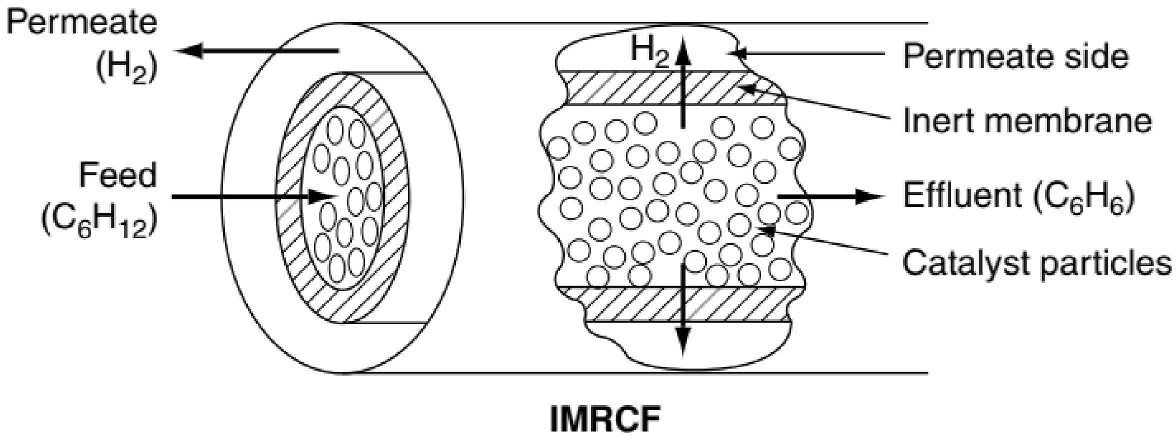
Suppose we need to decompose cyclohexane, C_6H_{12} into benzene, C_6H_6 and hydrogen, H_2 using a membrane reactor. Hydrogen is needed to be out of reactor once gets formed. Based on the size of the three components, hydrogen has the smallest molecule and can easily pass through the membrane once it gets formed.

$$C_6H_{12} \rightleftarrows 3H_2 + C_6H_6$$

$$A \rightleftarrows 3B + C$$



Here we have three components A, B and C and we need to write the design equation (mass balance) for each of these components.



For component A and C the mass balance is written as before, because these enter the reactor for one side and leaves from the exist side.

$$\boxed{\frac{dF_A}{dV} = r_A} \qquad \boxed{\frac{dF_C}{dV} = r_C}$$

However, for component B (H_2) we have side withdrawal and the mass balance becomes

$$\begin{bmatrix}\text{In}\\ \text{by flow}\end{bmatrix} - \begin{bmatrix}\text{Out}\\ \text{by flow}\end{bmatrix} - \begin{bmatrix}\text{Out}\\ \text{by diffusion}\end{bmatrix} + [\text{Generation}] = [\text{Accumulation}]$$

$$\begin{bmatrix}\text{In}\\ \text{by flow}\end{bmatrix} - \begin{bmatrix}\text{Out}\\ \text{by flow}\end{bmatrix} - \begin{bmatrix}\text{Out}\\ \text{by diffusion}\end{bmatrix} + [\text{Generation}] = [\text{Accumulation}]$$

$$\overbrace{F_{B}|_{V}} - \overbrace{F_{B}|_{V+\Delta V}} - \overbrace{R_{B}\Delta V} + \overbrace{r_{B}\Delta V} = 0$$

$$\boxed{\frac{dF_B}{dV} = r_B - R_B}$$

Where

$$R_B = W_B a = k_C' a(C_B - C_{BS}) \qquad (\text{mol/m}^3\text{/s}),$$

$$W_B = k_C'(C_B - C_{BS}) \qquad (\text{mol/m}^2\cdot\text{s}).$$

$$a = \frac{\text{Area}}{\text{Volume}} = \frac{\pi DL}{\frac{\pi D^2}{4}L} = \frac{4}{D} \qquad (\text{m}^2\text{/m}^3)$$

Where R_B is the molar flow of B out through the membrane per unit volume of the reactor, k_c' is the overall mass transfer coefficient in m/s and C_{BS} is the concentration of B in the sweep gas channel (mol/m3)

Assuming the concentration in the sweep gas is essentially zero as it flushed out ($C_{BS} \approx 0$), we obtain

$$\boxed{R_B = k_C C_B}$$

The rate of reaction of the equilibrium reaction aside is $\mathrm{A} \rightleftharpoons 3\mathrm{B} + \mathrm{C}$

$$\boxed{-r_A = k\left(C_A - \frac{C_B C_C}{K_C}\right)}$$

The relation between the rate of each species is shown $\boxed{\frac{-r_A}{1} = \frac{r_B}{3} = \frac{r_C}{1}}$

$$r_B = -3r_A \qquad r_C = -r_A$$

For the case of constant temperature and pressure, we have for ***isothermal operation***, and ***no pressure drop***. Thus

$$C_A = C_{T0}\frac{F_A}{F_T} \qquad C_B = C_{T0}\frac{F_B}{F_T} \qquad C_C = C_{T0}\frac{F_C}{F_T} \qquad F_T = F_A + F_B + F_C$$

Here we have **four** equations with **four** unknowns F_A, F_B, F_C and F_T. These equation can be solved by polymath.

$$\frac{dF_\mathrm{A}}{dV} = r_\mathrm{A}$$

$$\frac{dF_\mathrm{B}}{dV} = -r_\mathrm{A} - k_\mathrm{C} C_\mathrm{T0}\left(\frac{F_\mathrm{B}}{F_\mathrm{T}}\right)$$

$$\frac{dF_\mathrm{C}}{dV} = -r_\mathrm{A}$$

$$-r_\mathrm{A} = kC_\mathrm{T0}\left[\left(\frac{F_\mathrm{A}}{F_\mathrm{T}}\right) - \frac{C_\mathrm{T0}}{K_\mathrm{C}}\left(\frac{F_\mathrm{B}}{F_\mathrm{T}}\right)\left(\frac{F_\mathrm{C}}{F_\mathrm{T}}\right)\right]$$

$$F_\mathrm{T} = F_\mathrm{A} + F_\mathrm{B} + F_\mathrm{C}$$

Example 11.2 Reversible reaction in a membrane reactor

Consider the bellow rection takes place in membrane reactor:

$$A \rightleftarrows B + C$$

The equilibrium constant for this reaction is quite small at 227 C (e.g., $K_C = 0.05$ mol/dm^3). The membrane is permeable to B (e.g., H_2) but not to A and C. Pure gaseous A enters the reactor at 8.2 atm and 227 C ($C_{T0} = 0.2$ mol/dm^3) at a molar flow rate of 10 mol/min. The rate of diffusion of B out of the reactor per unit volume of reactor, R_B, is proportional to the concentration of B (i.e., $R_B = K_C\, C_B$).

a) Perform differential mole balances on A, B, and C to arrive at a set of coupled differential equations to solve.
b) Plot and analyze the molar flow rates of each species as a function of reactor volume.
c) Calculate the conversion of A at V = 500 dm^3.

Additional information: Even though this reaction is a gas–solid catalytic reaction, we will use the bulk catalyst density in order to write our balances in terms of reactor volume rather than catalyst weight (recall $-r_A = -r'_A \rho_b$). For the bulk catalyst density of $\rho_b = 1.5\ \text{g/cm}^3$ and a 2-cm inside-diameter tube containing the catalyst pellets, the specific reaction rate, k, and the transport coefficient, k_C, are $k = 0.7\ \text{min}^{-1}$ and $k_C = 0.2\ \text{min}^{-1}$, respectively.

Solution

$$C_{T0} = \frac{P_0}{RT_0} = \frac{830.6\ \text{kPa}}{[8.314\ \text{k Pa} \cdot \text{dm}^3/(\text{mol} \cdot \text{K})]\ (500\ \text{K})} = 0.2\ \frac{\text{mol}}{\text{dm}^3}$$

$$k = 0.7\ \text{min}^{-1},\ K_C = 0.05\ \text{mol/dm}^3,\ k_C = 0.2\ \text{min}^{-1}$$

$$F_{A0} = 10\ \text{mol/min}$$

$$F_{B0} = F_{C0} = 0$$

$$\mathrm{A} \rightleftarrows \mathrm{B} + \mathrm{C}$$

$$\frac{dF_A}{dV} = r_A \qquad -r_A = k\left(C_A - \frac{C_B C_C}{K_C}\right)$$

$$\frac{dF_B}{dV} = r_B - R_B \qquad \frac{r_A}{-1} = \frac{r_B}{1} = \frac{r_C}{1}$$

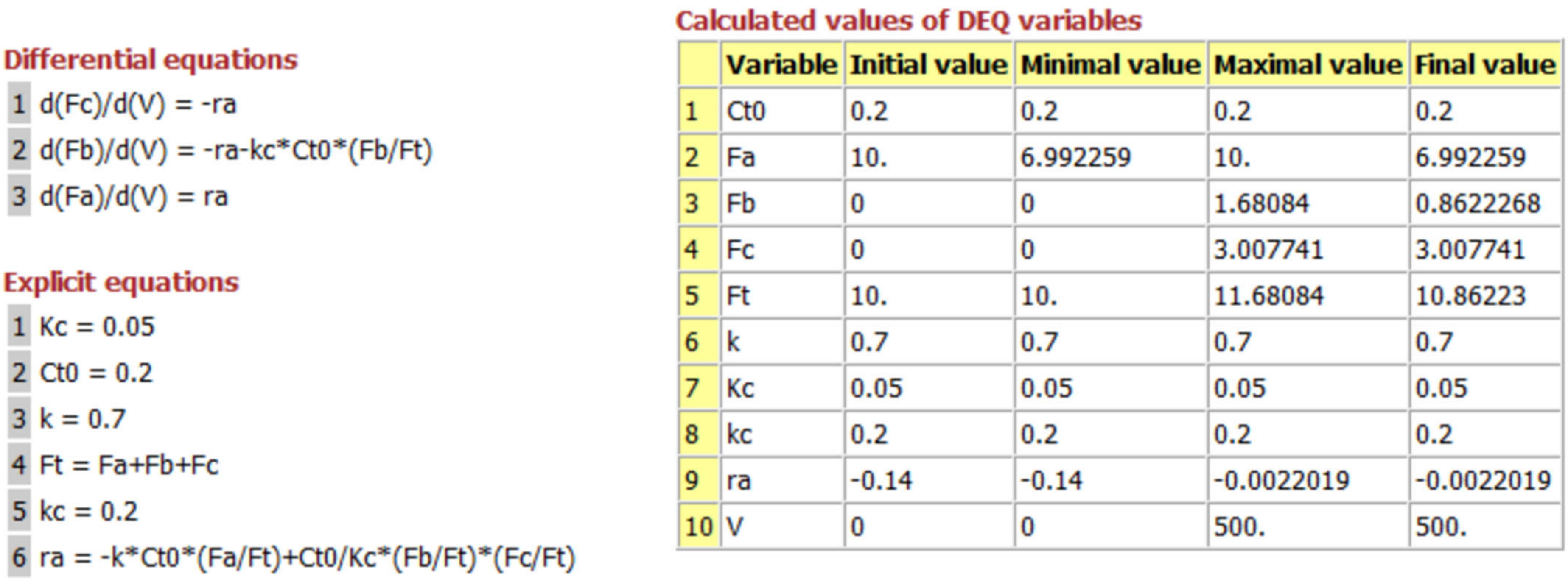
$$\frac{dF_C}{dV} = r_C \qquad R_B = k_C C_B$$

$$\boxed{\begin{aligned} \frac{dF_A}{dV} &= r_A \\ \frac{dF_B}{dV} &= -r_A - k_C C_{T0}\left(\frac{F_B}{F_T}\right) \\ \frac{dF_C}{dV} &= -r_A \\ -r_A &= kC_{T0}\left[\left(\frac{F_A}{F_T}\right) - \frac{C_{T0}}{K_C}\left(\frac{F_B}{F_T}\right)\left(\frac{F_C}{F_T}\right)\right] \\ F_T &= F_A + F_B + F_C \end{aligned}}$$

entering conditions.

$$V = 0: \quad F_A = F_{A0}, \quad F_B = 0, \quad F_C = 0$$

The equations above were solved using polymath to obtain F_A, F_B, F_C and F_T as shown bellow:



Differential equations

1 d(Fc)/d(V) = -ra
2 d(Fb)/d(V) = -ra-kc*Ct0*(Fb/Ft)
3 d(Fa)/d(V) = ra

Explicit equations

1 Kc = 0.05
2 Ct0 = 0.2
3 k = 0.7
4 Ft = Fa+Fb+Fc
5 kc = 0.2
6 ra = -k*Ct0*(Fa/Ft)+Ct0/Kc*(Fb/Ft)*(Fc/Ft)

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ct0	0.2	0.2	0.2	0.2
2	Fa	10.	6.992259	10.	6.992259
3	Fb	0	0	1.68084	0.8622268
4	Fc	0	0	3.007741	3.007741
5	Ft	10.	10.	11.68084	10.86223
6	k	0.7	0.7	0.7	0.7
7	Kc	0.05	0.05	0.05	0.05
8	kc	0.2	0.2	0.2	0.2
9	ra	-0.14	-0.14	-0.0022019	-0.0022019
10	V	0	0	500.	500.

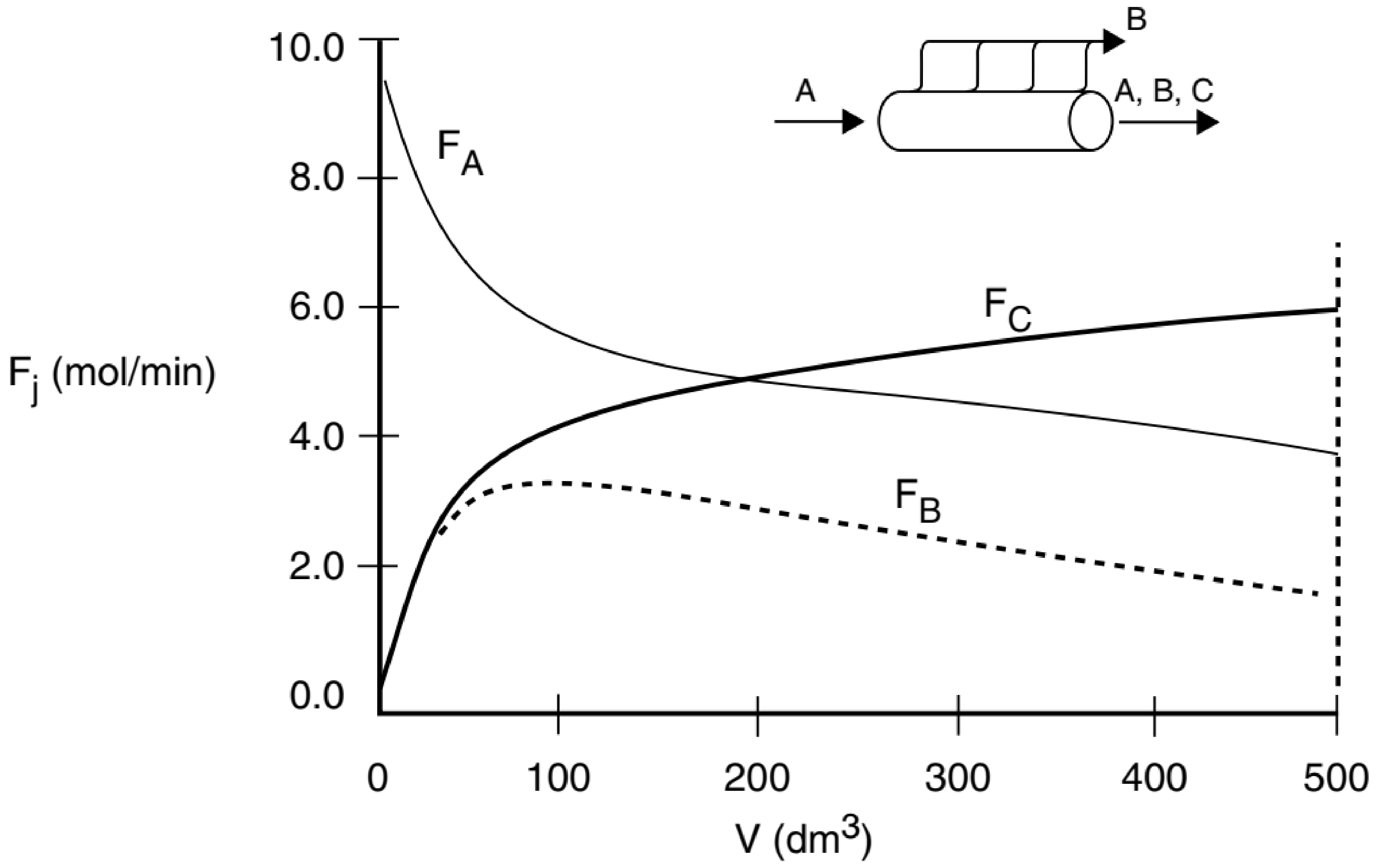


Figure E6-2.1 Polymath solution.

(c) From Figure E6-2.1, we see that the exit molar flow rate of A at 500 dm^3 is 4 mol/min, for which the corresponding conversion is

$$x = \frac{F_{Ao} - F_A}{F_{Ao}} = \frac{10 - 7}{10} = 0.3$$

Design of Isothermal, Liquid-phase CSTR for multiple reactions

Consider the following multiple reactions:

$$A + B \rightarrow C$$
$$E \rightarrow A + D$$

The mole balance for each individual species, i, in the reactor is written in the form:

$$F_{10} - F_1 = -r_1 V = V \sum_{i=1}^{q} -r_{i1} = V \cdot f_1(C_1 \ldots, C_N)$$

$$\vdots$$

$$F_{j0} - F_j = -r_j V = V \cdot f_j(C_1 \ldots, C_N)$$

$$\vdots$$

$$F_{N0} - F_N = -r_N V = V \cdot f_N(C_1 \ldots, C_N)$$

Here we get N nonlinear equations based on N number of species (reactants and products) that exist in the reactor.
These equations should be solved simultaneously to obtain the molar flowrate of each species.

Example 11.3 Multiple liquid-Phase Reactions in a CSTR

The following complex liquid-phase elementary reactions take place isothermally in a 2,500 L CSTR. The feed is equimolar in A and B with F_{A0}= 200 mol/min and the volumetric flow rate is 100 L/min. The total entering concentration is $C_{T0} = 0.2\ mol/L$.

$$\begin{array}{lll} (1) & A + 2B \rightarrow C & -r'_{1A} = k_{1A} C_A C_B^2 \\ (2) & 2A + 3C \rightarrow D & -r'_{2C} = k_{2C} C_A^2 C_C^3 \end{array}$$

$$k_{1A} = 10\left(\frac{\text{dm}^3}{\text{mol}}\right)^2 \Big/ \text{min} \quad \text{and} \quad k_{2C} = 15\left(\frac{\text{dm}^3}{\text{mol}}\right)^4 \Big/ \text{min}$$

Find the concentrations of A, B, C, and D exiting the reactor, along with the exiting overall selectivity, $S_{C/D}$.

Solution

Liquid-Phase CSTR: $v = v_0$

$$\boxed{\begin{aligned} &A + 2B \rightarrow C \\ &2A + 3C \rightarrow D \end{aligned}}$$

Mole Balances

$$(1) \qquad f(C_A) = v_0 C_{A0} - v_0 C_A + r_A V$$

$$(2) \qquad f(C_B) = v_0 C_{B0} - v_0 C_B + r_B V$$

$$(3) \qquad f(C_C) = \qquad - v_0 C_C + r_C V$$

$$(4) \qquad f(C_D) = \qquad - v_0 C_D + r_D V$$

Key components

$$r'_{1A} = -k_{1A} C_A C_B^2$$

$$r'_{2C} = -k_{2C} C_A^2 C_C^3$$

$$\frac{r'_{1A}}{-1} = \frac{r'_{1B}}{-2} = \frac{r'_{1C}}{1} \qquad \frac{r'_{2A}}{-2} = \frac{r'_{2C}}{-3} = \frac{r'_{2D}}{1}$$

$$r'_A = r'_{1A} + r'_{2A} = -k_{1A}C_AC_B^2 - \frac{2}{3}k_{2C}C_A^2C_C^3$$

$$r'_B = r'_{1B} = -2k_{1A}C_AC_B^2$$

$$r'_C = r'_{1C} + r'_{2C} = k_{1A}C_AC_B^2 - k_{2C}C_A^2C_C^3$$

$$r'_D = r'_{2D} = \frac{1}{3}k_{2C}C_A^2C_C^3$$

$$\boxed{\begin{array}{l} A + 2B \rightarrow C \\ 2A + 3C \rightarrow D \end{array}}$$

$$v_0 = 100\ \text{dm}^3/\text{min}$$

$$k_{1A} = 10\ \left(\text{dm}^3/\text{mol}\right)^2 \Big/ \text{min}$$

$$k_{2C} = 15\ \left(\text{dm}^3/\text{mol}\right)^4 \Big/ \text{min}$$

$$V = 2,500\ \text{dm}^3$$

$$C_{A0} = 2.0\,\text{mol / dm}^3$$

$$C_{B0} = 2.0\,\text{mol / dm}^3$$

$$f(C_A) = v_0 C_{A0} - v_0 C_A - \left(k_{1A} C_A C_B^2 - \frac{2}{3} k_{2C} C_A^2 C_C^3 \right) V$$

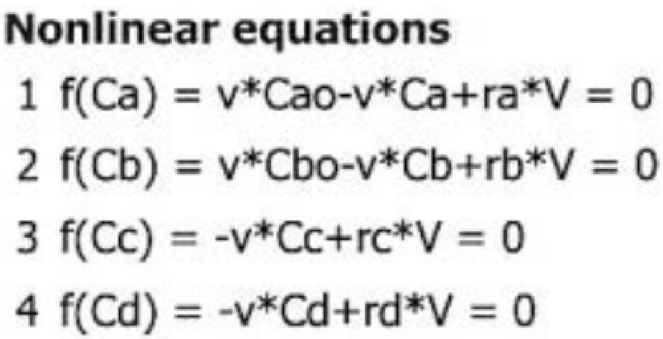
$$f(C_B) = v_0 C_{B0} - v_0 C_B - (2 k_{1A} C_A C_B^2) V$$

$$f(C_C) = -v_0 C_C + (k_{1A} C_A C_B^2 - k_{2C} C_A^2 C_C^3) V$$

$$f(C_D) = -v_0 C_D + \left(\frac{1}{3} k_{2C} C_A^2 C_C^3 \right) V$$

$A + 2B \rightarrow C$

$2A + 3C \rightarrow D$



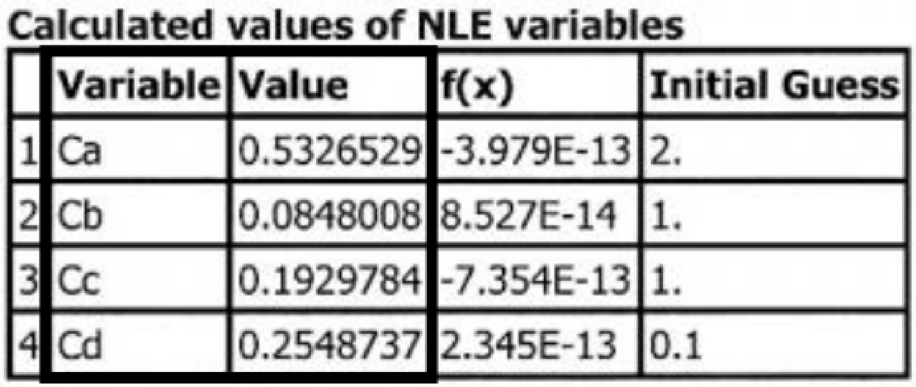
Nonlinear equations

1 f(Ca) = v*Cao-v*Ca+ra*V = 0

2 f(Cb) = v*Cbo-v*Cb+rb*V = 0

3 f(Cc) = -v*Cc+rc*V = 0

4 f(Cd) = -v*Cd+rd*V = 0



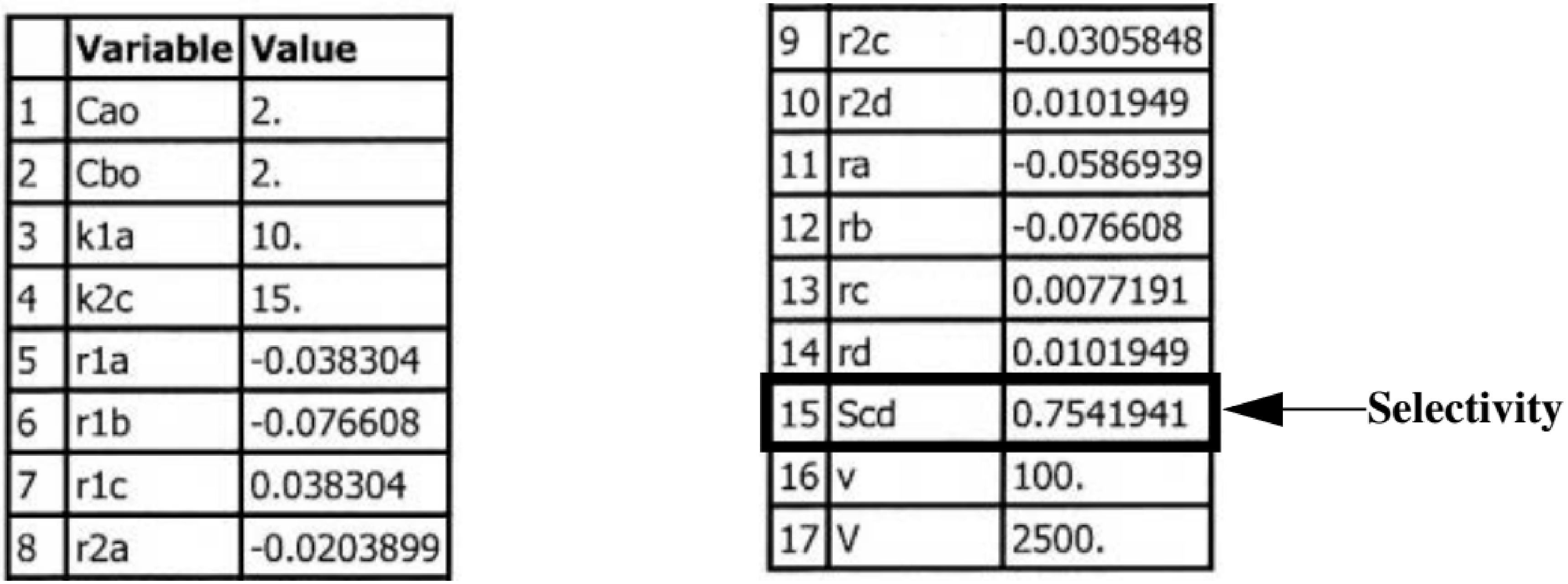
Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	Ca	0.5326529	-3.979E-13	2.
2	Cb	0.0848008	8.527E-14	1.
3	Cc	0.1929784	-7.354E-13	1.
4	Cd	0.2548737	2.345E-13	0.1

Results

The exit concentrations are $C_A = 0.53$ M, $C_B = 0.085$ M, $C_C = 0.19$ M, and $C_D = 0.25$ M with $\tilde{S}_{C/D} = 0.75$. The corresponding conversion of A is

$$\boxed{X = \frac{C_{A0} - C_A}{C_{A0}} = \frac{2 - 0.533}{2} = 0.73}$$

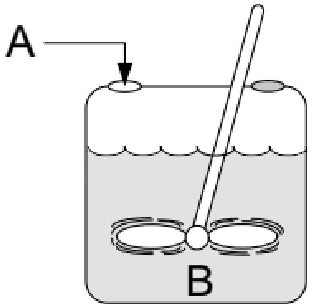


	Variable	Value
1	Cao	2.
2	Cbo	2.
3	k1a	10.
4	k2c	15.
5	r1a	-0.038304
6	r1b	-0.076608
7	r1c	0.038304
8	r2a	-0.0203899
9	r2c	-0.0305848
10	r2d	0.0101949
11	ra	-0.0586939
12	rb	-0.076608
13	rc	0.0077191
14	rd	0.0101949
15	Scd	0.7541941
16	v	100.
17	V	2500.

Complex Reactions in a Semibatch Reactor

semibatch reactor where A is fed to B with F_{A0} = 3 mol/min. The volumetric flow rate is 10 dm^3/min and the initial reactor volume is 1,000 dm^3. The rate constants are

$$k_{1A} = 10\left(\frac{\text{dm}^3}{\text{mol}}\right)^2 \Big/ \text{min} \text{ and } k_{2C} = 15\left(\frac{\text{dm}^3}{\text{mol}}\right)^4 \Big/ \text{min}$$



Semibatch Reactor

The maximum volume is 2,000 dm^3. The inlet concentration of A is C_{A0} = 0.3 mol/dm^3 and the initial concentration of B is C_{Bi} = 0.2 mol/dm^3.

(a) Plot and analyze N_A, N_B, N_C, N_D, and $S_{C/D}$ as a function of time.

Mole Balances

(1) $$\frac{dN_A}{dt} = r_A V + F_{A0} \qquad (N_{Ai} = 0)$$

(2) $$\frac{dN_B}{dt} = r_B V \qquad (N_{Bi} = C_{Bi} V_0 = 200 \text{ moles})$$

(3) $$\frac{dN_C}{dt} = r_C V \qquad (N_{Ci} = 0)$$

(4) $$\frac{dN_D}{dt} = r_D V \qquad (N_{Di} = 0)$$

$$C_A = N_A / V$$

$$C_D = N_D / V$$

$$C_B = N_B / V$$

$$V = V_0 + v_0 t$$

$$C_C = N_C / V$$

$$v_0 = 10 \text{ dm}^3 / \text{min}$$

$$V_0 = 1{,}000 \text{ dm}^3$$

$$F_{A0} = 3 \text{ mol} / \text{min}$$

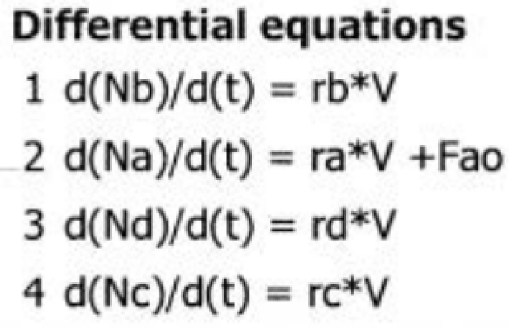
$$\boxed{\begin{array}{l} A + 2B \rightarrow C \\ 2A + 3C \rightarrow D \end{array}}$$

Key components

$$r'_{1A} = -k_{1A} C_A C_B^2$$

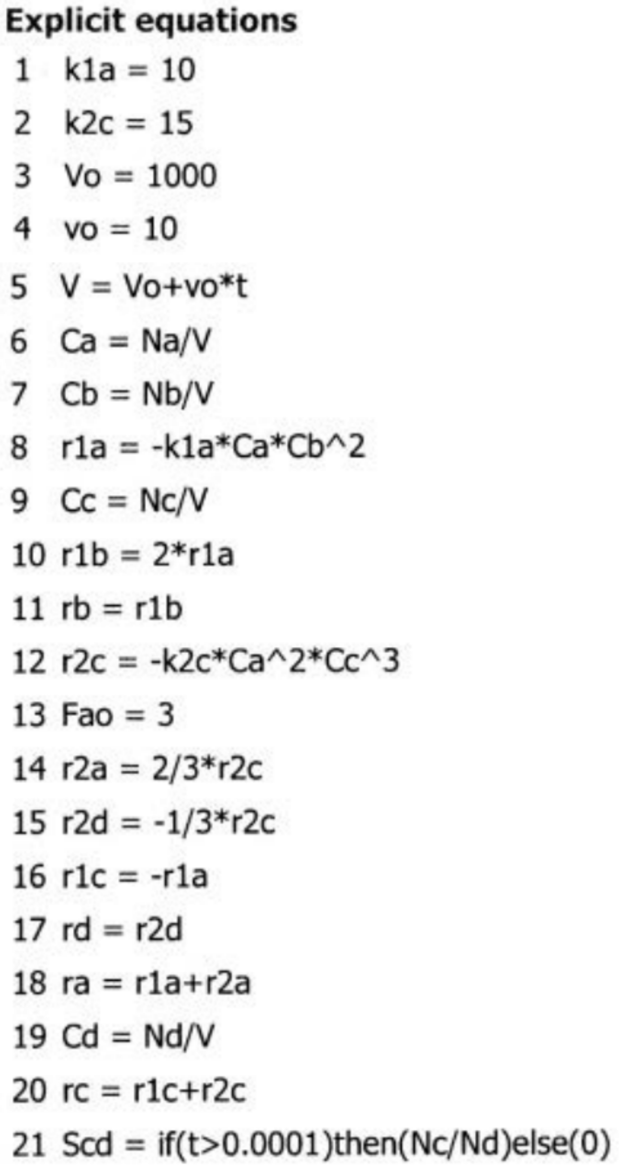
$$r'_{2C} = -k_{2C} C_A^2 C_C^3$$

$$\frac{r'_{1A}}{-1} = \frac{r'_{1B}}{-2} = \frac{r'_{1C}}{1} \qquad \frac{r'_{2A}}{-2} = \frac{r'_{2C}}{-3} = \frac{r'_{2D}}{1}$$



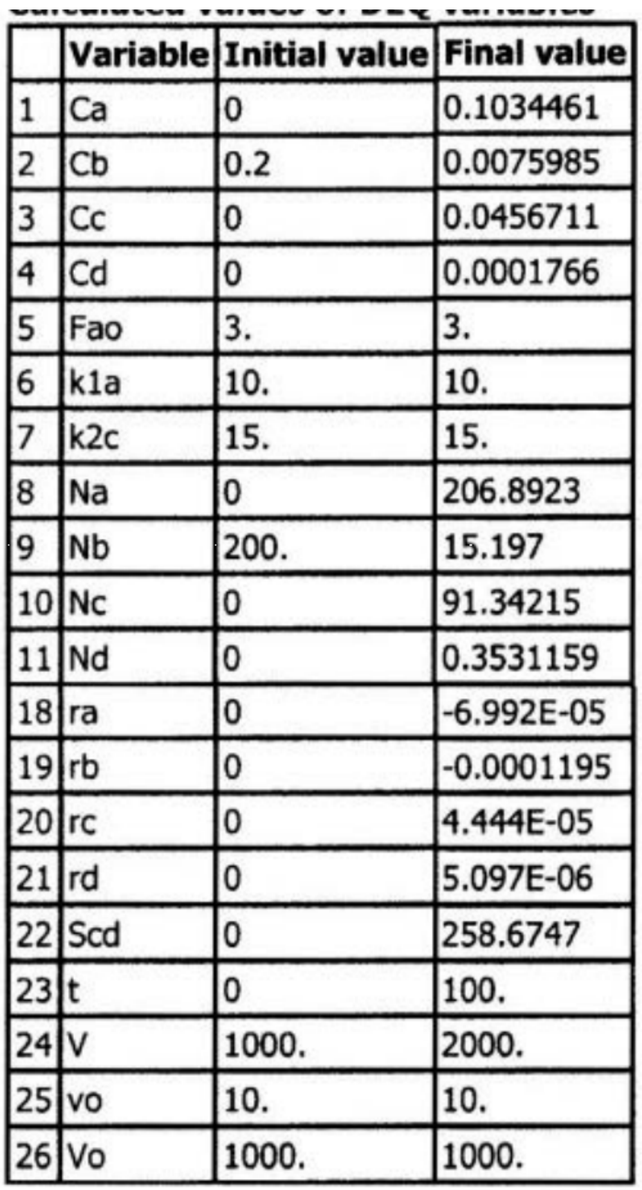
Differential equations

```
1 d(Nb)/d(t) = rb*V
2 d(Na)/d(t) = ra*V +Fao
3 d(Nd)/d(t) = rd*V
4 d(Nc)/d(t) = rc*V
```

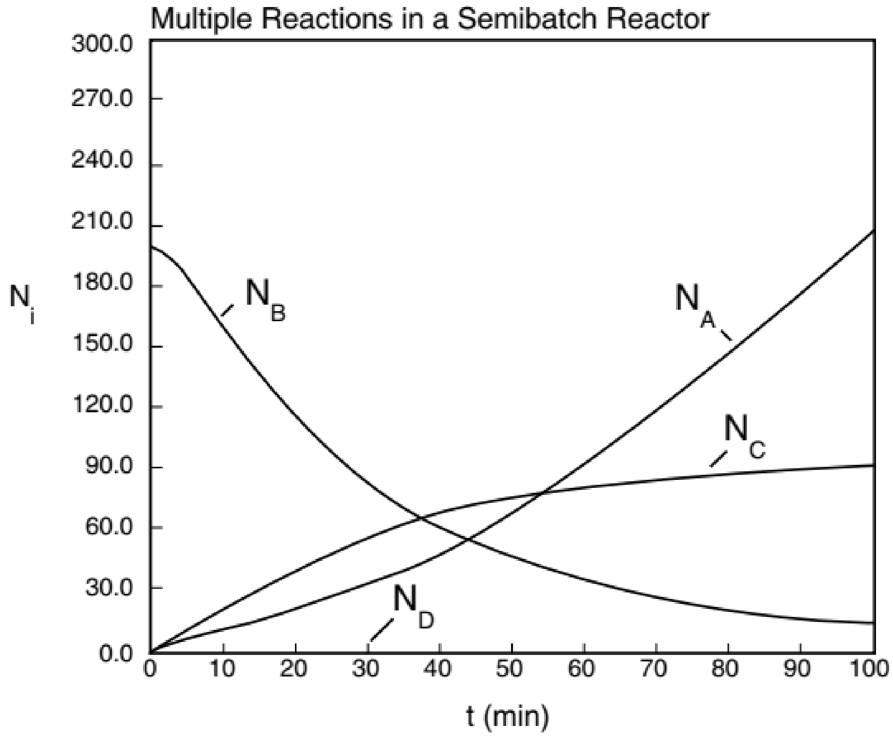


Explicit equations

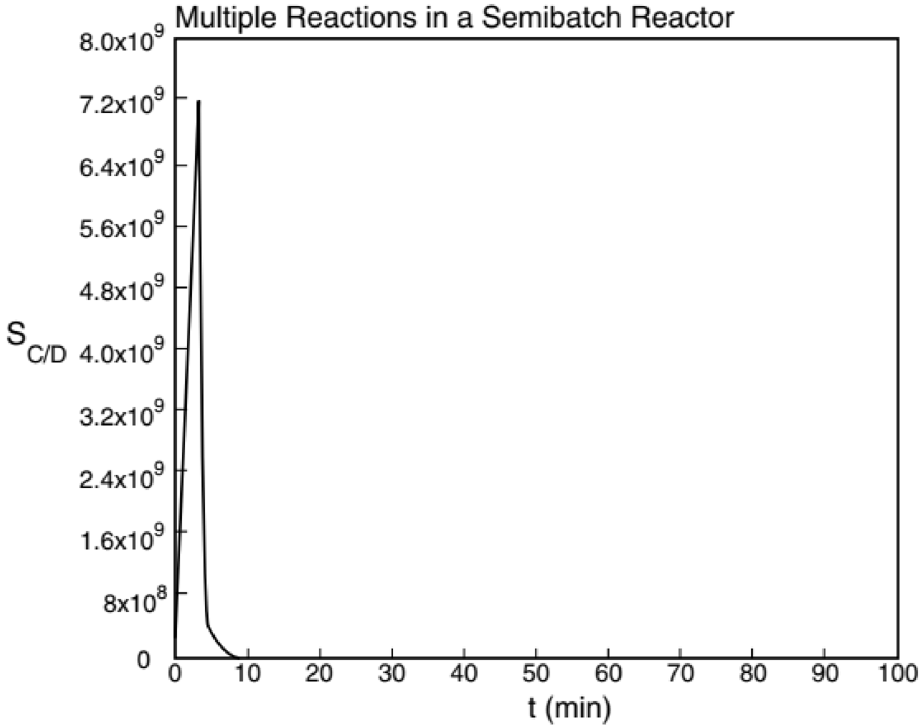
```
1   k1a = 10
2   k2c = 15
3   Vo = 1000
4   vo = 10
5   V = Vo+vo*t
6   Ca = Na/V
7   Cb = Nb/V
8   r1a = -k1a*Ca*Cb^2
9   Cc = Nc/V
10  r1b = 2*r1a
11  rb = r1b
12  r2c = -k2c*Ca^2*Cc^3
13  Fao = 3
14  r2a = 2/3*r2c
15  r2d = -1/3*r2c
16  r1c = -r1a
17  rd = r2d
18  ra = r1a+r2a
19  Cd = Nd/V
20  rc = r1c+r2c
21  Scd = if(t>0.0001)then(Nc/Nd)else(0)
```



	Variable	Initial value	Final value
1	Ca	0	0.1034461
2	Cb	0.2	0.0075985
3	Cc	0	0.0456711
4	Cd	0	0.0001766
5	Fao	3.	3.
6	k1a	10.	10.
7	k2c	15.	15.
8	Na	0	206.8923
9	Nb	200.	15.197
10	Nc	0	91.34215
11	Nd	0	0.3531159
18	ra	0	-6.992E-05
19	rb	0	-0.0001195
20	rc	0	4.444E-05
21	rd	0	5.097E-06
22	Scd	0	258.6747
23	t	0	100.
24	V	1000.	2000.
25	vo	10.	10.
26	Vo	1000.	1000.



Multiple Reactions in a Semibatch Reactor



Multiple Reactions in a Semibatch Reactor

Steady State Non-isothermal reactor Design

In this topic we will study the following:

- The energy balance
- Adiabatic operations
- Non-isothermal flow reactors with heat exchange
- Equilibrium conversion and adiabatic temperature
- Optimum feed temperature

Isothermal and non-isothermal reactions

Because most reactions we not carried out isothermally, we now focus on heat effect in chemical reactors.

The basic design equations, rate laws, and stoichiometric relationships discussed early for isothermal reactor design are still valid for the design of non-isothermal reactors.

The major difference lies in the method of evaluating the design equation when temperature varies along the length of a PFR or when heat is added/removed from a *CSTR.*

To identify the additional information necessary to design non-isothermal Reactors, let us check the example bellow:

Example 12.1:

Calculate the reactor volume necessary for 70% conversion: $\mathrm{A} \longrightarrow \mathrm{B}$

The reaction is exothermic and the reactor is operated adiabatically. As a result temperature will increase with conversion down the length of the reactor.

Solution

1. **Mole Balance (design equation):**

$$\frac{dX}{dV} = \frac{-r_{\mathrm{A}}}{F_{\mathrm{A0}}}$$

2. **Rate Law:**

$$-r_{\mathrm{A}} = kC_{\mathrm{A}}$$

Recalling the Arrhenius equation,

$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

we know that k is a function of temperature, T.

3. Stoichiometry (liquid phase): $v = v_0$

$$C_A = C_{A0}(1 - X)$$

4. Combining:

$$-r_A = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] C_{A0}(1 - X)$$

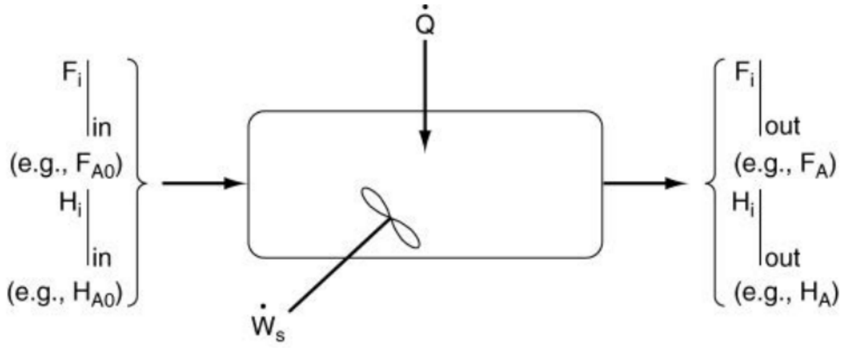
Combining the above Equations and canceling the entering concentration, C_{A0}, yields

$$\frac{dX}{dV} = \frac{k(1 - X)}{v_0} \quad \Longrightarrow \quad \frac{dX}{dV} = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \frac{1 - X}{v_0}$$

This ordinary differential equation estimates the variation of conversion as a function of volume of reactor, however, we do have another dependent variable (Temperature) that varies with volume of reactor. Therefore, how to get an expression of variation of reactor temperature as a function of volume?

The Energy Balance

Consider the schematic diagram for a representative reactor where the feed to this reactor is $Fi_{(IN)}$ enters with energy $Hi_{(IN)}$ and the products leave with $Fi_{(OUT)}$ and energy $Hi_{(OUT)}$. Heat is added to the reactor or removed (based on if the reaction is endothermic or exothermic, respectively), and a work is added to the reactor (as in the case of flow work or mechanical work).



The energy balance for the case of only one species entering and leaving becomes

$$\begin{bmatrix}\text{Rate of}\\ \text{accumulation}\\ \text{of energy}\\ \textit{within}\text{ the}\\ \text{system}\end{bmatrix} = \begin{bmatrix}\text{Rate of flow}\\ \text{of heat }\textit{to}\\ \text{the system}\\ \textit{from}\text{ the}\\ \text{surroundings}\end{bmatrix} - \begin{bmatrix}\text{Rate of work}\\ \textit{done}\text{ by}\\ \text{the system}\\ \textit{on}\text{ the}\\ \text{surroundings}\end{bmatrix} + \begin{bmatrix}\text{Rate of energy}\\ \text{added to the}\\ \text{system by mass}\\ \text{flow }\textit{into}\text{ the}\\ \text{system}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{energy leaving}\\ \text{the system by mass}\\ \text{flow }\textit{out}\text{ of}\\ \text{the system}\end{bmatrix}$$

Energy balance on an open system

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W} + F_{in}E_{in} - F_{out}E_{out} \qquad (11\text{-}2)$$

$$(\mathrm{J/s}) = (\mathrm{J/s}) - (\mathrm{J/s}) + (\mathrm{J/s}) - (\mathrm{J/s})$$

Typical units for each term in Equation (11-2) are (Joule/s).

The unsteady-state energy balance for an open well-mixed system that has ***n* species**, each entering and leaving the system at its respective molar flow rate *Fi* (moles of i per time) and with its respective energy *Ei* (joules per mole of i), is

$$\frac{d\hat{E}_{\text{sys}}}{dt} = \dot{Q} - \dot{W} + \sum_{i=1}^{n} E_i F_i \bigg|_{\text{in}} - \sum_{i=1}^{n} E_i F_i \bigg|_{\text{out}}$$

The work term, $\dot{W}$, into flow work and other work $\dot{W}_s$. The term $\dot{W}_s$, often referred to as the shaft work, could be produced from such things as a stirrer in a CSTR or a turbine in a PFR. Flow work is work that is necessary to get the mass into and out of the system.

$$\dot{W} = \overbrace{-\sum_{i=1}^{n} F_i P \tilde{V}_i \bigg|_{\text{in}} + \sum_{i=1}^{n} F_i P \tilde{V}_i \bigg|_{\text{out}}}^{\text{[Rate of flow work]}} + \dot{W}_s$$

where P is the pressure (Pa) [1 Pa = 1 Newton/m^2 = 1 kg·m/s^2/m^2] and $\tilde{V}_i$ is the specific molar volume of species i (m^3/mol of i).

Substituting the work equation into the energy equation and grouping terms, we have

$$\frac{d\hat{E}_{\text{sys}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_i(E_i + P\tilde{V}_i)\Big|_{\text{in}} - \sum_{i=1}^{n} F_i(E_i + P\tilde{V}_i)\Big|_{\text{out}}$$

The energy *Ei* can be approximated by the internal energy (*Ui*) other forms of energy are negligible compered to internal energy, substitute in the above equation and re-arrange

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_{i0}H_{i0} - \sum_{i=1}^{n} F_iH_i = \frac{d\hat{E}_{\text{sys}}}{dt}$$

Where the subscript "0" represent the inlet conditions, and

$$F_iH_i = F_i(U_i + P\tilde{V}_i)$$

Convention

Heat Added

$\dot{Q} = +10\text{J/s}$

Heat Removed

$\dot{Q} = -10\text{J/s}$

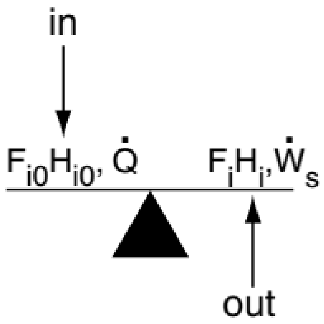
Work Done **by** System

$\dot{W}_S = +10\text{J/s}$

Work Done **on** System

$\dot{W}_S = -10\text{J/s}$

Energy Balance



$$\dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_i H_i = \frac{d\hat{E}_{\text{sys}}}{dt}$$

If the following reaction takes place inside the reactor

$$\mathrm{A} + \frac{b}{a}\mathrm{B} \longrightarrow \frac{c}{a}\mathrm{C} + \frac{d}{a}\mathrm{D}$$

The inlet and outlet summation terms in the energy equation are expanded to

$$\textbf{In:} \quad \Sigma H_{i0} F_{i0} = H_{\mathrm{A0}} F_{\mathrm{A0}} + H_{\mathrm{B0}} F_{\mathrm{B0}} + H_{\mathrm{C0}} F_{\mathrm{C0}} + H_{\mathrm{D0}} F_{\mathrm{D0}} + H_{\mathrm{I0}} F_{\mathrm{I0}}$$

$$\textbf{Out:} \quad \Sigma H_i F_i = H_{\mathrm{A}} F_{\mathrm{A}} + H_{\mathrm{B}} F_{\mathrm{B}} + H_{\mathrm{C}} F_{\mathrm{C}} + H_{\mathrm{D}} F_{\mathrm{D}} + H_{\mathrm{I}} F_{\mathrm{I}}$$

Where the subscript I represents inert species. Expressing the molar flow rates in terms of conversion for incompressible fluids we get

$$F_{\mathrm{A}} = F_{\mathrm{A0}}(1 - X)$$

$$F_{\mathrm{B}} = F_{\mathrm{A0}}\left(\Theta_{\mathrm{B}} - \frac{b}{a}X\right)$$

$$F_{\mathrm{C}} = F_{\mathrm{A0}}\left(\Theta_{\mathrm{C}} + \frac{c}{a}X\right)$$

$$F_{\mathrm{D}} = F_{\mathrm{A0}}\left(\Theta_{\mathrm{D}} + \frac{d}{a}X\right)$$

$$F_{\mathrm{I}} = \Theta_{\mathrm{I}} F_{\mathrm{A0}}$$

$$\text{where } \Theta_i = \frac{F_{i0}}{F_{\mathrm{A0}}}$$

Substitute these symbols for the molar flow rates into the energy equations

$$\boxed{\dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_i H_i = \frac{d\hat{E}_{\text{sys}}}{dt}}$$

$$\begin{aligned}\sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_i H_i = {} & F_{\text{A0}}[(H_{\text{A0}} - H_{\text{A}}) + (H_{\text{B0}} - H_{\text{B}})\Theta_{\text{B}} \\ & + (H_{\text{C0}} - H_{\text{C}})\Theta_{\text{C}} + (H_{\text{D0}} - H_{\text{D}})\Theta_{\text{D}} + (H_{\text{I0}} - H_{\text{I}})\Theta_{\text{I}}] \\ & \underbrace{-\left(\frac{d}{a} H_{\text{D}} + \frac{c}{a} H_{\text{C}} - \frac{b}{a} H_{\text{B}} - H_{\text{A}}\right)}_{\Delta H_{\text{Rx}}} F_{\text{A0}} X\end{aligned}$$

Heat of reaction at temperature T

$$\boxed{\Delta H_{\text{Rx}}(T) = \frac{d}{a} H_{\text{D}}(T) + \frac{c}{a} H_{\text{C}}(T) - \frac{b}{a} H_{\text{B}}(T) - H_{\text{A}}(T)}$$

Combining some of the terms in the energy equations above and assume steady-state condition, we get

$$\boxed{\dot{Q} - \dot{W}_s + F_{\text{A0}} \sum_{i=1}^{n} \Theta_i (H_{i0} - H_i) - \Delta H_{\text{Rx}}(T) F_{\text{A0}} X = 0}$$

The molal enthalpy of species i at a particular temperature and pressure, H_i, is usually expressed in terms of an *enthalpy of formation* of species i at some reference temperature T_R, $H_i^\circ(T_R)$, plus the change in enthalpy, ΔH_{Qi}, that results when the temperature is raised from the reference temperature, T_R, to some temperature T

$$H_i = H_i^\circ(T_R) + \Delta H_{Qi}$$

When No phase change exists $$\Delta H_{Qi} = \int_{T_1}^{T_2} C_{P_i}\, dT$$

Combine the above terms to have $$H_i(T) = H_i^\circ(T_R) + \int_{T_R}^{T} C_{P_i}\, dT$$

$$H_i - H_{i0} = \left[H_i^\circ(T_R) + \int_{T_R}^{T} C_{P_i}\, dT\right] - \left[H_i^\circ(T_R) + \int_{T_R}^{T_{i0}} C_{P_i}\, dT\right]$$

$$= \int_{T_{i0}}^{T} C_{P_i}\, dT = C_{P_i}\,[T - T_{i0}]$$

Constant C_p

Substituting for H_i and H_{i0} yields

$$\dot{Q}-\dot{W}_s-F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}\,[T-T_{i0}]-\Delta H_{Rx}(T)\,F_{A0}X=0$$

Also

$$\Delta H_{Rx}(T)=\frac{d}{a}H_D(T)+\frac{c}{a}H_C(T)-\frac{b}{a}H_B(T)-H_A(T)$$

Where the enthalpy of each species is given by

$$H_i(T)=H_i^{\circ}(T_R)+\int_{T_R}^{T}C_{P_c}\,dT=H_i^{\circ}(T_R)+C_{P_i}(T-T_R)$$

For the generic reaction

$$A+\frac{b}{a}B\rightarrow\frac{c}{a}C+\frac{d}{a}D$$

$$\boxed{\begin{aligned}\Delta H_{Rx}(T)=&\left[\frac{d}{a}H_D^{\circ}(T_R)+\frac{c}{a}H_C^{\circ}(T_R)-\frac{b}{a}H_B^{\circ}(T_R)-H_A^{\circ}(T_R)\right]\\&+\left[\frac{d}{a}C_{P_D}+\frac{c}{a}C_{P_C}-\frac{b}{a}C_{P_B}-C_{P_A}\right](T-T_R)\end{aligned}}$$

The heat of reaction at the reference temperature T_R

$$\Delta H^\circ_{Rx}(T_R) = \frac{d}{a}H^\circ_D(T_R) + \frac{c}{a}H^\circ_C(T_R) - \frac{b}{a}H^\circ_B(T_R) - H^\circ_A(T_R)$$

Also

$$\Delta C_P = \frac{d}{a}C_{P_D} + \frac{c}{a}C_{P_C} - \frac{b}{a}C_{P_B} - C_{P_A}$$

$$\Delta H_{Rx}(T) = \left[\frac{d}{a}H^\circ_D(T_R) + \frac{c}{a}H^\circ_C(T_R) - \frac{b}{a}H^\circ_B(T_R) - H^\circ_A(T_R)\right] + \left[\frac{d}{a}C_{P_D} + \frac{c}{a}C_{P_C} - \frac{b}{a}C_{P_B} - C_{P_A}\right](T - T_R)$$

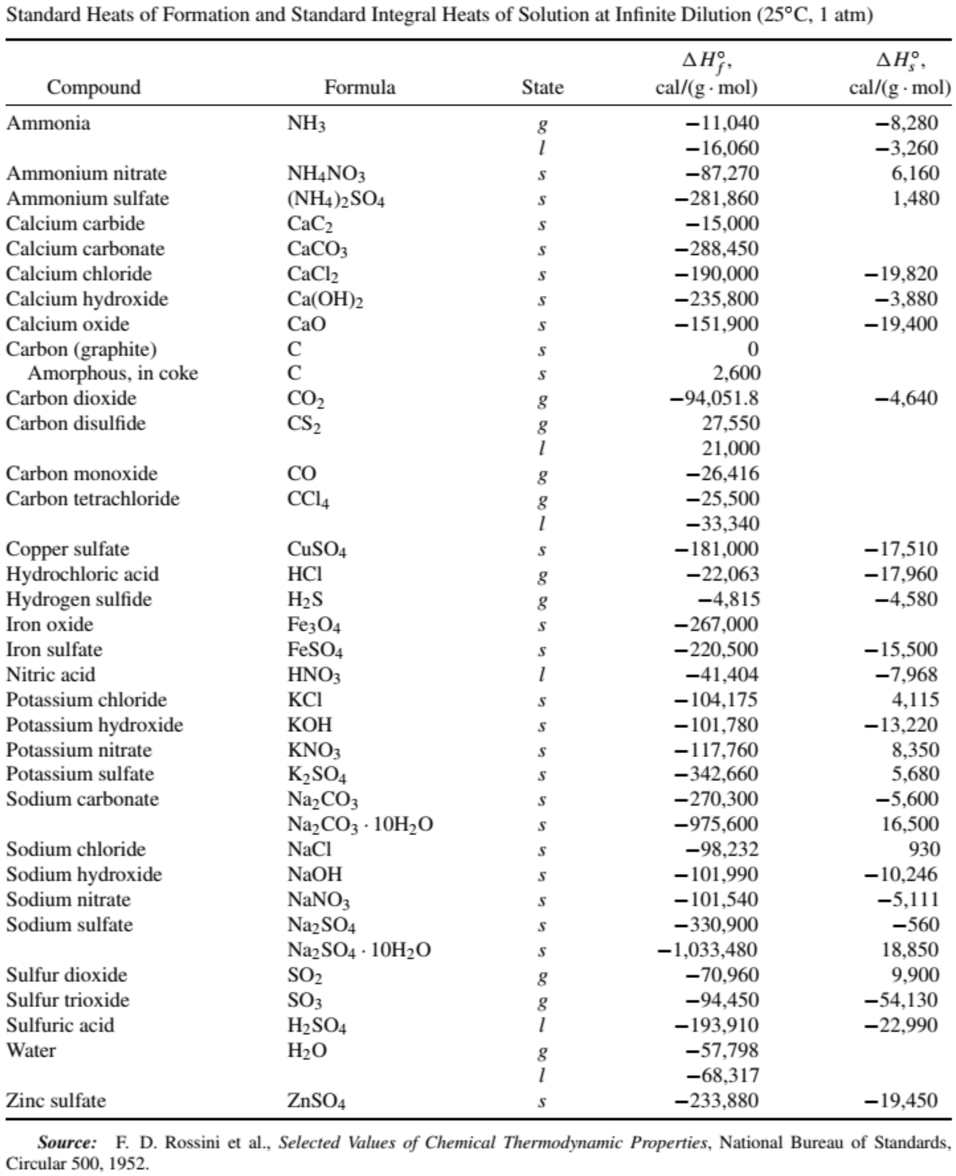
⇨

$$\Delta H_{Rx}(T) = \Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)$$

The Energy balance above in terms of mean or constant heat capacities

$$\boxed{\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0}$$

Standard **heats of formation** and standard **integral heats of solution** at infinite dilution (25◦C, 1 atm)



Standard Heats of Formation and Standard Integral Heats of Solution at Infinite Dilution (25°C, 1 atm)

Compound	Formula	State	ΔH_f°, cal/(g · mol)	ΔH_s°, cal/(g · mol)
Ammonia	NH_3	*g*	−11,040	−8,280
		l	−16,060	−3,260
Ammonium nitrate	NH_4NO_3	*s*	−87,270	6,160
Ammonium sulfate	$(NH_4)_2SO_4$	*s*	−281,860	1,480
Calcium carbide	CaC_2	*s*	−15,000	
Calcium carbonate	$CaCO_3$	*s*	−288,450	
Calcium chloride	$CaCl_2$	*s*	−190,000	−19,820
Calcium hydroxide	$Ca(OH)_2$	*s*	−235,800	−3,880
Calcium oxide	CaO	*s*	−151,900	−19,400
Carbon (graphite)	C	*s*	0	
Amorphous, in coke	C	*s*	2,600	
Carbon dioxide	CO_2	*g*	−94,051.8	−4,640
Carbon disulfide	CS_2	*g*	27,550	
		l	21,000	
Carbon monoxide	CO	*g*	−26,416	
Carbon tetrachloride	CCl_4	*g*	−25,500	
		l	−33,340	
Copper sulfate	$CuSO_4$	*s*	−181,000	−17,510
Hydrochloric acid	HCl	*g*	−22,063	−17,960
Hydrogen sulfide	H_2S	*g*	−4,815	−4,580
Iron oxide	Fe_3O_4	*s*	−267,000	
Iron sulfate	$FeSO_4$	*s*	−220,500	−15,500
Nitric acid	HNO_3	*l*	−41,404	−7,968
Potassium chloride	KCl	*s*	−104,175	4,115
Potassium hydroxide	KOH	*s*	−101,780	−13,220
Potassium nitrate	KNO_3	*s*	−117,760	8,350
Potassium sulfate	K_2SO_4	*s*	−342,660	5,680
Sodium carbonate	Na_2CO_3	*s*	−270,300	−5,600
	$Na_2CO_3 \cdot 10H_2O$	*s*	−975,600	16,500
Sodium chloride	NaCl	*s*	−98,232	930
Sodium hydroxide	NaOH	*s*	−101,990	−10,246
Sodium nitrate	$NaNO_3$	*s*	−101,540	−5,111
Sodium sulfate	Na_2SO_4	*s*	−330,900	−560
	$Na_2SO_4 \cdot 10H_2O$	*s*	−1,033,480	18,850
Sulfur dioxide	SO_2	*g*	−70,960	9,900
Sulfur trioxide	SO_3	*g*	−94,450	−54,130
Sulfuric acid	H_2SO_4	*l*	−193,910	−22,990
Water	H_2O	*g*	−57,798	
		l	−68,317	
Zinc sulfate	$ZnSO_4$	*s*	−233,880	−19,450

Source: F. D. Rossini et al., *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards, Circular 500, 1952.

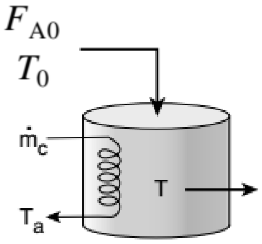
Neglecting $\dot{W}_s$, the energy balance becomes

$$\boxed{\dot{Q} - F_{A0}\Sigma\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0}$$

Special Case 1: Adiabatic Operation

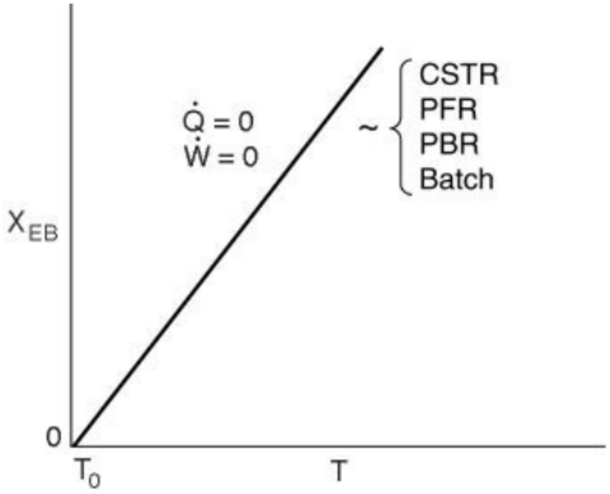
$$\dot{Q} = 0$$

$$T_{i0} = T_0$$



$$\boxed{X = \frac{\Sigma\ \Theta_i C_{P_i}(T - T_0)}{-[\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]}}$$

Relationship between X and T for *adiabatic* exothermic reactions



Special Case 2: Variation of Temperature with conversion for Adiabatic Tubular Reactor

Rearranging the energy equation and write it in term $T = f(X)$

$$\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0$$

$$T = \frac{X[-\Delta H^\circ_{Rx}(T_R)] + \Sigma\Theta_i C_{P_i} T_0 + X\Delta C_P T_R}{\Sigma\Theta_i C_{P_i} + X\Delta C_P}$$

Special Case 3: CSTR with heat exchange

Assumption

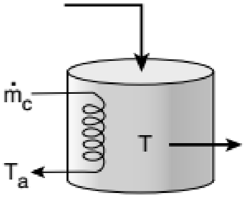
$\dot{W}_s = 0$

constant C_{P_i}

$\Delta C_P = 0$

large coolant flow rate

heat exchanger, UA $(T_a - T)$.



$$X_{EB} = \frac{\left(\frac{UA}{F_{A0}}(T - T_a)\right) + \Sigma\Theta_i C_{P_i}(T - T_0)}{-\Delta H^\circ_{Rx}}$$

Special Case 4: Batch and semi-batch / unsteady CSTR with heat exchange

Batch

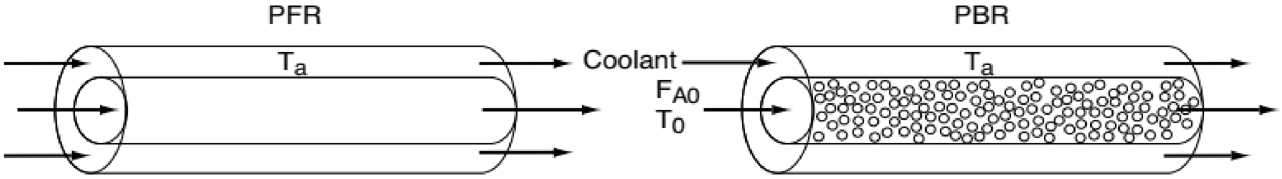
$$\boxed{\frac{dT}{dt} = \frac{(r_A V)(\Delta H_{Rx}) - UA(T - T_a)}{\sum N_i C_{P_i}}}$$

Semibatch or unsteady CSTR

$$\boxed{\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum_{i=1}^{n} F_{i0} C_{P_i}(T - T_{i0}) + [-\Delta H_{Rx}(T)](-r_A V)}{\sum_{i=1}^{n} N_i C_{P_i}}}$$

Special Case 5: Plug flow (PFR) / Packed bed reactors (PBR) with heat exchange

Here we have differential change in temperature across the length of the reactor



$$\frac{dT}{dV} = \frac{(\text{Heat “generated”}) - (\text{Heat “removed”})}{\sum F_i C_{P_i}} = \frac{Q_g - Q_r}{\sum F_i C_{P_i}}$$

PFR in terms of conversion

$$\boxed{\frac{dT}{dV} = \frac{\overbrace{r_A \Delta H_{Rx}(T)}^{Q_g} - \overbrace{Ua(T - T_a)}^{Q_r}}{F_{A0}\left(\sum \Theta_i C_{P_i} + \Delta C_P X\right)} = \frac{Q_g - Q_r}{F_{A0}\left(\sum \Theta_i C_{P_i} + \Delta C_P X\right)}}$$

PBR in terms of conversion

$$\boxed{\frac{dT}{dW} = \frac{r'_A \Delta H_{Rx}(T) - \dfrac{Ua}{\rho_b}(T - T_a)}{F_{A0}\left(\sum \Theta_i C_{P_i} + \Delta C_P X\right)}}$$

PBR in terms of molar flow rates

$$\boxed{\frac{dT}{dW} = \frac{r'_A \Delta H_{Rx}(T) - \frac{Ua}{\rho_b}(T - T_a)}{\sum F_i C_{P_i}}}$$

PFR in terms of molar flow rates

$$\boxed{\frac{dT}{dV} = \frac{r_A \Delta H_{Rx}(T) - Ua(T - T_a)}{\sum F_i C_{P_i}} = \frac{Q_g - Q_r}{\sum F_i C_{P_i}}}$$

For multiple reactions in a PFR

(*q* reactions and *m* species)

$$\boxed{\frac{dT}{dV} = \frac{\sum_{i=1}^{q} r_{ij} \Delta H_{Rxij} - Ua(T - T_a)}{\sum_{j=1}^{m} F_j C_{P_j}}}$$

i = reaction number, j = species

Example 12.2: Heat of reaction

Calculate the heat of reaction for the synthesis of ammonia from hydrogen and nitrogen at 150 °C in kcal/mol of N_2 reacted and also in kJ/mol of H_2 reacted.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Solution

The enthalpies of formation at 25°C are

$$H^\circ_{NH_3}(T_R) = -11{,}020 \frac{\text{cal}}{\text{mol NH}_3}, \quad H^\circ_{H_2} = 0, \text{ and } \quad H^\circ_{N_2} = 0$$

$$\Delta H^\circ_{Rx}(T_R) = 2H^\circ_{NH_3}(T_R) - 3H^\circ_{H_2}(T_R) - H^\circ_{N_2}(T_R)$$

$$\Delta H^\circ_{Rx}(T_R) = 2H^\circ_{NH_3}(T_R) - 3(0) - 0 = 2H^\circ_{NH_3} \quad = 2(-11{,}020)\,\frac{\text{cal}}{\text{mol N}_2}$$

$$\Delta H^\circ_{\mathrm{Rx}}(298\ \mathrm{K}) = -22.04\ \ \mathrm{kcal/mol}\ \ N_2\ \mathrm{reacted} = -92.22\ \ \mathrm{kJ/mol}\ \ N_2\ \mathrm{reacted}$$

$$C_{\mathrm{P_{H_2}}} = 6.992\ \mathrm{cal/mol\ H_2 \cdot K}$$

$$C_{\mathrm{P_{N_2}}} = 6.984\ \mathrm{cal/mol\ N_2 \cdot K}$$

$$C_{\mathrm{P_{NH_3}}} = 8.92\ \mathrm{cal/mol\ NH_3 \cdot K}$$

⇒

$$\begin{aligned}\Delta C_{\mathrm{P}} &= 2C_{\mathrm{P_{NH_3}}} - 3C_{\mathrm{P_{H_2}}} - C_{\mathrm{P_{N_2}}} \\ &= 2(8.92) - 3(6.992) - 6.984 \\ &= -10.12\ \mathrm{cal/mol\ N_2\ reacted \cdot K}\end{aligned}$$

$$\begin{aligned}\Delta H_{\mathrm{Rx}}(T) &= \Delta H^\circ_{\mathrm{Rx}}(T_{\mathrm{R}}) + \Delta C_{\mathrm{P}}(T - T_{\mathrm{R}}) \\ \Delta H_{\mathrm{Rx}}(423\ \mathrm{K}) &= -22{,}040 + (-10.12)(423 - 298) \\ &= -23{,}310\ \mathrm{cal/mol\ N_2} = -23.31\ \mathrm{kcal/mol\ N_2}\end{aligned}$$

$$\Delta H^\circ_{\mathrm{Rx}}(423\ \mathrm{K}) = -23.3\ \mathrm{kcal/mol\ N_2} \times 4.184\ \mathrm{kJ/kcal}$$

$$\boxed{\Delta H_{\mathrm{Rx}}(423\ \mathrm{K}) = -97.5\ \mathrm{kJ/mol\ N_2}}$$

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

The heat of reaction based on the moles of H_2 reacted is

$$\Delta H_{\mathrm{Rx}}(423\ \mathrm{K}) = \frac{1\ \mathrm{mol}\ N_2}{3\ \mathrm{mol}\ H_2}\left(-97.53\ \frac{\mathrm{kJ}}{\mathrm{mol}\ N_2}\right)$$

$$\Delta H_{\mathrm{Rx}}(423\ \mathrm{K}) = -32.51\ \frac{\mathrm{kJ}}{\mathrm{mol}\ H_2}\ \text{at 423 K}$$

Example 12.3: Adiabatic Liquid-Phase reaction in PFR and CSTR

The isomerization of n-butane is an elementary reversible reaction that is carried out *adiabatically* in the liquid phase under high pressure using essentially trace amounts of a liquid catalyst. It gives a specific reaction rate of 31.1 h^{-1} at 360 K. The feed enters the reactor at 330 K.

$$n\text{-}C_4H_{10} \rightleftarrows i\text{-}C_4H_{10}$$

a. Calculate the PFR volume necessary to process 163 kmol/h at 95% of equilibrium conversion.
b. Plot and analyze X, Xe, T, and $-r_A$ down the length of the reactor.
c. Calculate the CSTR volume for 40% conversion.

Additional information:

$$\Delta H^\circ_{Rx} = -6900 \text{ J/mol n-butane}, \quad \text{Activation energy} = 65.7 \text{ kJ/mol}$$

$$K_C = 3.03 \text{ at } 60°\text{C}, \quad C_{A0} = 9.3 \text{ mol/dm}^3 = 9.3 \text{ kmol/m}^3$$

<u>Butane</u>

$$C_{P_{n\text{-}B}} = 141 \text{ J/mol} \cdot \text{K}$$

$$C_{P_{i\text{-}B}} = 141 \text{ J/mol} \cdot \text{K} = 141 \text{ kJ/kmol} \cdot K$$

<u>*i*-Pentane</u>

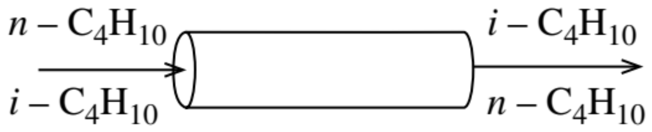
$$C_{P_{i\text{-}P}} = 161 \text{ J/mol} \cdot \text{K}$$

Solution

$$n\text{-}C_4H_{10} \rightleftarrows i\text{-}C_4H_{10}$$

$$\text{A} \rightleftarrows \text{B}$$

PFR algorithm



$$F_{A0}\frac{dX}{dV} = -r_A \qquad -r_A = k\left(C_A - \frac{C_B}{K_C}\right) \qquad k = k(T_1)e^{\left[\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T}\right)\right]}$$

$$K_C = K_C(T_2)\,e^{\left[\frac{\Delta H^\circ_{Rx}}{R}\left(\frac{1}{T_2}-\frac{1}{T}\right)\right]}$$

Stoichiometry (liquid phase, $v = v_0$):

$$C_A = C_{A0}(1-X)$$

$$C_B = C_{A0}X$$

$$-r_{\mathrm{A}} = k\left(C_{\mathrm{A}} - \frac{C_{\mathrm{B}}}{K_{\mathrm{C}}}\right) \quad \Rightarrow \quad -r_{\mathrm{A}} = kC_{\mathrm{A0}}\left[1 - \left(1 + \frac{1}{K_{\mathrm{C}}}\right)X\right]$$

Energy Balance:

$$\dot{Q} - \dot{W}_s - F_{\mathrm{A0}}\sum\Theta_i C_{\mathrm{P}_i}(T - T_0) - F_{\mathrm{A0}}X[\Delta H^\circ_{\mathrm{Rx}}(T_{\mathrm{R}}) + \Delta C_{\mathrm{P}}(T - T_{\mathrm{R}})] = 0$$

Adiabatic: $\dot{Q} = 0$

No work: $\dot{W} = 0$

$\Delta C_{\mathrm{P}} = C_{\mathrm{P_B}} - C_{\mathrm{P_A}} = 141 - 141 = 0$

$$\Rightarrow \quad T = T_0 + \frac{(-\Delta H^\circ_{\mathrm{Rx}})X}{\sum\Theta_i C_{\mathrm{P}_i}}$$

$$F_{A0} = 0.9F_{T0} = (0.9)\left(163\,\frac{\text{kmol}}{\text{h}}\right) = 146.7\,\frac{\text{kmol}}{\text{h}}$$

$$\Sigma\Theta_i C_{P_i} = C_{P_A} + \Theta_I C_{P_I} = \left(141 + \left(\frac{0.1}{0.9}\right)161\right)\ \text{J/mol}\cdot\text{K} \quad = 159\ \text{J/mol}\cdot\text{K}$$

$$T = T_0 + \frac{(-\Delta H^{\circ}_{Rx})X}{\Sigma\,\Theta_i C_{P_i}} \quad ⇨ \quad T = 330 + \frac{-(-6900)}{159}X$$

$$\boxed{T = 330 + 43.4X}$$

$$k = k(T_1)e^{\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]} \quad ⇨ \quad k = 31.1\ \exp\left[\frac{65{,}700}{8.31}\left(\frac{1}{360} - \frac{1}{T}\right)\right](h^{-1})$$

$$\boxed{k = 31.1\ \exp\left[7906\left(\frac{T - 360}{360T}\right)\right](h^{-1})}$$

$$K_C = 3.03\ \exp\left[\frac{-6900}{8.31}\left(\frac{1}{333}-\frac{1}{T}\right)\right]$$

⇨

$$\boxed{K_C = 3.03\ \exp\left[-830.3\left(\frac{T-333}{333T}\right)\right]}$$

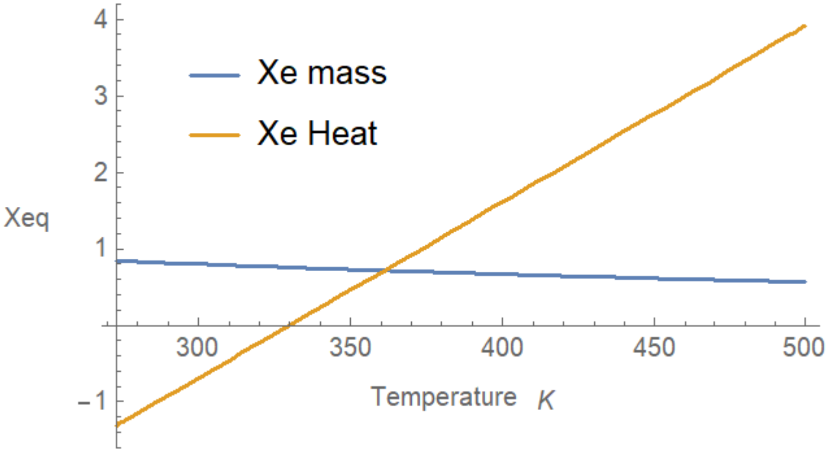
At equilibrium $-r_A \equiv 0$

$$-r_A = kC_{A0}\left[1-\left(1+\frac{1}{K_C}\right)X\right]$$

⇨

$$X_e = \frac{K_C}{1+K_C}$$

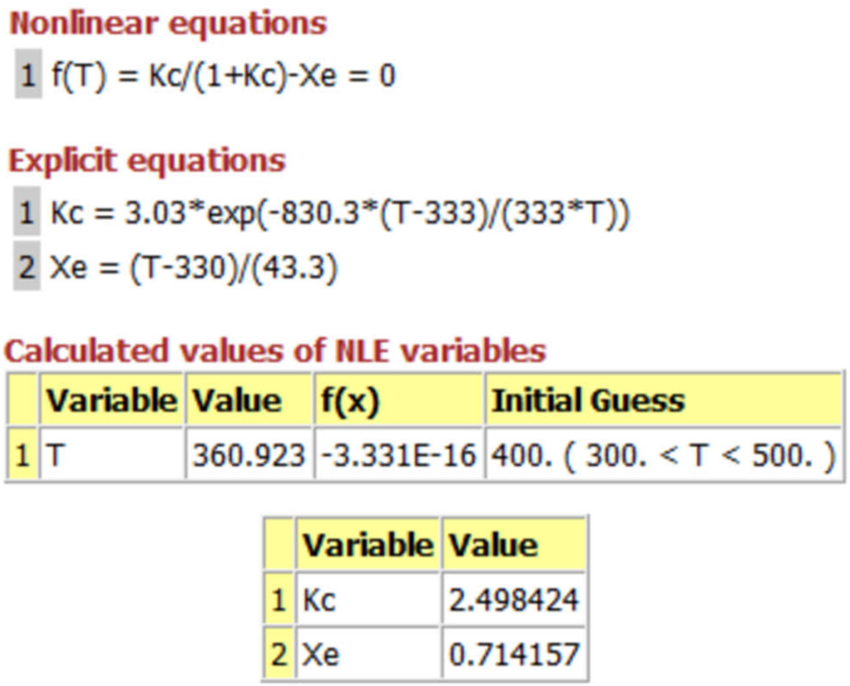
$$X_e = \frac{K_c}{1+K_c} = \frac{3.03\ e^{\left[-830.3\left(\frac{T-333}{333T}\right)\right]}}{1+3.03\ e^{\left[-830.3\left(\frac{T-333}{333T}\right)\right]}}$$



Substitute for T from energy equation into mass equation and solve for T, or perform a plot of X_e vs T yields the optimum value of T necessary to achieve equilibrium conversion:

$$\boxed{T = 330 + 43.4X}$$

$$X_e = \frac{K_c}{1 + K_c} = \frac{3.03\ e^{\left[-830.3\left(\frac{T-333}{333T}\right)\right]}}{1 + 3.03\ e^{\left[-830.3\left(\frac{T-333}{333T}\right)\right]}}$$



Nonlinear equations

1 f(T) = Kc/(1+Kc)-Xe = 0

Explicit equations

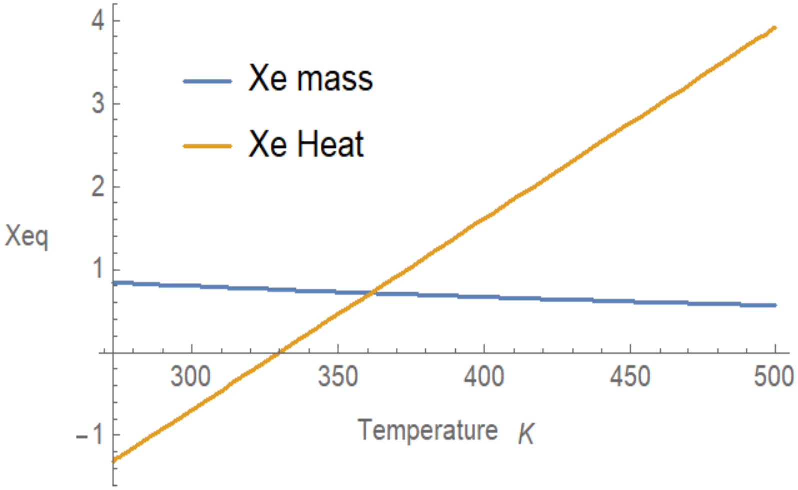
1 Kc = 3.03*exp(-830.3*(T-333)/(333*T))

2 Xe = (T-330)/(43.3)

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	T	360.923	-3.331E-16	400. (300. < T < 500.)

	Variable	Value
1	Kc	2.498424
2	Xe	0.714157



a. Volume of PFR at 95% of equilibrium conversion

$$X = 0.95\,X_e = 0.95(0.714) = 0.68$$

$$\boxed{T = 330 + 43.4X}$$

⇨

$$\boxed{k = 31.1\ \exp\left[7906\left(\frac{T-360}{360T}\right)\right](h^{-1})}$$

⇨

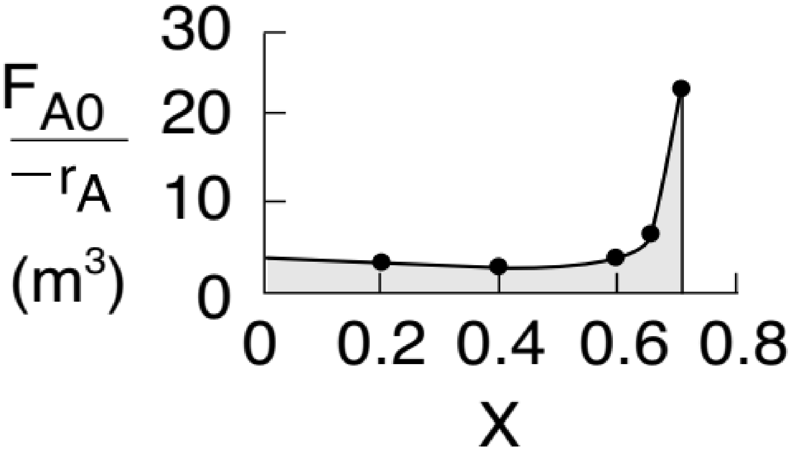
$$\boxed{K_C = 3.03\ \exp\left[-830.3\left(\frac{T-333}{333T}\right)\right]}$$

⇨

$$\boxed{-r_A = kC_{A0}\left[1-\left(1+\frac{1}{K_C}\right)X\right]}$$

X	T (K)	k (h^{-1})	K_C	X_e	$-r_A$(kmol/m$^3\cdot$h)	$\frac{F_{A0}}{-r_A}$ (m^3)
0	330	4.22	3.1	0.76	39.2	3.74
0.2	338.7	7.76	2.9	0.74	52.8	2.78
0.4	347.3	14.02	2.73	0.73	58.6	2.50
0.6	356.0	24.27	2.57	0.72	37.7	3.88
0.65	358.1	27.74	2.54	0.718	24.5	5.99
0.7	360.3	31.67	2.5	0.715	6.2	23.29

The reactor volume for 70% conversion will be evaluated using the quadrature formulas. Because (F_{A0}/r_A) increases rapidly as we approach the adiabatic equilibrium conversion, 0.71, we will break the integral into two parts

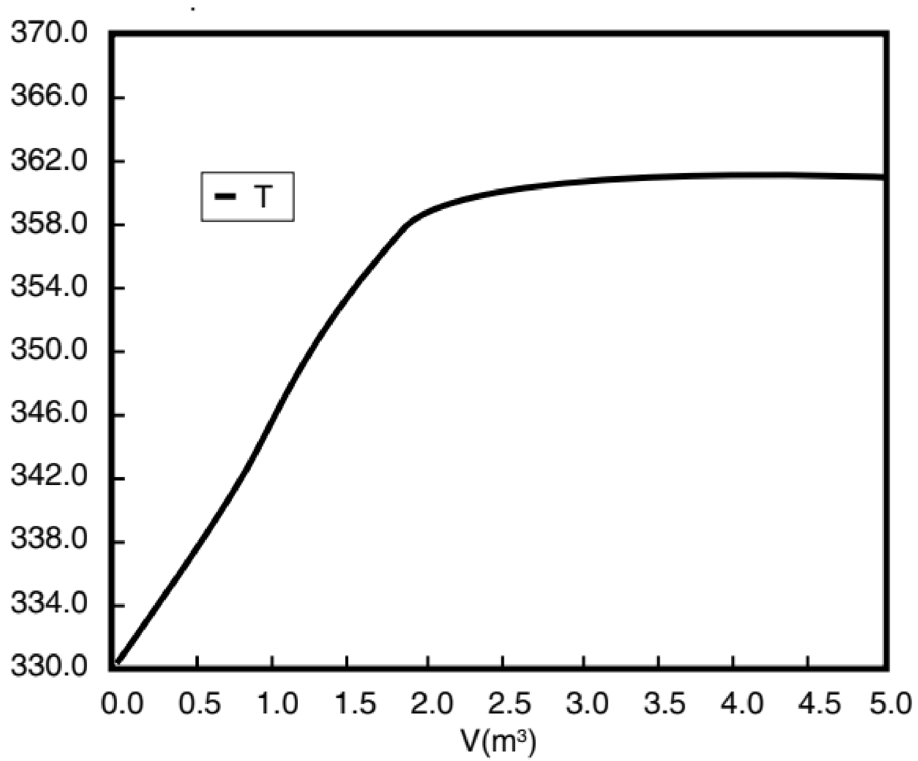


$$V = \int_0^{0.7} \frac{F_{A0}}{-r_A}\,dX = \int_0^{0.6} \frac{F_{A0}}{-r_A}\,dX + \int_{0.6}^{0.7} \frac{F_{A0}}{-r_A}\,dX$$

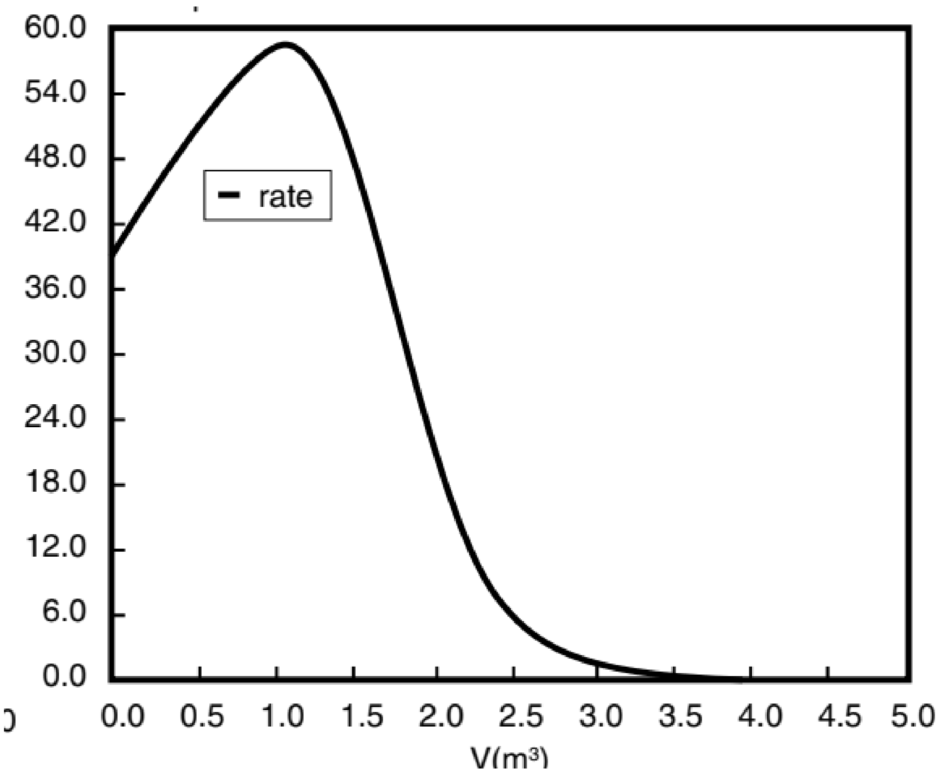
$$V = \frac{3}{8} \times \frac{0.6}{3}[3.74 + 3 \times 2.78 + 3 \times 2.50 + 3.88]\mathrm{m}^3 + \frac{1}{3} \times \frac{0.1}{2}[3.88 + 4 \times 5.99 + 23.29]\mathrm{m}^3$$

$$\boxed{V = 2.60\ m^3}$$

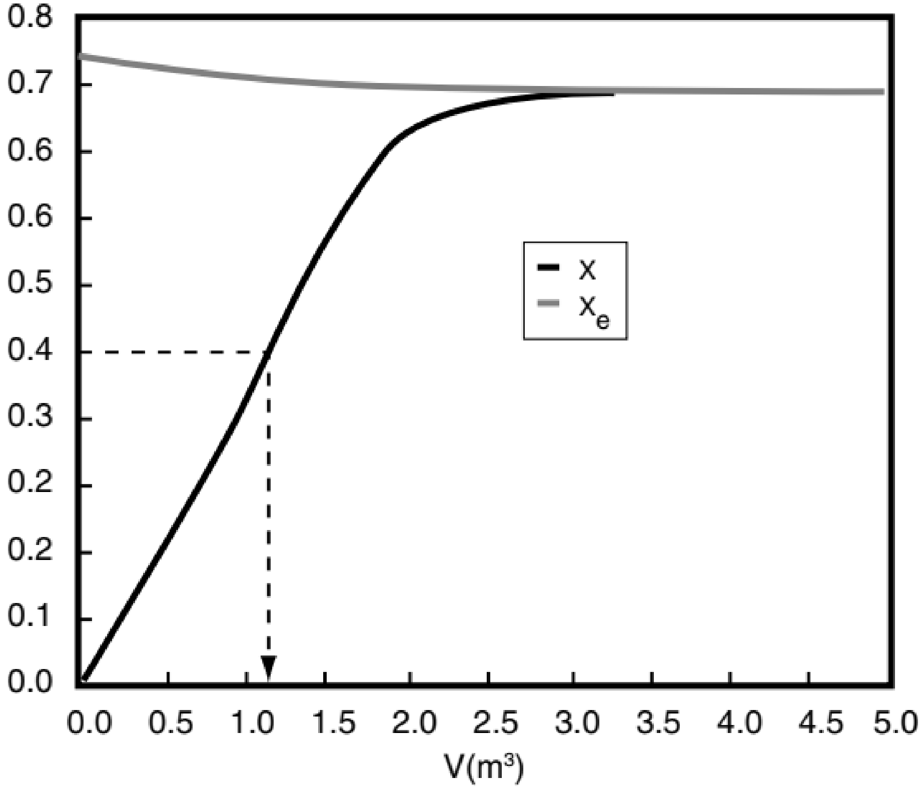
Temperature vs. volume



Rate vs. volume



Conversion and equilibrium conversion vs. reactor volume



Part (c) CSTR Solution

$$V = \frac{F_{A0}X}{-r_A}$$

$$V = \frac{F_{A0}X}{kC_{A0}\left[1-\left(1+\frac{1}{K_C}\right)X\right]}$$

⇨

$$k = 14.02 \text{ h}^{-1}$$

$$K_C = 2.73$$

$$-r_A = 58.6 \text{ kmol/m}^3\cdot\text{h}$$

$$V = \frac{(146.7 \text{ kmol butane/h})(0.4)}{58.6 \text{ kmol/m}^3\cdot\text{h}}$$

$$V = 1.0 \text{ m}^3$$

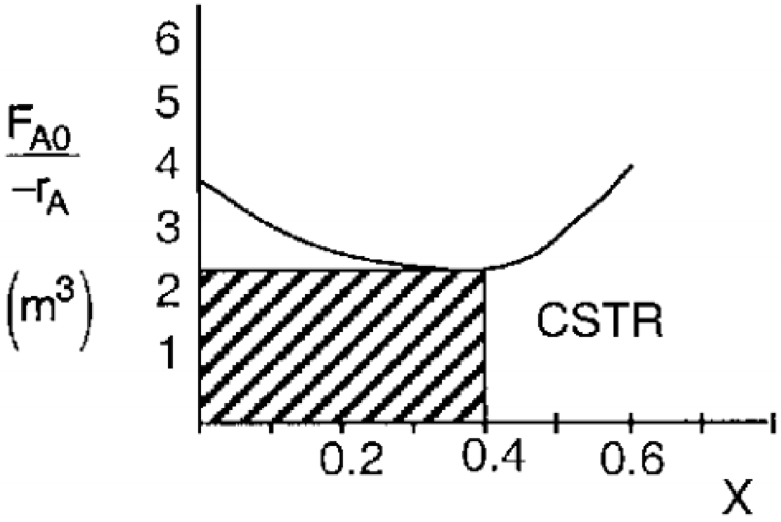
$$\boxed{T = 330 + 43.4X}$$

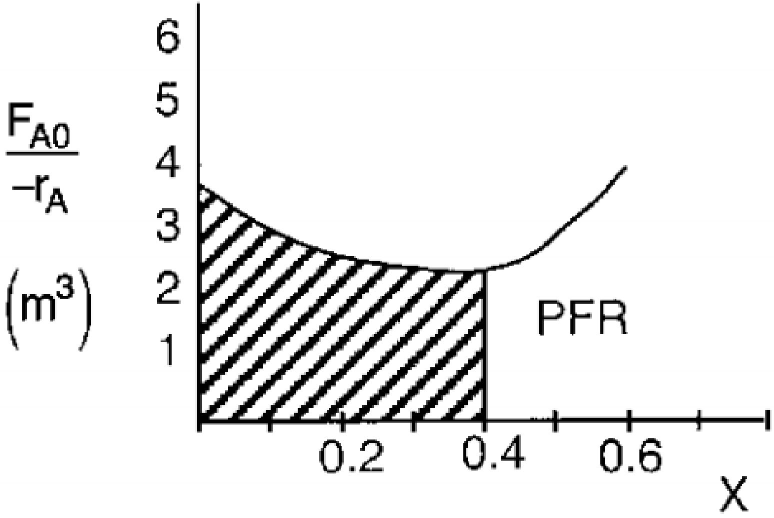
For 40% conversion

$$T = 330 + 43.4X$$

$$T = 330 + 43.4(0.4) = 347.3\text{K}$$

Comparison between size of CSTR and PFR for the given rate of isomerization of n-butane





We see that the CSTR volume (1 m^3) to achieve 40% conversion in this adiabatic reaction is less than the PFR volume (1.15 m^3).

Adiabatic operation & interstage cooling for non-isothermal reactors

In this topic we will study the following:

- Adiabatic operations
- Interstage cooling

Adiabatic Equilibrium Conversion

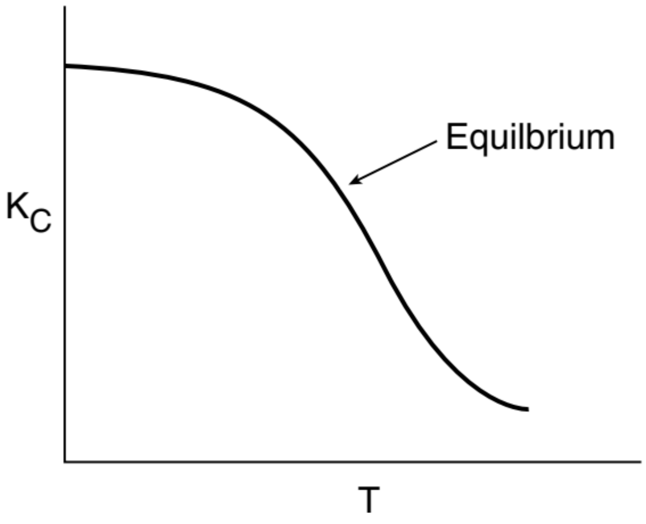
Given the following first order reversible and exothermic reaction:

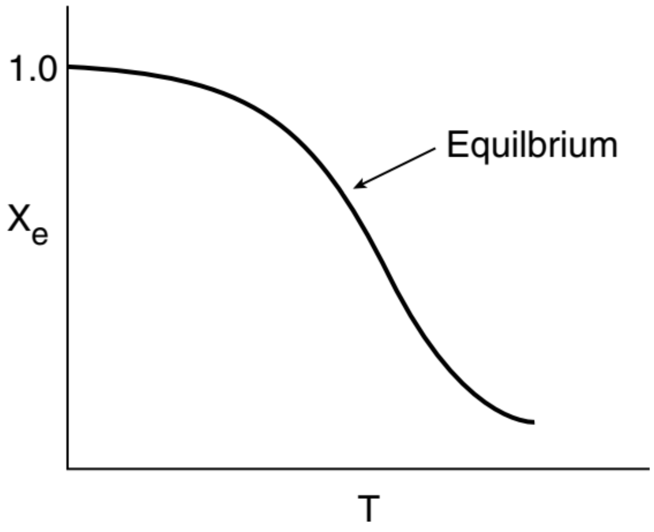
$$A \rightleftarrows B$$

The equilibrium conversion:

$$X_e = \frac{K_C}{1 + K_C}$$

Therefore, for exothermic reactions, the equilibrium constant and conversion decrease with increasing temperature.





What is the maximum equilibrium conversion that can be achieved in an exothermic reaction carried out adiabatically?

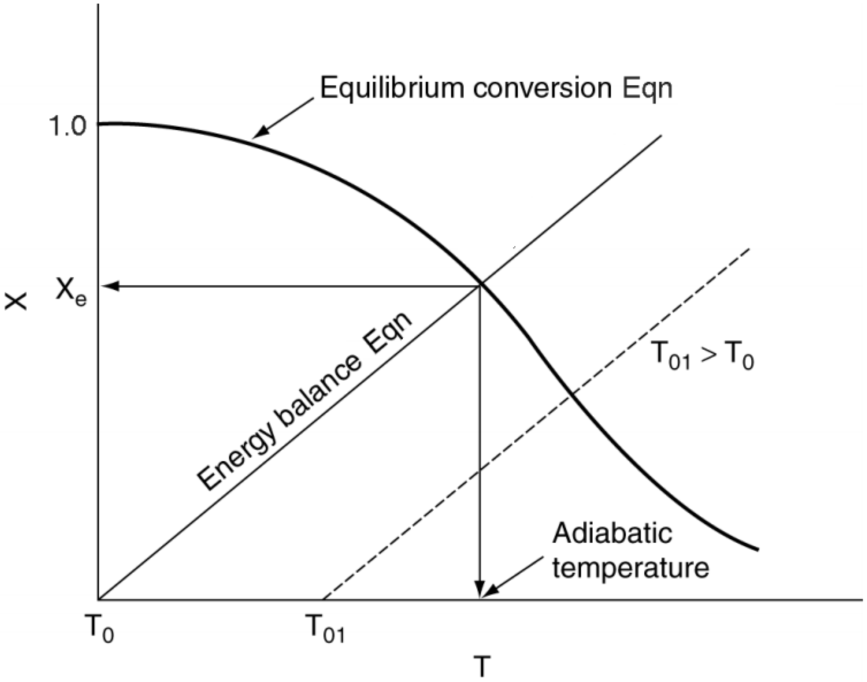
Energy Balance

$$\boxed{\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0}$$

$$\boxed{X = \frac{\Sigma\ \Theta_i C_{P_i}(T - T_0)}{-[\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]}}$$

Mass Balance

$$\boxed{X_e = \frac{K_c}{1 + K_c} = \frac{K_c(T_1)\ e^{\left[\frac{\Delta H^o_{Rx}}{R}\left(\frac{1}{T_R} - \frac{1}{T}\right)\right]}}{1 + K_c(T_1)\ e^{\left[\frac{\Delta H^o_{Rx}}{R}\left(\frac{1}{T_R} - \frac{1}{T}\right)\right]}}}$$



Example 13.1: Adiabatic Equilibrium Temperature

For the elementary liquid-phase reaction takes place in an adiabatic CSTR, determine the adiabatic equilibrium temperature and conversion when pure A is fed to the reactor at a temperature of 300 K. What is the CSTR volume necessary to achieve 90% of the adiabatic equilibrium conversion for $v_o = 5\ L/min$?

$$\mathrm{A} \rightleftarrows \mathrm{B}$$

Solution

$$H_{\mathrm{A}}^{\circ}(298\ \mathrm{K}) = -40{,}000\ \mathrm{cal/mol} \qquad H_{\mathrm{B}}^{\circ}(298\ \mathrm{K}) = -60{,}000\ \mathrm{cal/mol}$$

$$C_{P_{\mathrm{A}}} = 50\ \mathrm{cal/mol \cdot K} \qquad C_{P_{\mathrm{B}}} = 50\ \mathrm{cal/mol \cdot K}$$

$$K_e = 100{,}000 \text{ at } 298\ \mathrm{K},\ k = 10^{-3} \exp\left(\frac{E}{R}\left(\frac{1}{298} - \frac{1}{T}\right)\mathrm{min}^{-1}\right) \text{with } E = 10{,}000\ \frac{\mathrm{cal}}{\mathrm{mol}}$$

$$K_e = \frac{C_{\mathrm{B}e}}{C_{\mathrm{A}e}}$$

$$C_{\mathrm{A}} = C_{\mathrm{A0}}(1-X)$$

$$C_b = C_{\mathrm{A0}}X$$

⇨

$$K_e = \frac{C_{\mathrm{A0}}X_e}{C_{\mathrm{A0}}(1-X_e)} = \frac{X_e}{(1-X_e)}$$

⇨

$$\boxed{X_e = \frac{K_e(T)}{1+K_e(T)}}$$

$$K_e(T) = K_e(T_1)\ \exp\left[\frac{\Delta H^\circ_{\mathrm{Rx}}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

⇨

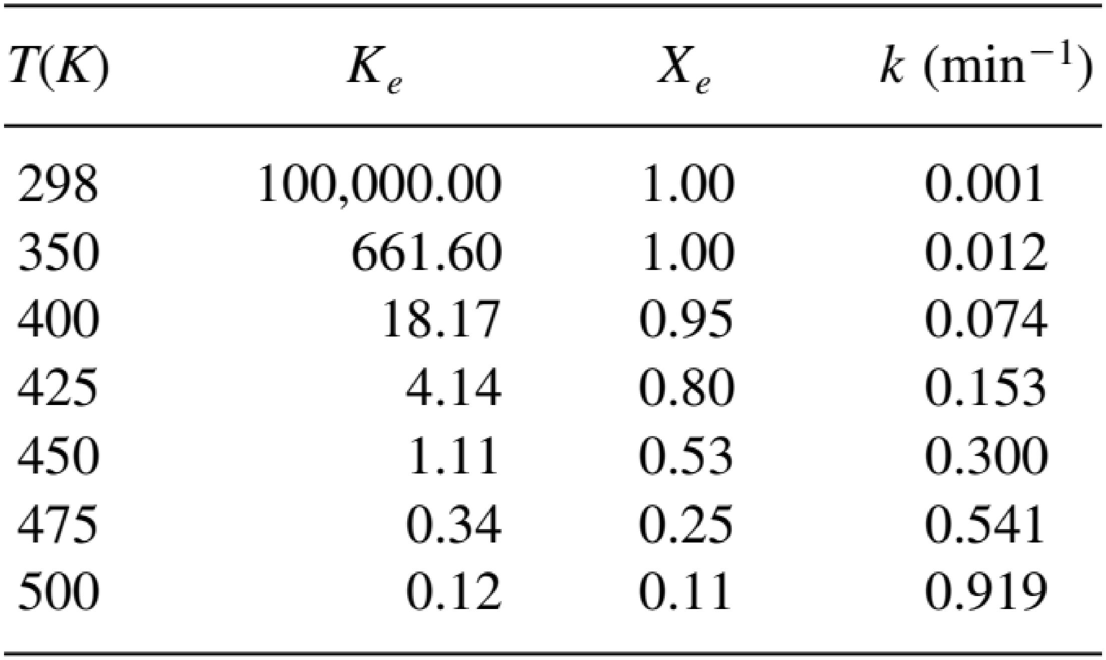
$$\Delta H^\circ_{\mathrm{Rx}} = H^\circ_{\mathrm{B}} - H^\circ_{\mathrm{A}} = -20{,}000\ \mathrm{cal/mol}$$

$$K_e(T) = 100{,}000\ \exp\left[\frac{-20{,}000}{1.987}\left(\frac{1}{298} - \frac{1}{T}\right)\right]$$

$$K_e = 100{,}000\ \exp\left[-33.78\left(\frac{T-298}{T}\right)\right]$$

$$\boxed{X_e = \frac{100{,}000\ \exp[-33.78(T-298)/T]}{1+100{,}000\ \exp[-33.78(T-298)/T]}}$$

TABLE: EQUILIBRIUM CONVERSION AS A FUNCTION OF TEMPERATURE



$T(K)$	K_e	X_e	k (min^{-1})
298	100,000.00	1.00	0.001
350	661.60	1.00	0.012
400	18.17	0.95	0.074
425	4.14	0.80	0.153
450	1.11	0.53	0.300
475	0.34	0.25	0.541
500	0.12	0.11	0.919

$$\boxed{X_e = \frac{100{,}000\ \exp[-33.78(T-298)/T]}{1+100{,}000\ \exp[-33.78(T-298)/T]}}$$

Energy Balance:

$$\boxed{X = \frac{\Sigma\, \Theta_i C_{P_i}(T - T_0)}{-[\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]}}$$

$$\Delta C_P = C_{P_B} - C_{P_A} = 50 - 50 = 0 \text{ cal/mol} \cdot \text{K}$$

$$\Rightarrow \quad X_{EB} = \frac{\Sigma\, \Theta_i C_{P_i}(T - T_0)}{-\Delta H_{Rx}} = \frac{C_{P_A}(T - T_0)}{-\Delta H^\circ_{Rx}}$$

$$\boxed{X_{EB} = \frac{50(T - 300)}{20{,}000} = 2.5 \times 10^{-3}(T - 300)}$$

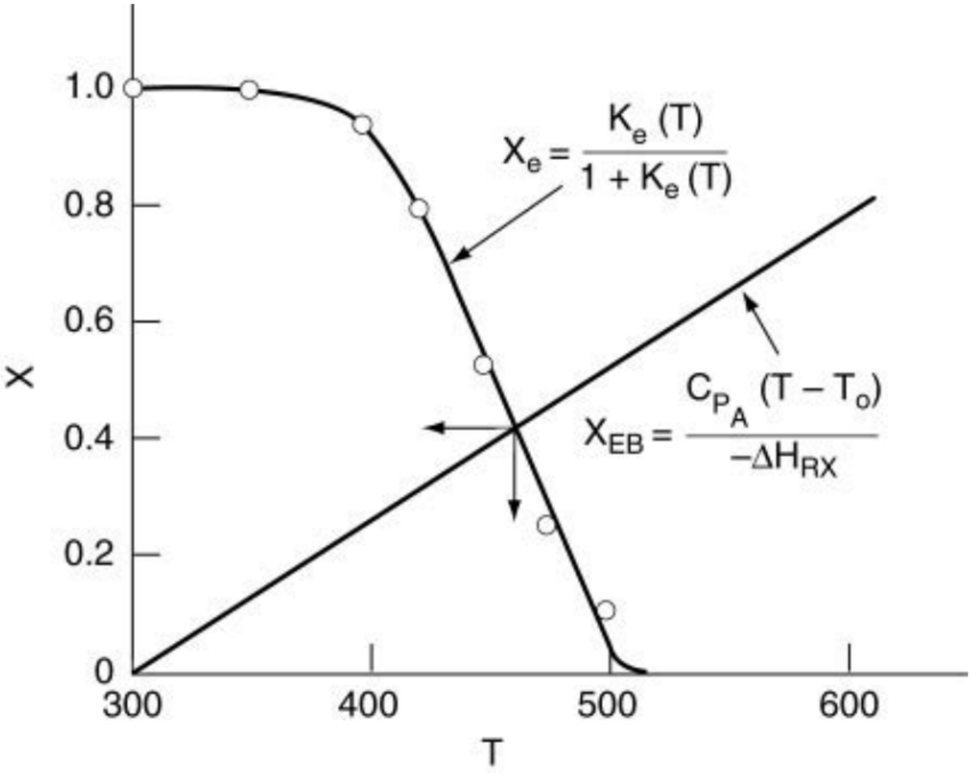
$T(K)$	300	400	500	600
X_{EB}	0	0.25	0.50	0.75

Mass Balance (Design equation):

$T(K)$	K_e	X_e	k (min^{-1})
298	100,000.00	1.00	0.001
350	661.60	1.00	0.012
400	18.17	0.95	0.074
425	4.14	0.80	0.153
450	1.11	0.53	0.300
475	0.34	0.25	0.541
500	0.12	0.11	0.919

Energy Balance:

$T(K)$	300	400	500	600
X_{EB}	0	0.25	0.50	0.75



The intersection of $X_{EB}(T)$ and $X_e(T)$ gives $X_e = 0.42$ and $T_e = 465$ K.

Calculate the CSTR Volume to achieve 90% of the adiabatic equilibrium conversion corresponding to an entering temperature of 300 K.

$$\mathrm{A} \rightleftarrows \mathrm{B}$$

$$V = \frac{F_{\mathrm{A0}}X}{-r_{\mathrm{A}}} = \frac{C_{\mathrm{A0}}v_0X}{kC_{\mathrm{A0}}\left(1-\frac{X}{X_{\mathrm{e}}}\right)} = \frac{v_0X}{k\left(1-\frac{X}{X_{\mathrm{e}}}\right)}$$

$$\boxed{-r_{\mathrm{A}} = kC_{\mathrm{A0}}\left(1-\frac{X}{X_e}\right)}$$

$$k = 10^{-3}\exp\left(\frac{E}{R}\left(\frac{1}{298}-\frac{1}{T}\right)\mathrm{min}^{-1}\right) \quad ⇨ \quad k = \left(0.001\exp\left[\frac{10{,}000}{1.987}\left(\frac{1}{298}-\frac{1}{T}\right)\right]\right) = 0.01\exp 16.89\left(\frac{T-298}{T}\right)$$

$$\text{at } X = 0.9\,X_e = 0.9(0.42) = 0.38$$

From the adiabatic energy balance, the temperature corresponding to $X = 0.38$ is

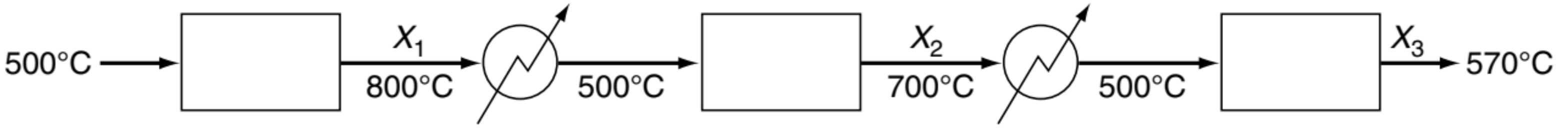
$$T = T_0 + \left(\frac{-\Delta H_{\mathrm{Rx}}}{C_{\mathrm{P_A}}}\right) = 300\ \mathrm{K} + \frac{20{,}000\ \frac{\mathrm{cal}}{\mathrm{mol}}}{50\frac{\mathrm{cal}}{\mathrm{molK}}}(0.38) = 452\ \mathrm{K}$$

From mass balance:

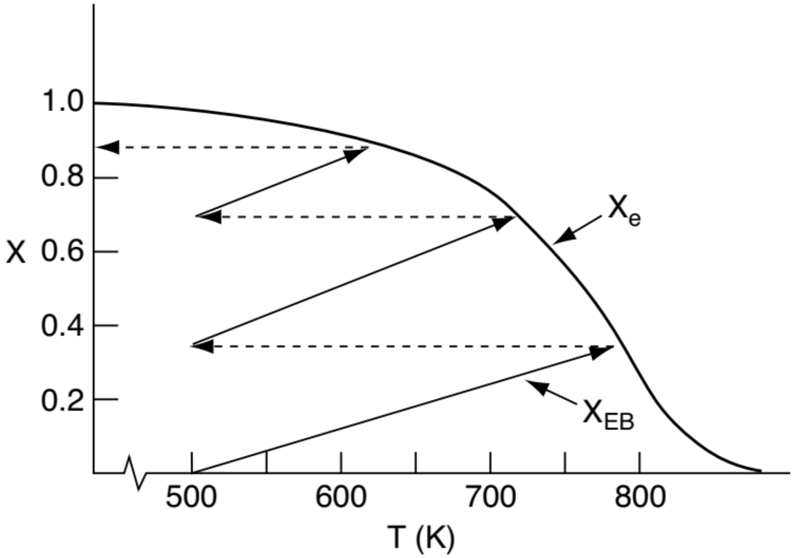
at $T = 452$ K $\quad X_e = 0.50$ and $k = 0.322\ \text{min}^{-1}$

$$\boxed{V = \frac{(0.38)(5\ \text{dm}^3/\text{min})}{0.322\ \text{min}^{-1}\left(1 - \frac{0.38}{0.50}\right)} = 24.5\ \text{dm}^3}$$

How to increase conversion for the exothermic reaction? ⇨ Use series CSTRs with interstage cooling



Interstage cooling used for exothermic reversible reactions



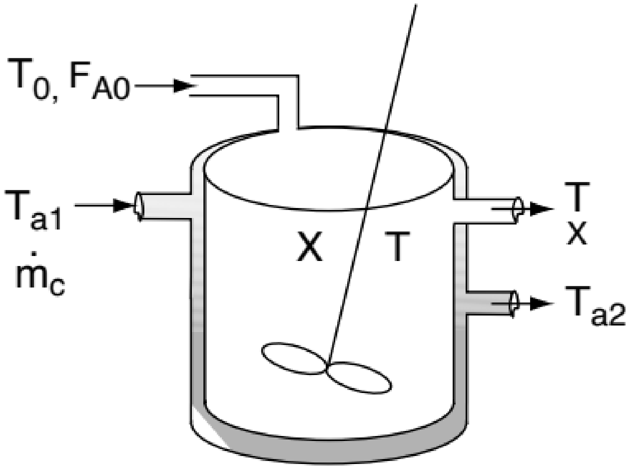
Heat transfer in Non-isothermal reactors

In this topic we will study the following:

- The effect of heat exchange in non-isothermal reactors on conversion

Heat transfer in non-isothermal CSTR

Suppose the below reaction takes place in a non-isothermal CSTR, where a heating/cooling utility is introduced into the jacket around the reactor.



$$A \rightarrow B + C$$

The design equation

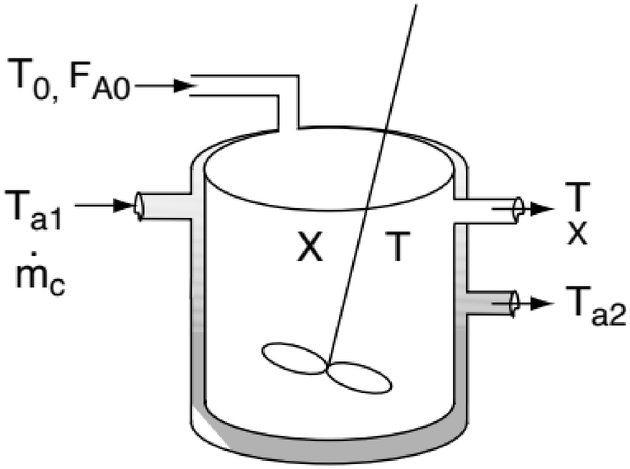
$$\boxed{V = \frac{F_{A0}X}{-r_A(X,T)}}$$

The energy equation

$$\boxed{\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0}$$

Where at this time $\dot{Q}$ varies based on the heat generated or consumed within the reaction, i.e. $\dot{Q} = f(T)$

An energy balance on the heat-exchanger fluid entering and leaving the exchanger is



$$\begin{bmatrix}\text{Rate of}\\ \text{energy}\\ \textit{in}\\ \text{by flow}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{energy}\\ \textit{out}\\ \text{by flow}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{heat transfer}\\ \textit{from}\text{ exchanger}\\ \textit{to}\text{ reactor}\end{bmatrix} = 0$$

$$\dot{m}_c C_{P_c}(T_{a1} - T_R) - \dot{m}_c C_{P_c}(T_{a2} - T_R) - \frac{UA\,(T_{a1} - T_{a2})}{\ln[(T - T_{a1})/(T - T_{a2})]} = 0$$

Where C_{Pc} is the heat capacity of the heat exchanger fluid and T_R is the reference temperature

However, the heat exchange by the utility fluid is $\dot{Q} = \dot{m}_c C_{P_c}(T_{a1} - T_{a2})$

Substitute in the above energy balance ⇨ $\dot{Q} = \dot{m}_c C_{P_c}(T_{a1} - T_{a2}) = \dfrac{UA\,(T_{a1} - T_{a2})}{\ln[(T - T_{a1})/(T - T_{a2})]}$

Solving for the exit temperature of the heat-exchanger fluid yields

$$T_{a2} = T - (T - T_{a1}) \exp\left(\frac{-UA}{\dot{m}_c C_{\mathrm{P}_c}}\right)$$

Substitute for unknow T_{a2} in $\dot{Q} = \dot{m}_c C_{\mathrm{P}_c}(T_{a1} - T_{a2})$

$$\dot{Q} = \dot{m}_c C_{\mathrm{P}_c}\left\{(T_{a1} - T)\left[1 - \exp\left(\frac{-UA}{\dot{m}_c C_{\mathrm{P}_c}}\right)\right]\right\}$$

For large values of the heat-exchanger fluid flow rate, $\dot{m}_c$, the exponent will be small and can be expanded in a Taylor series ($e^{-x} = 1 - x + \cdots$) where second-order terms are neglected in order to give

$$\dot{Q} = \dot{m}_c C_{\mathrm{P}_c}(T_{a1} - T)\left[1 - \left(1 - \frac{UA}{\dot{m}_c C_{\mathrm{P}_c}}\right)\right]$$

$T_{a1} \cong T_{a2} = T_a.$ $\Rightarrow$ $\boxed{\dot{Q} = UA(T_a - T)}$

The energy equation becomes

$$\boxed{\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^{\circ}_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0}$$

$$UA(T_a - T) - \dot{W}s - F_{A0}\sum_{i=1}^{n}\theta_i C_{pi}(T - T_{i0}) - \left[\Delta H^{o}_{Rx}(T_R) + \Delta C_p(T - T_R)\right]F_{A0}X = 0$$

rearrange

$$\boxed{X = \frac{UA(T - T_a) + \dot{W}s + F_{A0}\sum_{i=1}^{n}\theta_i C_{pi}(T - T_{i0})}{-F_{A0}\left[\Delta H^{o}_{Rx}(T_R) + \Delta C_p(T - T_R)\right]}}$$

Special Case:

No shaft work and $\Delta C_p = 0$ ⇨

$$\boxed{X = \frac{\frac{UA}{F_{A0}}(T - T_a) + \Sigma\Theta_i C_{P_i}(T - T_0)}{[-\Delta H^{\circ}_{Rx}(T_R)]}}$$

To further simplify, let $\Sigma\Theta_i C_{\mathrm{P}_i} = C_{\mathrm{P}_0}$ $\qquad \kappa = \dfrac{UA}{F_{\mathrm{A}0} C_{\mathrm{P}_0}}$ $\qquad T_c = \dfrac{\kappa T_a + T_0}{1+\kappa}$

$$\boxed{X = \frac{\dfrac{UA}{F_{\mathrm{A}0}}(T - T_a) + \Sigma\Theta_i C_{\mathrm{P}_i}(T - T_0)}{[-\Delta H^\circ_{\mathrm{Rx}}(T_\mathrm{R})]}}$$

$$\Rightarrow$$

$$\boxed{X = \frac{C_{\mathrm{P}_0}(1+\kappa)(T - T_c)}{-\Delta H^\circ_{\mathrm{Rx}}}}$$

$$\boxed{T = T_c + \frac{(-\Delta H^\circ_{\mathrm{Rx}})(X)}{C_{\mathrm{P}_0}(1+\kappa)}}$$

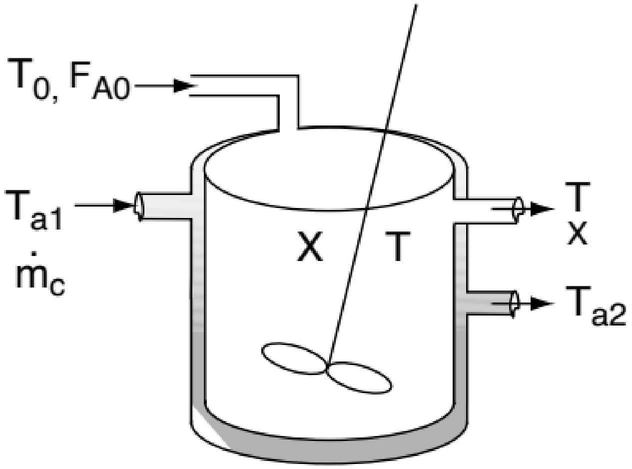
How to design a non-isothermal CSTR

There are three ways to specify the sizing of the CSTR:

A. From the energy balance equation, Specify X then Find V and T

B. From the energy balance equation, Specify T then Find X and V

C. From the energy balance equation, Specify V then Find X and T



A

Specify X

Find V and T

↓

Calculate T

$$\boxed{T = T_c + \frac{(-\Delta H^\circ_{\mathrm{Rx}})(X)}{C_{\mathrm{P}_0}(1+\kappa)}}$$

↓

Calculate k

$k = Ae^{-E/RT}$

↓

Calculate $-r_A(X,T)$

(e.g., $-r_A = k\,C_{A0}(1-X)$)

↓

Calculate V

$$V = \frac{F_{A0}X}{-r_A}$$

B

Specify T

Find X and V

↓

Calculate X_{EB}

$$\boxed{X_{\mathrm{EB}} = \frac{C_{\mathrm{P}_0}(1+\kappa)(T-T_c)}{-\Delta H^\circ_{\mathrm{Rx}}}}$$

↓

Calculate k

$k = Ae^{-E/RT}$

↓

Calculate $-r_A(X,T)$

(e.g., $-r_A = k\,C_{A0}(1-X)$)

↓

Calculate V

$$V = \frac{F_{A0}X}{-r_A}$$

C

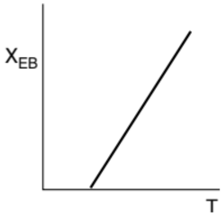
Specify V

Find X and T

↓

plot X_{EB} vs. T

$$\boxed{X_{\mathrm{EB}} = \frac{C_{\mathrm{P}_0}(1+\kappa)(T-T_c)}{-\Delta H^\circ_{\mathrm{Rx}}}}$$



↓

Solve $V = \dfrac{F_{A0}X}{-r_A(X,T)}$

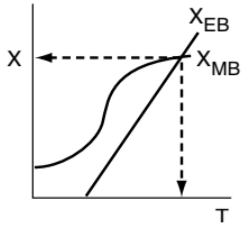
(e.g., for a first-order reaction)

$$X_{\mathrm{MB}} = \frac{\tau A\exp[-E/(RT)]}{1+\tau A\exp[-E/(RT)]}$$

↓

Plot X_{EB} and X_{MB} as a function of T on the same figure

↓



X_{MB} = Conversion calculated from the mole balance

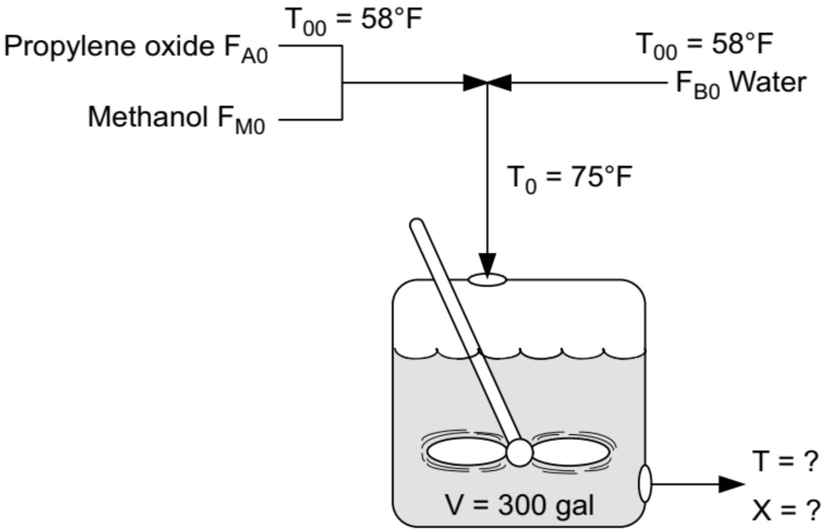
X_{EB} = Conversion calculated from the energy balance

Example 14.1: Production of Propylene Glycol in non-adiabatic CSTR

Propylene glycol is produced by the hydrolysis of propylene oxide according to the below reaction. If a feed of 43.04 lb-mol/h of propylene oxide (46.62 ft^3/h), 71.87 lb-mol/h methanol (46.62 ft^3/h), and 802.8 lb-mol/h water (233.1 ft^3/h) containing 0.1 wt % H2SO4 is fed to a non-isothermal, nonadiabatic CSTR.

The temperature of both feed streams is 58 F prior to mixing, but there is an immediate 17 F temperature rise upon mixing of the two feed streams caused by the heat of mixing. The entering temperature of all feed streams is thus taken to be 75 F.

Propylene oxide is a rather low-boiling-point substance. With the mixture you are using, you feel that you cannot exceed an operating temperature of 125 F, or you will lose too much oxide by vaporization through the vent system.



The reaction is first-order in propylene oxide concentration and apparent zero-order in excess of water with the specific reaction rate

$$k = A\,e^{-E/RT} = 16.96 \times 10^{12}\,(e^{-32{,}400/RT})\ \mathrm{h}^{-1}$$

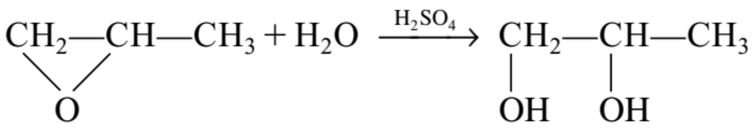
The units of E are Btu/lb-mol and T is in °R.

A is propylene oxide $(C_{P_A} = 35\ \text{Btu/lb-mol}\cdot{}^\circ\text{F})^{5}$

B is water $(C_{P_B} = 18\ \text{Btu/lb-mol}\cdot{}^\circ\text{F})$

C is propylene glycol $(C_{P_C} = 46\ \text{Btu/lb-mol}\cdot{}^\circ\text{F})$

M is methanol $(C_{P_M} = 19.5\ \text{Btu/lb-mol}\cdot{}^\circ\text{F})$



$$A + B \longrightarrow C$$

1. Can you use a CSTR as a replacement for the leaking one if it will be operated adiabatically? If so, what will be the conversion of propylene oxide to glycol?

2. If a cooling coil with 40 ft^2 surface is used to remove the excess heat using a large amount of cooling-water flow rate at temperature of 85 $^\circ$F can be maintained. A typical overall heat-transfer coefficient for such a coil is 100 Btu/h. ft^2.F. Will the reactor satisfy the previous constraint of 125 $^\circ$F maximum temperature if the cooling coil is used?

Solution

$$A + B \longrightarrow C$$

The reaction is predicted experimentally to be first-order in propylene oxide concentration and apparent zero-order in excess of water

$$-r_A = kC_A$$

$$k = 16.96\ 10^{12} \exp[-32{,}400/R/T]\ \text{h}^{-1}$$

The design equation in terms of X is

$$V = \frac{F_{A0}X}{-r_A}$$

(liquid phase, $v = v_0$): $C_A = C_{A0}(1-X)$

⇨

$$V = \frac{F_{A0}X}{kC_{A0}(1-X)} = \frac{v_0 X}{k(1-X)}$$

Solving for X as a function of T and recalling that $\tau = V/v_0$ gives

$$\boxed{X_{MB} = \frac{\tau k}{1+\tau k} = \frac{\tau A e^{-E/RT}}{1+\tau A e^{-E/RT}}}$$

The **energy balance** for this adiabatic reaction

$$\boxed{X=\frac{UA(T-T_a)+\dot{W}s+F_{A0}\sum_{i=1}^{n}\theta_i C_{pi}(T-T_{i0})}{-F_{A0}\left[\Delta H^{o}_{Rx}(T_R)+\Delta C_p(T-T_R)\right]}}$$

$$X_{\mathrm{EB}}=\frac{\sum\Theta_i C_{\mathrm{P}_i}(T-T_{i0})}{-[\Delta H^{\circ}_{\mathrm{Rx}}(T_{\mathrm{R}})+\Delta C_{\mathrm{P}}(T-T_{\mathrm{R}})]}$$

Calculations:

$$\begin{aligned}v_0&=v_{\mathrm{A0}}+v_{\mathrm{M0}}+v_{\mathrm{B0}}\\&=46.62+46.62+233.1=326.3\ \mathrm{ft^3/h}\\V&=300\ \mathrm{gal}=40.1\ \mathrm{ft^3}\end{aligned}$$

$$\tau=\frac{V}{v_0}=\frac{40.1\ \mathrm{ft^3}}{326.3\ \mathrm{ft^3/h}}=0.123\ \mathrm{h}$$

$$\begin{aligned}C_{\mathrm{A0}}&=\frac{F_{\mathrm{A0}}}{v_0}=\frac{43.0\ \text{lb-mol/h}}{326.3\ \mathrm{ft^3/h}}\\&=0.132\ \text{lb-mol/ft}^3\end{aligned}$$

For methanol: $\Theta_M = \dfrac{F_{M0}}{F_{A0}} = \dfrac{71.87\ \text{lb-mol/h}}{43.0\ \text{lb-mol/h}} = 1.67$

For water: $\Theta_B = \dfrac{F_{B0}}{F_{A0}} = \dfrac{802.8\ \text{lb-mol/h}}{43.0\ \text{lb-mol/h}} = 18.65$

$$\boxed{X_{MB} = \frac{\tau k}{1+\tau k} = \frac{\tau A e^{-E/RT}}{1+\tau A e^{-E/RT}}}$$

$$-r_A = kC_A$$

k = 16.96 10^{12} exp[–32,400/R/T] h^{-1}

⇨

$$X_{MB} = \frac{(16.96\times 10^{12}\ \text{h}^{-1})(0.1229\ \text{h})\ \exp(-32{,}400/1.987T)}{1+(16.96\times 10^{12}\ \text{h}^{-1})(0.1229\ \text{h})\ \exp(-32{,}400/1.987T)}$$

$$\boxed{X_{MB} = \frac{(2.084\times 10^{12})\ \exp(-16{,}306/T)}{1+(2.084\times 10^{12})\ \exp(-16{,}306/T)},\ T\text{ is in °R}}$$

(b) *Evaluating the energy balance terms*

(1) Heat of reaction at temperature T

$$\boxed{\Delta H_{\mathrm{Rx}}(T) = \Delta H^{\circ}_{\mathrm{Rx}}(T_{\mathrm{R}}) + \Delta C_{\mathrm{P}}(T - T_{\mathrm{R}})}$$

$$\Delta C_{\mathrm{P}} = C_{\mathrm{P_C}} - C_{\mathrm{P_B}} - C_{\mathrm{P_A}} = 46 - 18 - 35 = -7 \text{Btu/lb-mol/°F}$$

$$\Delta H_{\mathrm{Rx}} = -36,000 - 7(T - T_{\mathrm{R}})$$

(2) Heat capacity term

$$\begin{aligned} \Sigma \Theta_i C_{\mathrm{P}_i} &= C_{\mathrm{P_A}} + \Theta_{\mathrm{B}} C_{\mathrm{P_B}} + \Theta_{\mathrm{M}} C_{\mathrm{P_M}} \\ &= 35 + (18.65)(18) + (1.67)(19.5) \\ &= 403.3 \text{ Btu/lb-mol} \cdot \text{°F} \end{aligned}$$

$$\begin{aligned} T_0 &= T_{00} + \Delta T_{\mathrm{mix}} = 58\text{°F} + 17\text{°F} = 75\text{°F} \\ &= 535\text{°R} \\ T_{\mathrm{R}} &= 68\text{°F} = 528\text{°R} \end{aligned}$$

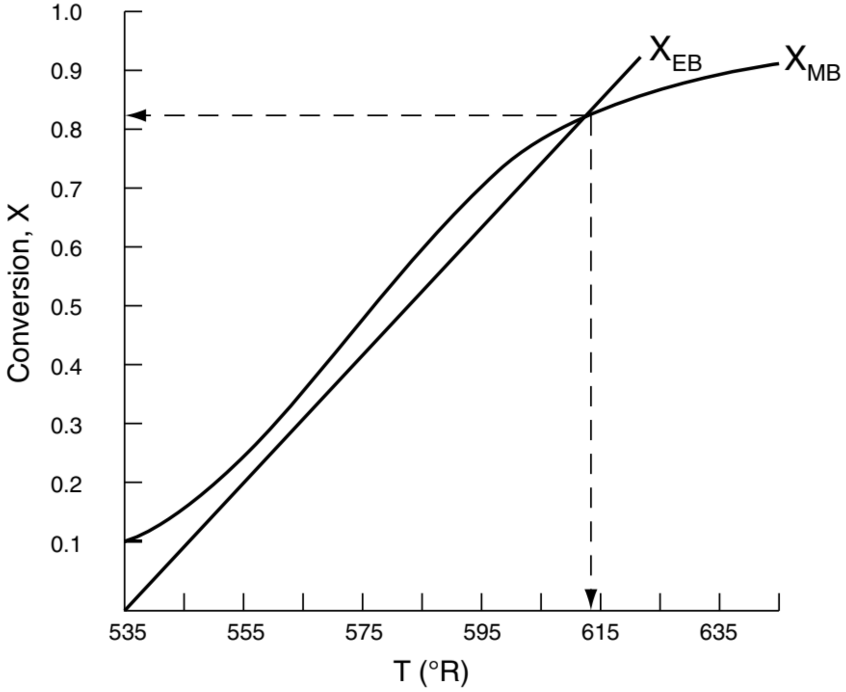
$$X_{\mathrm{EB}} = -\frac{\Sigma\, \Theta_i C_{\mathrm{P}_i}(T - T_{i0})}{\Delta H^{\circ}_{\mathrm{Rx}}(T_{\mathrm{R}}) + \Delta C_{\mathrm{P}}(T - T_{\mathrm{R}})} \quad \Rightarrow \quad X_{\mathrm{EB}} = \frac{(403.3 \text{ Btu/lb-mol} \cdot \text{°F})(T - 535)\text{°F}}{-[-36{,}400 - 7(T - 528)] \text{ Btu/lb-mol}}$$

$$\boxed{X_{EB} = \frac{403.3(T-535)}{36{,}400 + 7(T-528)}}$$

⇔

$$\boxed{X_{MB} = \frac{(2.084\times 10^{12})\exp(-16{,}306/T)}{1+(2.084\times 10^{12})\exp(-16{,}306/T)},\ T \text{ is in } {}^{\circ}\text{R}}$$

T (°R)	X_{MB} [Eq. (E12-3.10)]	X_{EB} [Eq. (E12-3.14)]
535	0.108	0.000
550	0.217	0.166
565	0.379	0.330
575	0.500	0.440
585	0.620	0.550
595	0.723	0.656
605	0.800	0.764
615	0.860	0.872
625	0.900	0.980



Intersection point is at 83% conversion and 613 R. At this point, both the energy balance and mole balance are satisfied. Because the temperature must remain below 125 F (585°R), we **cannot** use the 300-gal reactor as it is now

Part b: using a cooling to remove excess heat

The **energy balance**

$$\boxed{X = \frac{UA(T - T_a) + \dot{W}s + F_{A0}\sum_{i=1}^{n}\theta_i C_{pi}(T - T_{i0})}{-F_{A0}\left[\Delta H^{o}_{Rx}(T_R) + \Delta C_p(T - T_R)\right]}}$$

$$\Downarrow$$

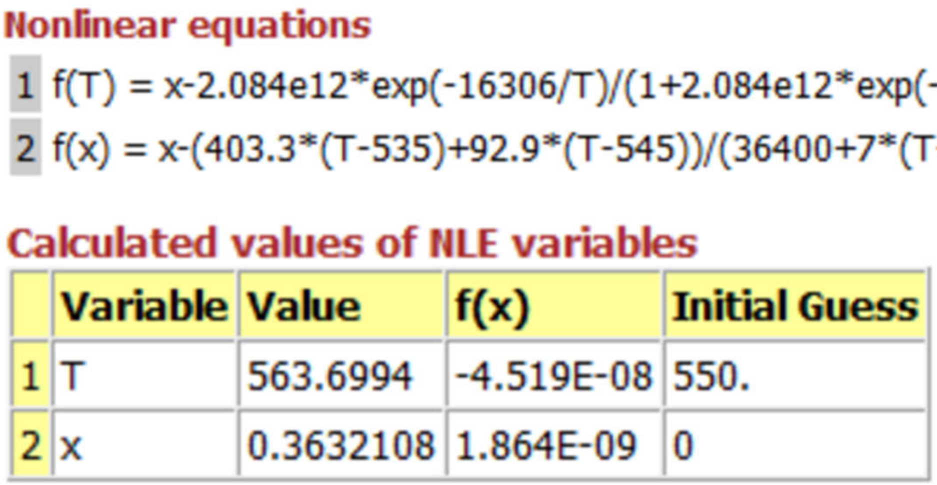
$$\boxed{X_{\mathrm{EB}} = \frac{\Sigma\Theta_i C_{\mathrm{P}_i}(T - T_0) + [UA(T - T_a)/F_{\mathrm{A0}}]}{-[\Delta H^{\circ}_{\mathrm{Rx}}(T_{\mathrm{R}}) + \Delta C_{\mathrm{P}}(T - T_{\mathrm{R}})]}}$$

$$\frac{UA}{F_{\mathrm{A0}}} = \left(100\ \frac{\mathrm{Btu}}{\mathrm{h \cdot ft^2 \cdot {}^{\circ}F}}\right)\frac{(40\ \mathrm{ft}^2)}{(43.04\ \mathrm{lb\text{-}mol/h})} = \frac{92.9\ \mathrm{Btu}}{\mathrm{lb\text{-}mol \cdot {}^{\circ}F}}$$

Recall that the cooling temperature is

$$T_a = 85°\text{F} = 545°\text{R}$$

$$\boxed{X_{\text{EB}} = \frac{403.3(T-535)+92.9(T-545)}{36{,}400+7(T-528)}} \Longleftrightarrow \boxed{X_{\text{MB}} = \frac{(2.084\times 10^{12})\ \exp(-16{,}306/T)}{1+(2.084\times 10^{12})\ \exp(-16{,}306/T)},\ T \text{ is in °R}}$$



Nonlinear equations

```
1 f(T) = x-2.084e12*exp(-16306/T)/(1+2.084e12*exp(-16306/T)) = 0
2 f(x) = x-(403.3*(T-535)+92.9*(T-545))/(36400+7*(T-528)) = 0
```

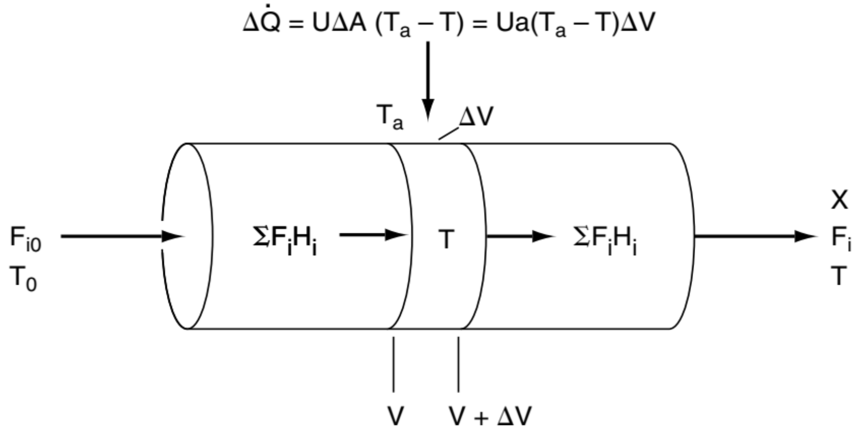
Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	T	563.6994	-4.519E-08	550.
2	x	0.3632108	1.864E-09	0

$$\boxed{T = 564°\text{R and } X = 0.36}$$

Heat transfer in non-isothermal PFR

Heat transfer across the length of the PFR varies with reactor length and the type of the reaction.



$$A \rightarrow B + C$$

The design equation $$\frac{dF_i}{dV} = r_i = \nu_i(-r_A)$$

The energy equation $$\boxed{\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^{\circ}_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0}$$

Where at this time $\dot{Q}$ varies based on the heat generated or consumed within the reaction, i.e. $\dot{Q} = f(T)$

Differentiate the energy equation w.r.t. volume, V

$$\boxed{\dot{Q} - \dot{W}_s - F_{A0}\sum_{i=1}^{n}\Theta_i C_{P_i}(T - T_{i0}) - [\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)]F_{A0}X = 0}$$

$$\frac{d\dot{Q}}{dV} - F_{A0}\sum_{i=1}^{n}\theta_i C_{pi}\frac{dT}{dV} - \left[\Delta H^o_{Rx}(T_R)F_{A0}\frac{dX}{dV} + \left(\int_{T_R}^{T}\Delta C_p\, dT\right)F_{A0}\frac{dX}{dV} + F_{A0}X\,\Delta C_p\frac{dT}{dV}\right] = 0$$

Re-arrange

$$\frac{d\dot{Q}}{dV} - F_{A0}\left(\sum_{i=1}^{n}\theta_i C_{pi} + X\,\Delta C_p\right)\frac{dT}{dV} - \left[\Delta H^o_{Rx}(T_R) + \left(\int_{T_R}^{T}\Delta C_p\, dT\right)\right]F_{A0}\frac{dX}{dV} = 0$$

Substitute for the rate of reaction $-r_A = F_{A0}\dfrac{dX}{dV}$

$$\frac{d\dot{Q}}{dV} - F_{A0}\left(\sum_{i=1}^{n} \theta_i C_{pi} + X\,\Delta C_p\right)\frac{dT}{dV} - \left[\Delta H^{o}_{Rx}(T_R) + \left(\int_{T_R}^{T} \Delta C_p\, dT\right)\right](-r_A) = 0$$

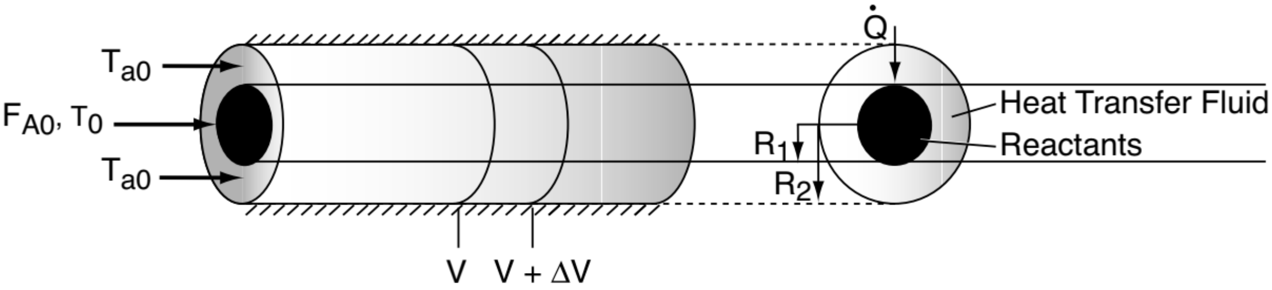
$$\frac{d\dot{Q}}{dV} = \frac{d\left(\dot{m}C_p(T_a - \mathrm{T})\right)}{dV} = Ua(T_a - \mathrm{T})$$

$$\boxed{\frac{dT}{dV} = \frac{Ua(T_a - \mathrm{T}) + \left[-\,\Delta H^{o}_{Rx}(T_R) - \left(\int_{T_R}^{T} \Delta C_p\, dT\right)\right](-r_A)}{F_{A0}\left(\sum_{i=1}^{n} \theta_i C_{pi} + X\,\Delta C_p\right)} = f(X, T, T_a)}$$

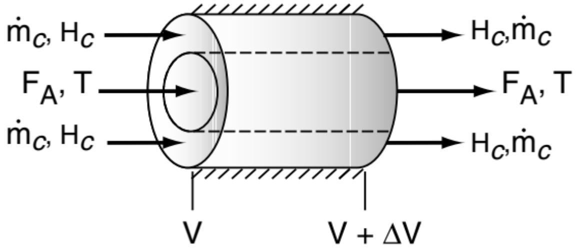
We need to have a relation between $T_a\ and\ T$

Balance on the Heat-Transfer Fluid

A. Co-current Flow



$$\begin{bmatrix}\text{Rate of energy}\\ \text{in at } V\end{bmatrix} - \begin{bmatrix}\text{Rate of energy}\\ \text{out at } V+\Delta V\end{bmatrix} + \begin{bmatrix}\text{Rate of heat added}\\ \text{by conduction through}\\ \text{the inner wall}\end{bmatrix} = 0$$



$$\dot{m}_c H_c|_V \quad - \quad \dot{m}_c H_c|_{V+\Delta V} \quad + \quad Ua(T-T_a)\Delta V \quad = 0$$

$$-\dot{m}_c \frac{dH_c}{dV} + Ua(T-T_a) = 0$$

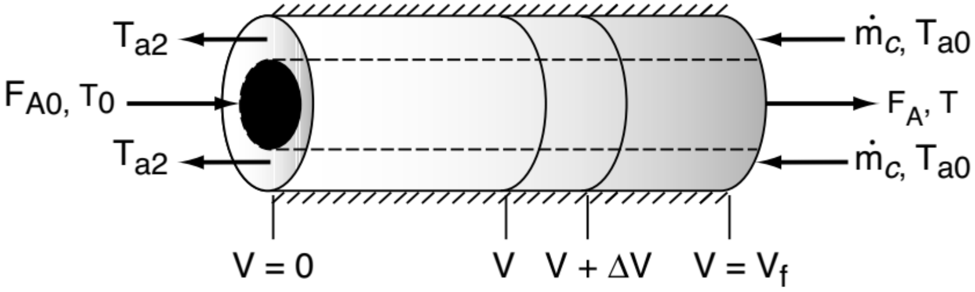
$$\frac{dH_c}{dV} = C_{P_c}\frac{dT_a}{dV}$$

$$\boxed{\frac{dT_a}{dV} = \frac{Ua(T-T_a)}{\dot{m}C_p} = f(T, T_a)}$$

B. Counter-current Flow

$$\boxed{\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}C_p} = f(T, T_a)}$$

Balance on the Heat-Transfer Fluid



Mole balance

$$\boxed{\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = f\left(X, T, p\right)}$$

Pressure drop

$$\boxed{\frac{dp}{dV} = -h\left(p, X, T\right)}$$

$$\frac{dP}{dz} = -\underbrace{\frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right]}_{\beta_0} \frac{P_0}{P}\left(\frac{T}{T_0}\right)\frac{F_T}{F_{T0}}$$

$$\frac{F_T}{F_{T0}} = 1 + \varepsilon X$$

Special case: For liquid-phase reactions, the rate is not a function of total pressure, the mole balance is

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = f(X, T)$$

Design of non-isothermal PFR with heat exchange
(conversion approach)

Suppose the following reversible reaction takes place in a plug flow reactor where the pressure drop is negligible. The cooling/heating utility flows co-current with the reaction effluents to the reactor::

$$\mathrm{A} + \mathrm{B} \rightleftarrows 2\mathrm{C}$$

1. Mole Balance:

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

2. Rate Law:

$$-r_A = k_1\left(C_A C_B - \frac{C_C^2}{K_C}\right)$$

$$k = k_1(T_1)\exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$K_C = K_{C2}(T_2)\exp\left[\frac{\Delta H^\circ_{Rx}}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right]$$

3. Stoichiometry (gas phase, **no ΔP**):

$$C_A = C_{A0}(1-X)\,\frac{T_0}{T} \qquad C_B = C_{A0}(\Theta_B - X)\,\frac{T_0}{T} \qquad C_C = 2C_{A0}X\,\frac{T_0}{T}$$

4. Energy Balances:

Reactor: $$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_{Rx})}{F_{A0}[C_{P_A} + \Theta_B C_{P_B} + X\,\Delta C_P]}$$

Co-current Coolant: $$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_{P_c}}$$

Three equations: $\frac{dX}{dV}$, $\frac{dT}{dV}$ and $\frac{dT_a}{dV}$ are varies with the volume, V with three unknowns: X, T and T_a

Design of non-isothermal PFR with heat exchange

(molar flowrate approach)

Similar to the reversible reaction takes place in a plug flow reactor where the pressure drop is negligible. The cooling/heating utility flows either co-current or counter-current with the reaction effluents to the reactor::

$$\mathrm{A} + \mathrm{B} \rightleftarrows 2\mathrm{C}$$

1. Mole Balance:

$$\frac{dF_\mathrm{A}}{dV} = r_\mathrm{A} \qquad \frac{dF_\mathrm{B}}{dV} = r_\mathrm{B} \qquad \frac{dF_\mathrm{C}}{dV} = r_\mathrm{C}$$

2. Rate Law:

$$-r_\mathrm{A} = k_1\left(C_\mathrm{A}C_\mathrm{B} - \frac{C_\mathrm{C}^2}{K_\mathrm{C}}\right)$$

$$k = k_1(T_1)\exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$K_\mathrm{C} = K_{\mathrm{C}2}(T_2)\exp\left[\frac{\Delta H^\circ_\mathrm{Rx}}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right]$$

3. Stoichiometry (gas phase, **no ΔP**):

$$\mathrm{A} + \mathrm{B} \rightleftarrows 2\mathrm{C}$$

$$r_{\mathrm{B}} = r_{\mathrm{A}}$$

$$r_{\mathrm{C}} = -2r_{\mathrm{A}}$$

$$-r_{\mathrm{A}} = k_1\left(C_{\mathrm{A}}C_{\mathrm{B}} - \frac{C_{\mathrm{C}}^2}{K_{\mathrm{C}}}\right)$$

$$C_{\mathrm{A}} = C_{T0}\,\frac{F_{\mathrm{A}}}{F_T}\,\frac{T_0}{T} \qquad C_{\mathrm{B}} = C_{T0}\,\frac{F_{\mathrm{B}}}{F_T}\,\frac{T_0}{T} \qquad C_{\mathrm{C}} = C_{T0}\,\frac{F_{\mathrm{C}}}{F_T}\,\frac{T_0}{T}$$

$$F_{\mathrm{T}} = F_{\mathrm{A}} + F_{\mathrm{B}} + F_{\mathrm{C}}$$

4. Energy Balances:

Reactor:

$$\frac{dT}{dV}=\frac{Ua(T_a-T)+(-r_A)(-\Delta H_{Rx})}{F_A C_{P_A}+F_B C_{P_B}+F_C C_{P_C}}$$

Co-current flow

$$\frac{dT_a}{dV}=\frac{Ua(T-T_a)}{\dot{m}_c C_{P_c}}$$

Countercurrent flow

$$\frac{dT_a}{dV}=\frac{Ua(T_a-T)}{\dot{m}_c C_{P_c}}$$

Five equations: $\frac{dF_A}{dV}$, $\frac{dF_B}{dV}$, $\frac{dF_C}{dV}$, $\frac{dT}{dV}$ and $\frac{dT_a}{dV}$ are varies with the volume, V with five unknowns:F_A, F_B, F_C, T and T_a

Example 14.2: Isomerization of an exothermic reaction of n-butane to i-butane in non-isothermal, non-adiabatic PFR

The isomerization of n-butane is an elementary, reversible and exothermic reaction that is carried out in the liquid phase PFR under high pressure using essentially trace amounts of a liquid catalyst. It gives a specific reaction rate of 31.1 h^{-1} at 360 K. The feed enters the reactor at 305 K. The coolant media enters at 315 K with $\dot{m}_c = 500\ kg/h$ and heat capacity of $C_{pc} = 28\ kJ/kg.K$.

$$n\text{-}C_4H_{10} \rightleftarrows i\text{-}C_4H_{10}$$

Additional information:

$\Delta H_{Rx} = -34{,}500\ \text{kJ/kmol}$

$Ua = 5{,}000\ \text{kJ/m}^3\cdot\text{h}\cdot\text{K}.$

$C_{A0} = 1.86\ \text{kmol/m}^3$

$F_{A0} = 14.7\ \text{kmol A/h}$

Butane

$C_{P_{n\text{-}B}} = 141\ \text{J/mol}\cdot\text{K}$

$C_{P_{i\text{-}B}} = 141\ \text{J/mol}\cdot\text{K} = 141\ \text{kJ/kmol}\cdot K$

i-Pentane

$C_{P_{i\text{-}P}} = 161\ \text{J/mol}\cdot\text{K}$

Solution

$$n\text{-C}_4\text{H}_{10} \rightleftarrows i\text{-C}_4\text{H}_{10}$$

$$\text{A} \rightleftarrows \text{B}$$

$$k = 31.1 \exp\left[7906\left(\frac{T-360}{360T}\right)\right] \text{h}^{-1}$$

$$K_C = 3.03 \exp\left[-830.3\left(\frac{T-333}{333T}\right)\right]$$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

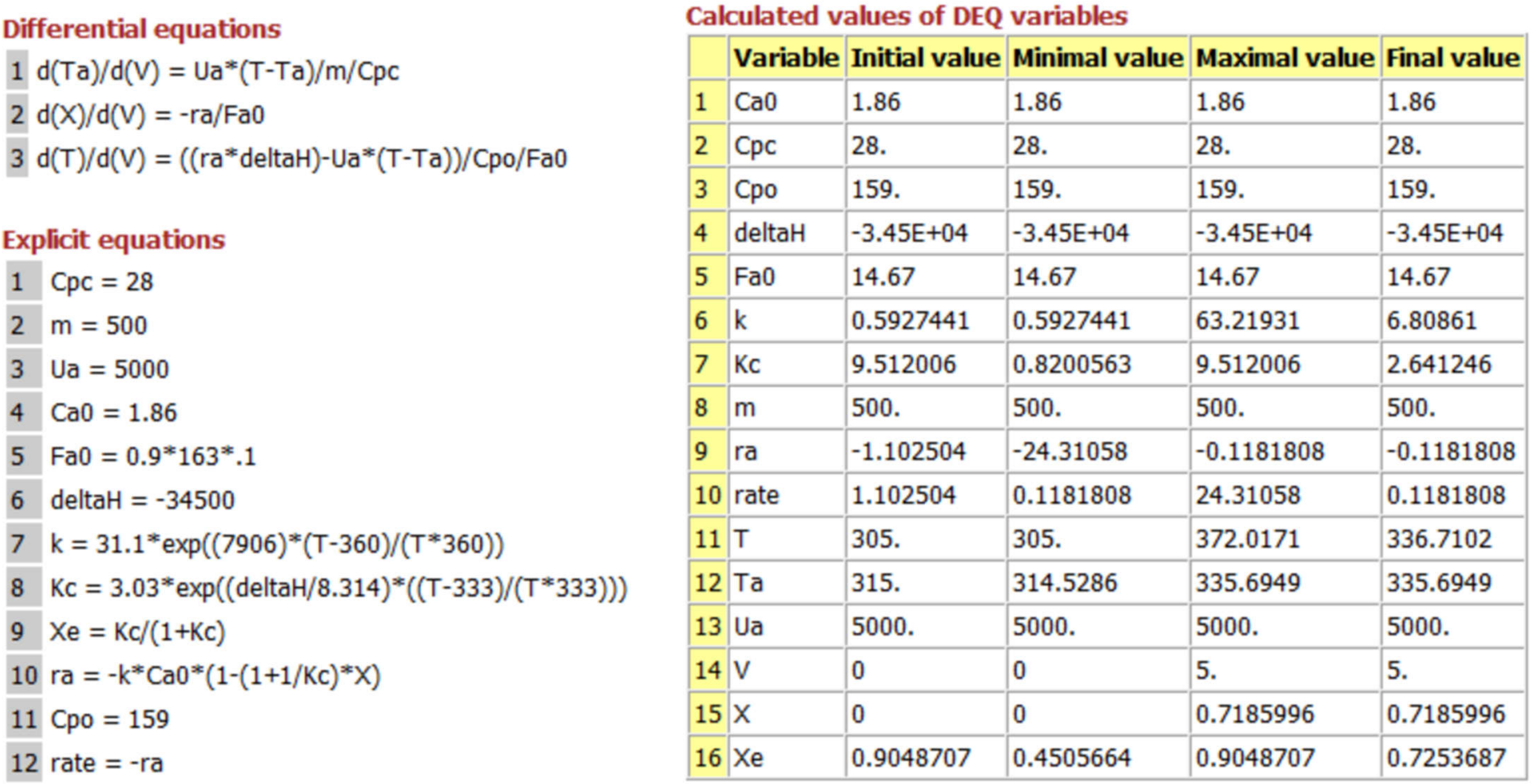
$$r_A = -kC_{A0}\left[1-\left(1+\frac{1}{K_C}\right)X\right]$$

$$X_e = \frac{K_C}{1+K_C}$$

$$\frac{dT}{dV} = \frac{r_A \Delta H_{Rx} - Ua(T-T_a)}{F_{A0}\underbrace{\sum \Theta_i C_{P_i}}_{C_{P_0}}} = \frac{r_A \Delta H_{Rx} - Ua(T-T_a)}{F_{A0} C_{P_0}}$$

Co-current Heat Exchange

$$\frac{dT_a}{dV} = \frac{Ua(T-T_a)}{\dot{m}_C C_{P_C}}$$



Differential equations

1 d(Ta)/d(V) = Ua*(T-Ta)/m/Cpc
2 d(X)/d(V) = -ra/Fa0
3 d(T)/d(V) = ((ra*deltaH)-Ua*(T-Ta))/Cpo/Fa0

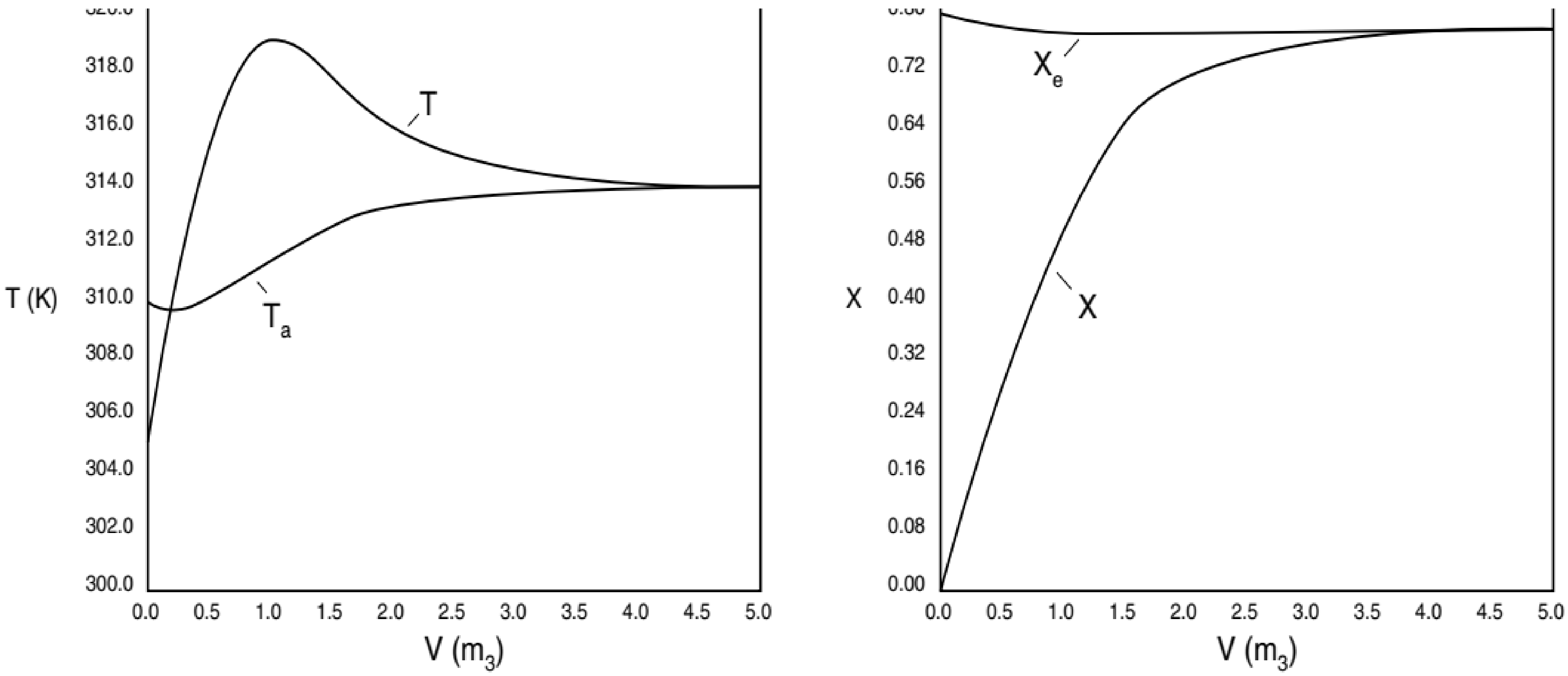
Explicit equations

1 Cpc = 28
2 m = 500
3 Ua = 5000
4 Ca0 = 1.86
5 Fa0 = 0.9*163*.1
6 deltaH = -34500
7 k = 31.1*exp((7906)*(T-360)/(T*360))
8 Kc = 3.03*exp((deltaH/8.314)*((T-333)/(T*333)))
9 Xe = Kc/(1+Kc)
10 ra = -k*Ca0*(1-(1+1/Kc)*X)
11 Cpo = 159
12 rate = -ra

Calculated values of DEQ variables

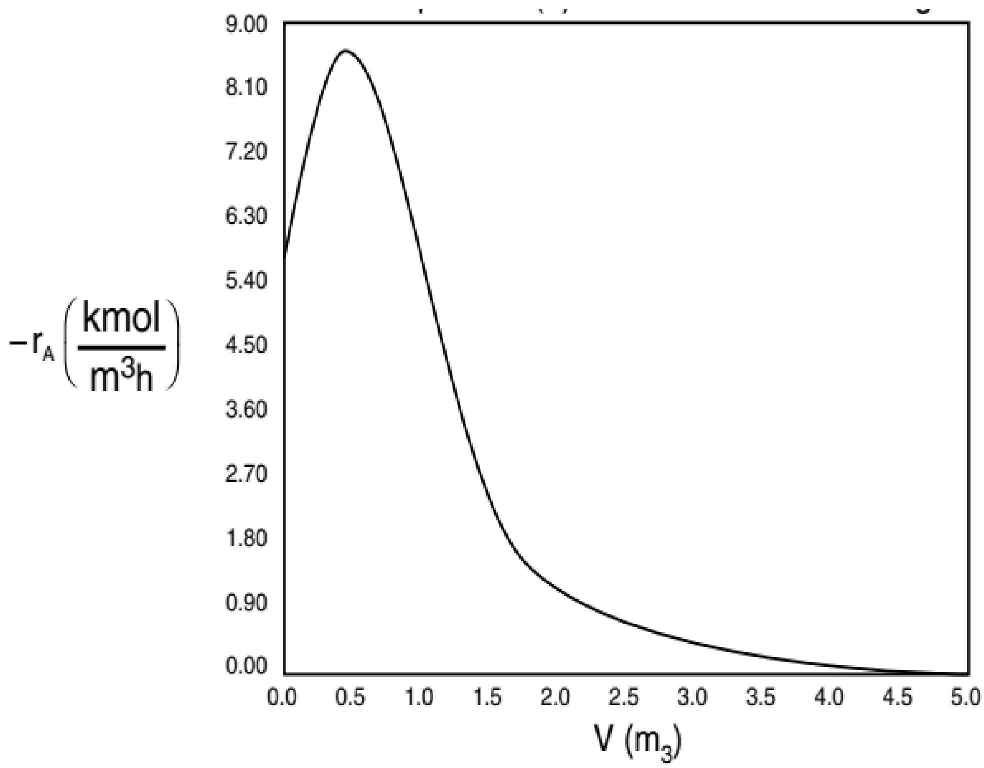
	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca0	1.86	1.86	1.86	1.86
2	Cpc	28.	28.	28.	28.
3	Cpo	159.	159.	159.	159.
4	deltaH	-3.45E+04	-3.45E+04	-3.45E+04	-3.45E+04
5	Fa0	14.67	14.67	14.67	14.67
6	k	0.5927441	0.5927441	63.21931	6.80861
7	Kc	9.512006	0.8200563	9.512006	2.641246
8	m	500.	500.	500.	500.
9	ra	-1.102504	-24.31058	-0.1181808	-0.1181808
10	rate	1.102504	0.1181808	24.31058	0.1181808
11	T	305.	305.	372.0171	336.7102
12	Ta	315.	314.5286	335.6949	335.6949
13	Ua	5000.	5000.	5000.	5000.
14	V	0	0	5.	5.
15	X	0	0	0.7185996	0.7185996
16	Xe	0.9048707	0.4505664	0.9048707	0.7253687

Variation of T and X vs V in exothermic, non-isothermal, non-adiabatic isomerization reaction with co-current heat exchange



(a) (b)

Effect of reactor volume on rate of isomerization of n-butane in exothermic, non-isothermal, non-adiabatic reaction with co-current heat exchange



(c)

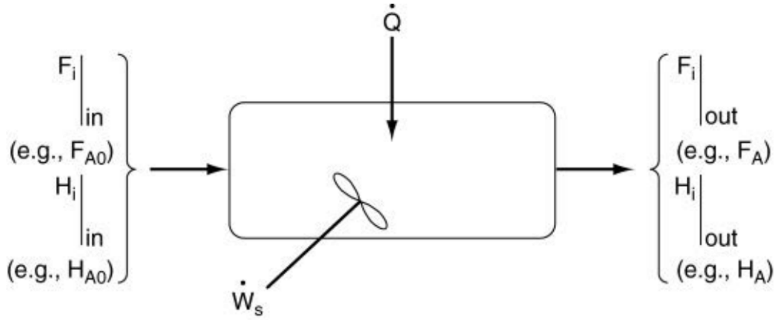
Topic 15. Unsteady-State, Non-isothermal Reactor Designs

This lecture

- ✓ The Unsteady-State Energy Balance
- ✓ Energy Balance on Batch Reactors
- ✓ Semi-batch Reactors with a Heat Exchanger
- ✓ Unsteady Operation of a CSTR
- ✓ Non-isothermal Multiple Reactions

The Unsteady-State Energy Balance

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^{m} F_i H_i\big|_{\text{in}} - \sum_{i=1}^{m} F_i H_i\big|_{\text{out}} = \left(\frac{d\hat{E}_{\text{sys}}}{dt}\right)$$



$$\hat{E}_{\text{sys}} = \sum_{i=1}^{m} N_i E_i = N_A E_A + N_B E_B + N_C E_C + N_D E_D + N_I E_I$$

$$\hat{E}_{\text{sys}} = \sum_{i=1}^{m} N_i E_i = \sum_{i=1}^{m} N_i U_i = \left[\sum_{i=1}^{m} N_i (H_i - PV_i)\right]_{\text{sys}} = \sum_{i=1}^{m} N_i H_i - \overset{\text{Neglect}}{\cancel{P \underbrace{\sum_{i=1}^{m} N_i \tilde{V}_i}_{V}}}$$

The term $P \sum_{i=1}^{m} N_i \tilde{V}_i$ always smaller than the other terms in this equation and can be neglected

$$\hat{E}_{\text{sys}} = \sum_{i=1}^{m} N_i H_i \quad \Rightarrow \quad \left(\frac{d\hat{E}_{\text{sys}}}{dt}\right) = \left[\Sigma N_i \frac{dH_i}{dt} + \Sigma H_i \frac{dN_i}{dt}\right]_{\text{sys}}$$

$$H_i = H_i^{\circ}(T_{\text{R}}) + \int_{T_{\text{R}}}^{T} C_{\text{P}_i}\, dT \quad \Rightarrow \quad \frac{dH_i}{dt} = C_{\text{P}_i} \frac{dT}{dt}$$

$$\boxed{\dot{Q} - \dot{W}_s + \Sigma F_{i0} H_{i0}\big|_{\text{in}} - \Sigma F_i H_i\big|_{\text{out}} = \left[\Sigma N_i \frac{dH_i}{dt} + \Sigma H_i \frac{dN_i}{dt}\right]_{\text{sys}}}$$

$$\Downarrow$$

$$\dot{Q} - \dot{W}_s + \Sigma F_{i0} H_{i0} - \Sigma F_i H_i = \Sigma N_i C_{\text{P}_i} \frac{dT}{dt} + \Sigma\, H_i \frac{dN_i}{dt}$$

The mole balance on species *i* is

$$\frac{dN_i}{dt} = -\nu_i\, r_A V + F_{i0} - F_i$$

$$\dot{Q} - \dot{W}_s + \Sigma F_{i0} H_{i0} - \Sigma F_i H_i = \Sigma N_i C_{P_i} \frac{dT}{dt} + \Sigma\, H_i \frac{dN_i}{dt}$$

$$\Downarrow$$

$$\dot{Q} - \dot{W}_s + \Sigma\, F_{i0} H_{i0} - \Sigma\, F_i H_i = \Sigma\, N_i C_{P_i} \frac{dT}{dt} + \Sigma\, \nu_i H_i (-r_A V) + \Sigma\, F_{i0} H_i - \Sigma\, F_i H_i$$

$$\sum \nu_i H_i = \Delta H_{Rx} \quad \Rightarrow \quad \boxed{\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \Sigma\, F_{i0}(H_i - H_{i0}) + (-\Delta H_{Rx})(-r_A V)}{\Sigma\, N_i C_{P_i}}}$$

Substituting for H_i and H_{i0} for the case of no phase change yields the energy balance on a **transient CSTR** or **semi-batch reactor**

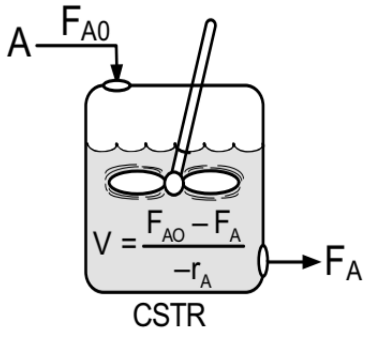
$$\boxed{\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum F_{i0} C_{\mathrm{P}_i} (T - T_{i0}) + [-\Delta H_{\mathrm{Rx}}(T)](-r_{\mathrm{A}} V)}{\sum N_i C_{\mathrm{P}_i}}}$$

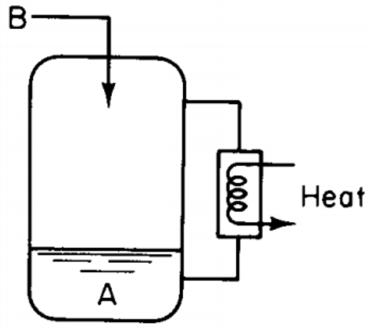
For l**iquid-phase** reactions where C_P is usually small and can be neglected, the following approximation is often made

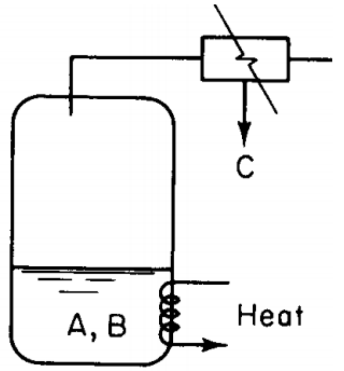
$$\sum N_i C_{\mathrm{P}_i} \cong \sum N_{i0} C_{\mathrm{P}_i} = N_{\mathrm{A0}} \overbrace{\Sigma \Theta_i C_{\mathrm{P}_i}}^{C_{\mathrm{P}_s}} = N_{\mathrm{A0}} C_{\mathrm{P}_s} \quad (\mathrm{J/K})$$

Also $\sum F_{i0} C_{\mathrm{P}_i} = F_{\mathrm{A0}} C_{\mathrm{P}_s} \quad (\mathrm{J/s \cdot K})$

C_{P_s} is the heat capacity of the solution.



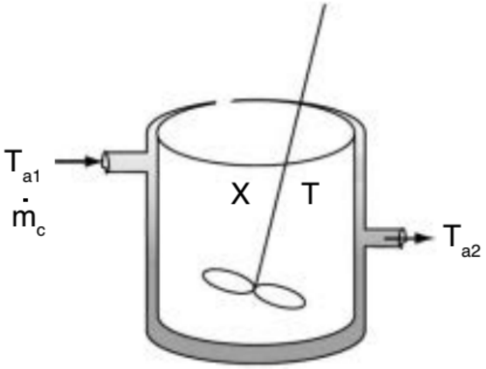




Energy Balance on Batch Reactors (BRs)

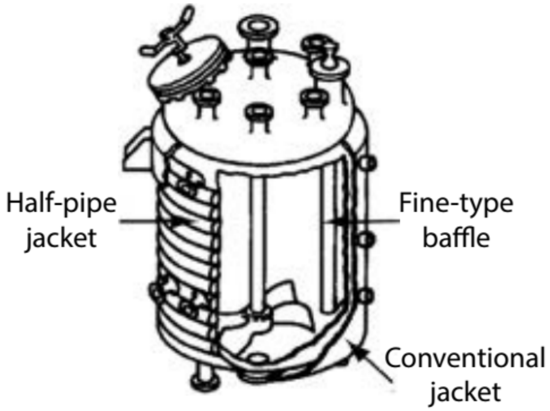
The general transient energy balance:

$$\boxed{\frac{dT}{dt}=\frac{\dot{Q}-\dot{W}_s-F_{A0}C_{P_s}(T-T_0)+[-\Delta H_{Rx}(T)](-r_AV)}{N_{A0}C_{P_s}}}$$



Reduces to:

$$\boxed{\frac{dT}{dt}=\frac{\dot{Q}-\dot{W}_s+(-\Delta H_{Rx})(-r_AV)}{\sum N_iC_{P_i}}}$$



At steady state condition, where there is no shaft work, the heat generates, Q_{gb} equals the heat removed by the jacket, Q_{rb}

$$\dot{Q}_{gb} = (-\Delta H_{\mathrm{Rx}})(-r_{\mathrm{A}} V) \quad \Longleftrightarrow \quad \dot{Q}_{rb} = \dot{m} C_{\mathrm{P_C}}(T - T_{a1})\left[1 - \exp\left[-\frac{UA}{\dot{m} C_{\mathrm{P_C}}}\right]\right]$$

$$T_{a2} = T - (T - T_{a1})\left[1 - \exp\left[-\frac{UA}{\dot{m} C_{\mathrm{P_C}}}\right]\right]$$

For liquid phase reaction, the number of moles are related to conversion

$$N_i = N_{\mathrm{A0}}(\Theta_i + v_i X)$$

The unsteady energy balance

$$\boxed{\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s + (-\Delta H_{\mathrm{Rx}})(-r_{\mathrm{A}} V)}{\sum N_i C_{\mathrm{P}_i}}}$$

$$\Rightarrow \quad \boxed{\frac{dT}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{N_{\mathrm{A0}}(\sum \Theta_i C_{\mathrm{P}_i} + \Delta C_{\mathrm{P}} X)}}$$

Reminder: The sign convention

Heat **Added**

$\dot{Q} = +10\mathrm{J/s}$

Heat **Removed**

$\dot{Q} = -10\mathrm{J/s}$

Work Done **by** System

$\dot{W}_S = +10\mathrm{J/s}$

Work Done **on** System

$\dot{W}_S = -10\mathrm{J/s}$

Special Case 1: Adiabatic operation in unsteady batch reactor

$$N_{A0}\frac{dX}{dt} = -r_A V \qquad \Longleftrightarrow \qquad \frac{dT}{dt} = \frac{(-\Delta H_{Rx})(-r_A V)}{\Sigma N_i C_{P_i}}$$

Substitute for $-r_A V$ from design equation into the energy equation, and multiply by dt

$$dT = \frac{(-\Delta H_{Rx})\,(N_{A0}\,dX)}{\sum N_i\,C_{pi}}$$

Integrate the above equation to get

$$\boxed{X = \frac{\sum \Theta_i C_{P_i}(T - T_0)}{-\Delta H_{Rx}(T)}}$$

or

$$\boxed{T = T_0 + \frac{[-\Delta H_{Rx}(T_0)]X}{\sum \Theta_i C_{P_i} + X\,\Delta C_P}}$$

Special Case 2: Heat Exchanger in a Batch Reactor

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$$

Neglecting ΔC_P the energy balance is $$\frac{dT}{dt} = \frac{\dot{Q}_g - \dot{Q}_r}{N_{A0} C_{P_s}}$$

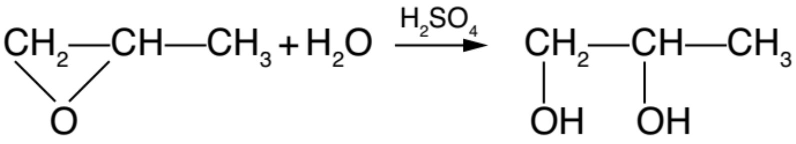
$$\dot{Q}_r = \dot{m}_c C_{P_C} \left\{ (T - T_{a1}) \left[1 - exp\left(\frac{-UA}{\dot{m}_c C_{P_C}} \right) \right] \right\}$$

$$\dot{Q}_g = (-r_A V)(-\Delta H^\circ_{Rx})$$

$$-r_A V = N_{A0} k (1 - X)$$

Example 15.1 Unsteady state batch reactor with heat exchange

Suppose a batch reactor is used for the production of propylene glycol from hydrolysis of propylene oxide according



$$A + B \longrightarrow C$$

The reactor is charged with 4 L of ethylene oxide, 4 L of methanol, and 10 L of water containing 0.1 wt % H_2SO_4. The concentration of pure ethylene oxide and methanol are 13.7 mol/L and 24.7 mol/L respectively. The initial temperature of all materials after mixing is 286 K (13˚C).

If the reactor temperature increases above 350 K (77˚C), a secondary, more exothermic reaction will take over, causing runaway and subsequent explosion. The coolant enters at 290 K (17˚C) and the flow rate through the exchanger is 10 g/s.

$$\Delta H_{Rx} = -20{,}202 \text{ cal/mol}, \; C_{P_A} = 35 \text{ cal/mol/K}, \; C_{P_B} = 18 \text{ cal/mol/K},$$
$$C_{P_C} = 46 \text{ cal/mol/K, and } C_{P_M} = 19.5 \text{ cal/mol/K}.$$

Solution

The number of moles of species fed to the reactor

A: Ethylene oxide: $N_{A0} = (13.7\ \text{mol/dm}^3)\ (4\ \text{dm}^3) = 54.8\ \text{mol}$

B: Water: $N_{B0} = (55.5\ \text{mol/dm}^3)\ (10\ \text{dm}^3) = 555\ \text{mol}$

M: Methanol: $N_{M} = (24.7\ \text{mol/dm}^3)\ (4\ \text{dm}^3) = 98.8\ \text{mol}$

$$C_{P_S} = \Sigma\, \Theta_i C_{P_i} = C_{P_A} + C_{P_B}\Theta_B + C_{P_M}\Theta_M$$

$$\Sigma\Theta_i C_{P_i} = C_{P_S} = 35 + 18\left(\frac{555}{54.8}\right) + 19.5\left(\frac{98.8}{54.8}\right)$$

$$= 35 + 182.3 + 35.2 = 252.5\frac{\text{cal}}{\text{mol}\cdot\text{K}}$$

$$C_{P_S} = 252.5\ \text{cal/mol/K} \quad C_{P_C} = 4.16\ \text{cal/g/s} \quad \dot{m}_c = 10\ \text{g/s}$$

$$N_{A0} = 54.8\ \text{mol, UA} = 10\ \text{cal/K/s}$$

$$T_{a1} = 290\ \text{K, T}_0 = 286\ \text{K}$$

1. Mole Balance, $\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$

2. Rate Law: $-r_A = kC_A$

3. Stoichiometry: $N_A = N_{A0}(1 - X)$

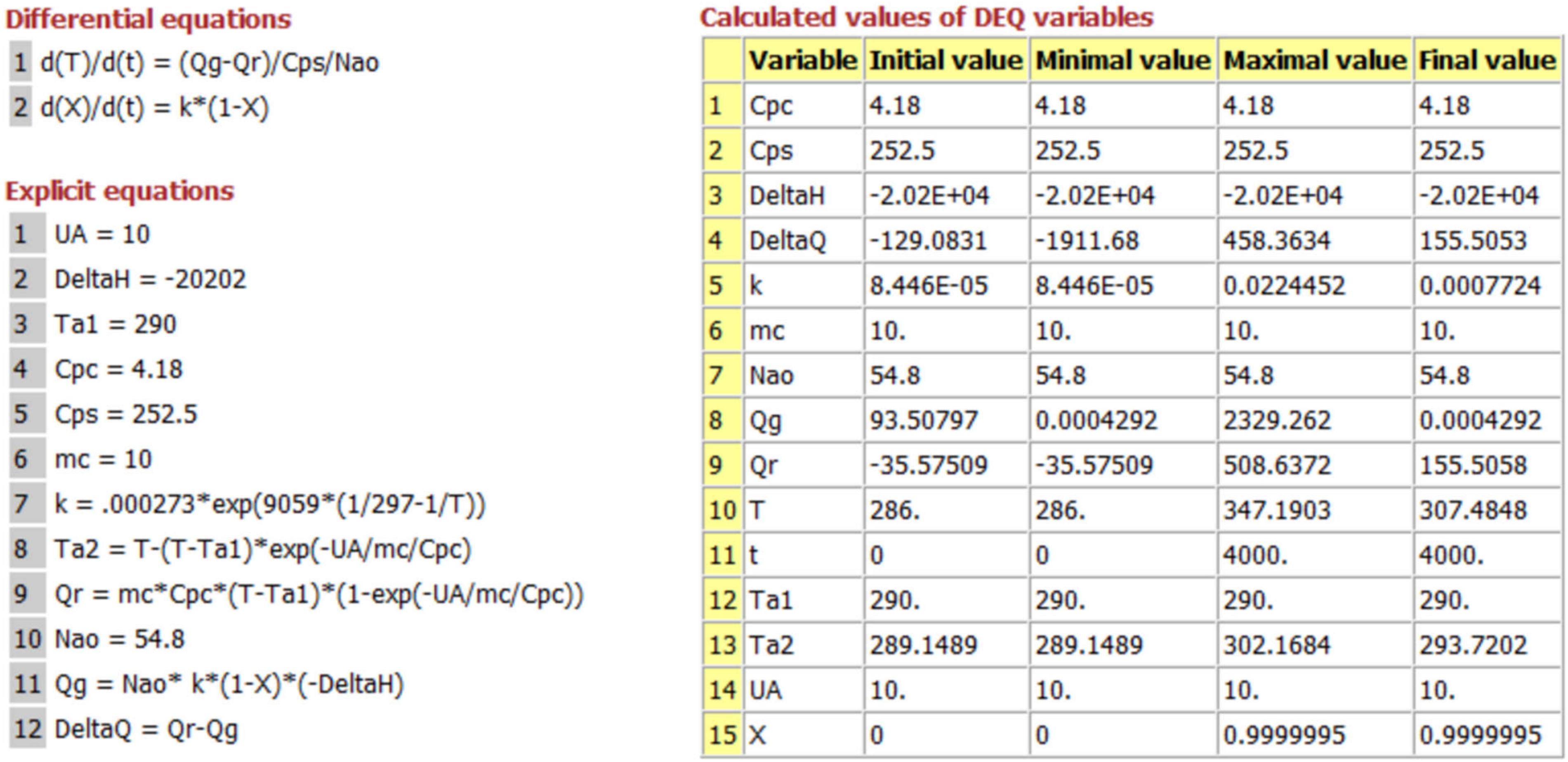
⇨

$$\left\{\begin{array}{l} \text{for liquid batch } V = V_0 \\ \frac{dX}{dt} = k(1 - X) \\ k = (4.71 \times 10^9)\exp\left[\left(\frac{E}{R}\right)\frac{1}{T}\right] s^{-1} \end{array}\right.$$

with $\frac{E}{R} = 9059K$ ⇨ $k = (2.73 \times 10^{-4})\exp\left[9059K\left(\frac{1}{297} - \frac{1}{T}\right)\right] s^{-1}$

4. Energy Balance: $\frac{dT}{dt} = \frac{\dot{Q}_g - \dot{Q}_r}{N_{A0} C_{P_s}}$ ⇨

$$\left\{\begin{array}{l} \dot{Q}_r = \dot{m}_c C_{P_C}\left\{(T - T_{a1})\left[1 - exp\left(\frac{-UA}{\dot{m}_c C_{P_C}}\right)\right]\right\} \\ \dot{Q}_g = (-r_A V)(-\Delta H^\circ_{Rx}) \\ -r_A V = N_{A0} k(1 - X) \end{array}\right.$$



Differential equations

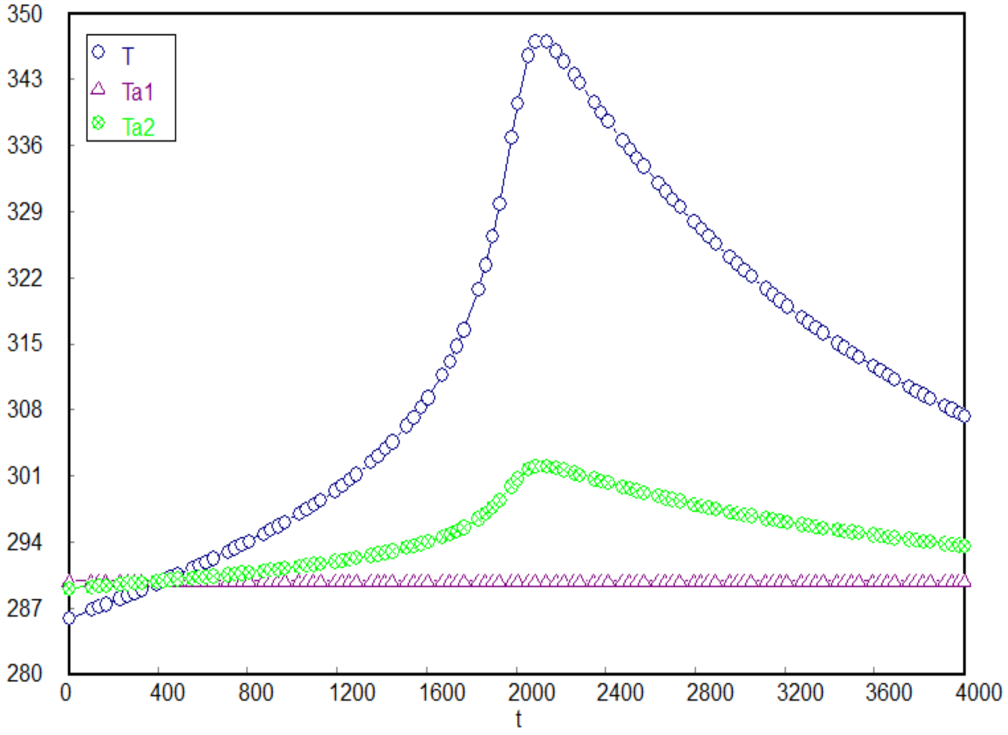
1 d(T)/d(t) = (Qg-Qr)/Cps/Nao
2 d(X)/d(t) = k*(1-X)

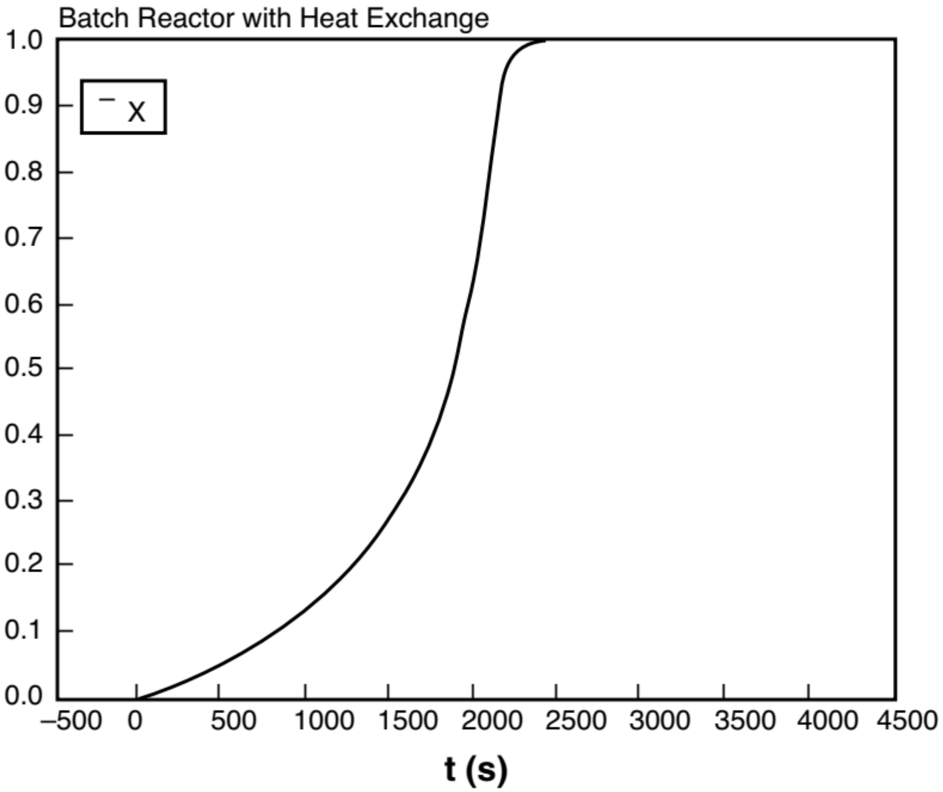
Explicit equations

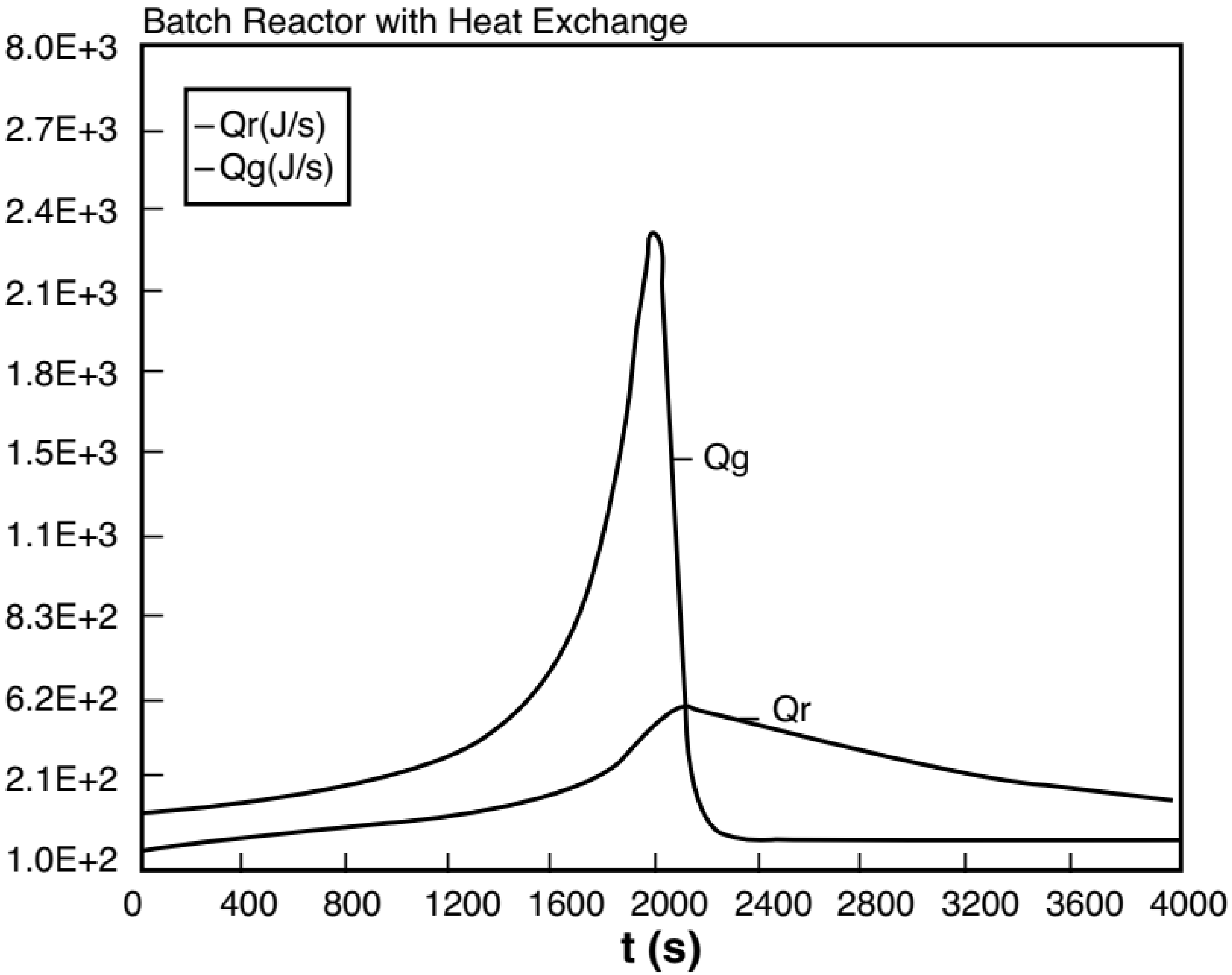
1 UA = 10
2 DeltaH = -20202
3 Ta1 = 290
4 Cpc = 4.18
5 Cps = 252.5
6 mc = 10
7 k = .000273*exp(9059*(1/297-1/T))
8 Ta2 = T-(T-Ta1)*exp(-UA/mc/Cpc)
9 Qr = mc*Cpc*(T-Ta1)*(1-exp(-UA/mc/Cpc))
10 Nao = 54.8
11 Qg = Nao* k*(1-X)*(-DeltaH)
12 DeltaQ = Qr-Qg

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	Cpc	4.18	4.18	4.18	4.18
2	Cps	252.5	252.5	252.5	252.5
3	DeltaH	-2.02E+04	-2.02E+04	-2.02E+04	-2.02E+04
4	DeltaQ	-129.0831	-1911.68	458.3634	155.5053
5	k	8.446E-05	8.446E-05	0.0224452	0.0007724
6	mc	10.	10.	10.	10.
7	Nao	54.8	54.8	54.8	54.8
8	Qg	93.50797	0.0004292	2329.262	0.0004292
9	Qr	-35.57509	-35.57509	508.6372	155.5058
10	T	286.	286.	347.1903	307.4848
11	t	0	0	4000.	4000.
12	Ta1	290.	290.	290.	290.
13	Ta2	289.1489	289.1489	302.1684	293.7202
14	UA	10.	10.	10.	10.
15	X	0	0	0.9999995	0.9999995

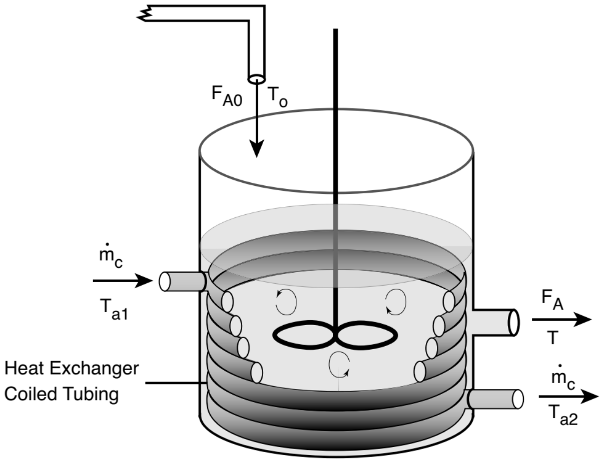

350
343
336
329
322
315
308
301
294
287
280
T
Ta1
Ta2
0
400
800
1200
1600
2000
2400
2800
3200
3600
4000
t


Batch Reactor with Heat Exchange
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
X
–500
0
500
1000
1500
2000
2500
3000
3500
4000
4500
t (s)



Batch Reactor with Heat Exchange
8.0E+3
2.7E+3
2.4E+3
2.1E+3
1.8E+3
1.5E+3
1.1E+3
8.3E+2
6.2E+2
2.1E+2
1.0E+2
—Qr(J/s)
—Qg(J/s)
Qg
Qr
0
400
800
1200
1600
2000
2400
2800
3200
3600
4000
t (s)

Unsteady state semi-batch Reactors



The general transient energy balance:

$$\boxed{\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \Sigma F_{i0} C_{\mathrm{P}_i}(T - T_{i0}) - [\Delta H_{\mathrm{Rx}}(T)](-r_{\mathrm{A}} V)}{\sum N_i C_{\mathrm{P}_i}}}$$

Reduces to:

$$\boxed{\frac{dT}{dt} = \frac{\dot{Q}_{gs} - \dot{Q}_{rs}}{\Sigma N_i C_{\mathrm{P}_i}}}$$

Where

$$\boxed{\dot{Q}_{gs} = (r_{\mathrm{A}} V)(\Delta H_{\mathrm{Rx}})}$$

$$\boxed{\dot{Q}_{rs} = \sum F_{i0} C_{\mathrm{P}_i}(T - T_{i0}) + \dot{m} C_P[T - T_{a1}]\left[1 - exp\left[\frac{-UA}{\dot{m} C_{P_i}}\right]\right]}$$

For large coolant flow rates, the energy balance reduces to

$$\boxed{\frac{dT}{dt} = \frac{\overbrace{(r_A V)(\Delta H_{Rx})}^{Q_{gs}} - \overbrace{[\Sigma F_{i0} C_{P_i}(T - T_{i0}) + UA(T - T_a)]}^{Q_{rs}}}{\Sigma N_i C_{P_i}}}$$

The design equation is written based only on one flow stream; whether there is a feed **IN** or product **OUT**. The general mass balance is

$$\begin{bmatrix}\text{Mass}\\ \text{rate}\\ \text{in}\end{bmatrix} - \begin{bmatrix}\text{Mass}\\ \text{rate}\\ \text{out}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{mass}\\ \text{generation}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\ \text{mass}\\ \text{accumulation}\end{bmatrix}$$

Example 15.2 Unsteady state semi-batch reactor with heat exchange

The second-order saponification of ethyl acetate is to be carried out in a semi-batch reactor according

$$C_2H_5(CH_3COO)(aq) + NaOH(aq) \rightleftharpoons Na(CH_3COO)(aq) + C_2H_5OH(aq)$$

$$A \quad + \quad B \quad \rightleftharpoons \quad C \quad + \quad D$$

Aqueous sodium hydroxide is to be fed at a concentration of 1.0 kmol/m^3, a temperature of 300 K, and a volumetric rate of 0.004 m^3/s to an initial volume of 0.2 m^3 of water and ethyl acetate. The concentration of water in the feed, C_{W0} = 55 kmol/m^3. The initial concentrations of ethyl acetate and water in the reactor are 5 kmol/m3 and 30.7 kmol/m^3, respectively. The reaction is exothermic and it is necessary to add a heat exchanger to keep its temperature below 315 K. A heat exchanger with UA = 3000 J/s·K is available for use. The coolant enters at a mass flow rate of 100 kg/s and a temperature of 285 K.
Plot the reactor temperature, T, and the concentrations, C_A, C_B, and C_C as a function of time.

Solution

Additional information:[3]

$$k = 0.39175 \exp\left[5472.7\left(\frac{1}{273} - \frac{1}{T}\right)\right] \ \mathrm{m^3/kmol \cdot s}$$

$$K_C = 10^{3885.44/T}$$

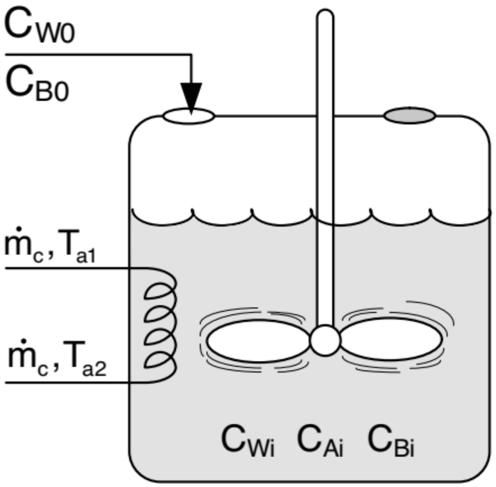
$$\Delta H^\circ_{Rx} = -79{,}076 \text{ kJ/ kmol}$$

$$C_{P_A} = 170.7 \text{ kJ/kmol/K} = 170{,}700 \text{ J/mol/K}$$

$$C_{P_B} = C_{P_C} = C_{P_D} \cong C_{P_W} = C_P = 75.24 \text{ kJ/kmol} \cdot \text{K} = 75{,}246 \text{ J/mol/K}$$

Feed: $C_{W0} = 55 \text{ kmol/m}^3$ $C_{B0} = 1.0 \text{ kmol/m}^3$

Initially: $C_{Wi} = 30.7 \text{ kmol/m}^3$ $C_{Ai} = 5 \text{ kmol/m}^3$ $C_{Bi} = 0$



1. Mole Balances:

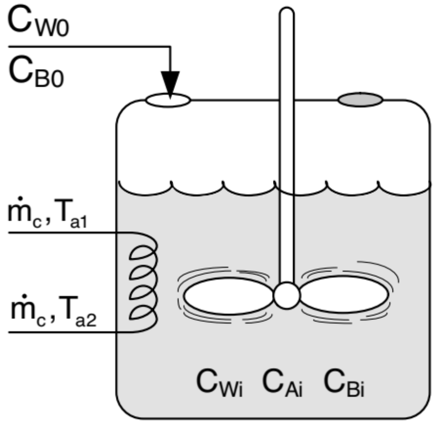
$$C_2H_5(CH_3COO)(aq) + NaOH(aq) \rightleftarrows Na(CH_3COO)(aq) + C_2H_5OH(aq)$$

$$A + B \rightleftarrows C + D$$

$$\frac{dN_A}{dt} = 0 - 0 + r_A V$$

Also, the rate of disappearance of A is

$$r_A V = \frac{dN_A}{dt} = \frac{d(C_A V)}{dt} = \frac{V dC_A}{dt} + C_A \frac{dV}{dt}$$



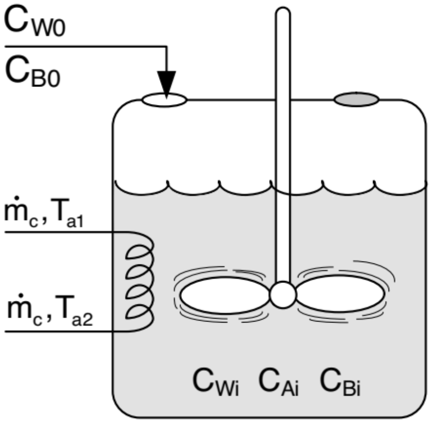
The overall mass balance $\quad \dot{m}_0 - 0 - 0 = \frac{dm}{dt}$

$$\overbrace{\rho_0 v_0} - \overbrace{0} + \overbrace{0} = \overbrace{\frac{d(\rho V)}{dt}}$$

For a constant-density system $\quad \rho_0 = \rho \qquad \frac{dV}{dt} = v_0 \quad ⇒$

$$\boxed{\frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A}$$

For component B (**which is only fed IN**)



$$\frac{dN_B}{dt} = r_B V + F_{B0}$$

$$\frac{dN_B}{dt} = \frac{d(VC_B)}{dt} = \frac{dV}{dt}C_B + \frac{VdC_B}{dt} = r_B V + F_{B0} = r_B V + v_0 C_{B0}$$

$$\Rightarrow \boxed{\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V}}$$

Similarly for C and D

$$\frac{dC_C}{dt} = r_C - \frac{C_C v_0}{V}$$

$$C_D = C_C$$

And water

$$\frac{dN_W}{dt} = C_{W0} v_0$$

2. Rate Law:

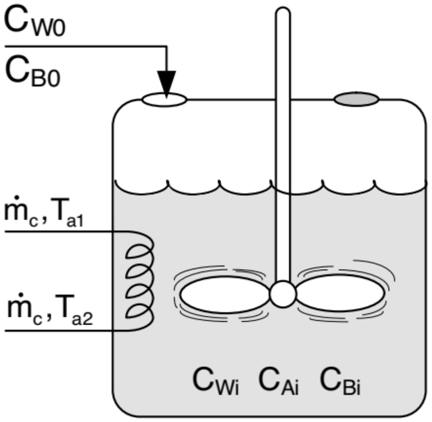
$$-r_A = k\left(C_A C_B - \frac{C_C C_D}{K_C}\right)$$

3. Stoichiometry:

$$-r_A = -r_B = r_C = r_D$$

$$N_A = C_A V$$

$$V = V_0 + v_0 t$$



$$N_{Wi} = V_i C_{W0} = (0.2\ \text{m}^3)(30.7\ \text{kmol/m}^3) = 6.14\ \text{kmol}$$

4. Energy Balance:

$$\boxed{\frac{dT}{dt} = \frac{\dot{Q}_{gs} - \dot{Q}_{rs}}{\Sigma N_i C_P}}$$

$$\dot{Q}_{gs} = (r_A V)(\Delta H_{Rx})$$

$$\dot{Q}_{rs} = \sum F_{i0} C_{P_i} (T - T_{i0}) + \dot{m}_c C_P [T - T_{a1}] \left[1 - exp\left[\frac{-UA}{\dot{m}_c C_{P_i}}\right]\right]$$

Only species **B** (NaOH) and **water** flow into the reactor, The heat removal term reduces to

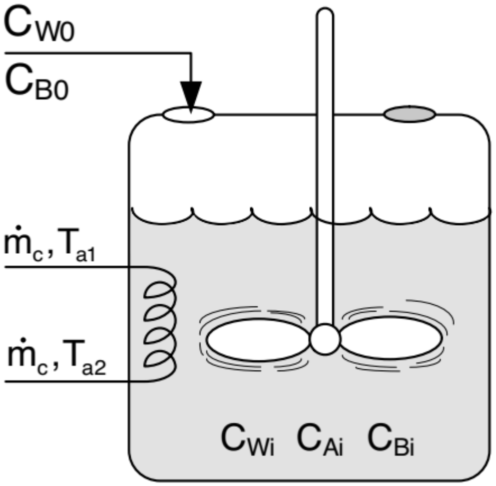
$$\boxed{Q_{rs} = \overbrace{(F_{B0} C_{P_B} + F_w C_{Pw})(T - T_0)}^{\dot{Q}_{rs1}} + \overbrace{\dot{m}_c C_{P_C} [T - T_{a1}] \left[1 - exp\left[\frac{-UA}{\dot{m}_c C_{P_C}}\right]\right]}^{\dot{Q}_{rs2}}}$$

$$F_{B0} = \upsilon_0 C_{B0} = \left(0.004\frac{m^3}{s}\right)\left(1\frac{kmol}{m^3}\right) = 0.004\frac{kmol}{s},$$

$$F_w = \upsilon_0 C_w = \left(0.004\frac{m^3}{s}\right)\left(55\frac{kmol}{m^3}\right) = 0.220\frac{kmol}{s}$$

$$C_{P_A} = 170{,}700 \text{ J/kmol/K}, \;\; C_P = 75{,}246 \text{ J/kmol/K}$$

$$NC_P = C_{P_A} N_A + C_P\,(N_B + N_C + N_D + N_W)$$



Differential equations

1 d(Ca)/d(t) =ra-(v0*Ca)/V

2 d(Cb)/d(t) =rb+(v0*(Cb0-Cb)/V)

3 d(Cc)/d(t) = rc -(Cc*-v0)/N

4 d(T)/d(t) = (Qgs-Qrs)/NCp

5 d(Nw)/d(t) = v0*Cw0

Explicit equations

1 v0 = 0.004

2 Cb0 =1

3 UA = 300

4 cp = 75240

5 T0 = 300

6 Cw0 = 55

7 dh = -7.9076e7

8 k = 0.39175*exp (5472.7*((1/273)-(1/T)))

9 Cd = Cc

10 Vl = 0.2

11 Kc = 10^(3885.44/T)

12 cpa = 170700

13 V = Vi+v0*t

14 ra = -k*((Ca*Cb)-((Cc*Cd)/Kc))

15 Na = V*Ca

16 Nb = V*Cb

17 Nb = V*Cc

18 rb = ra

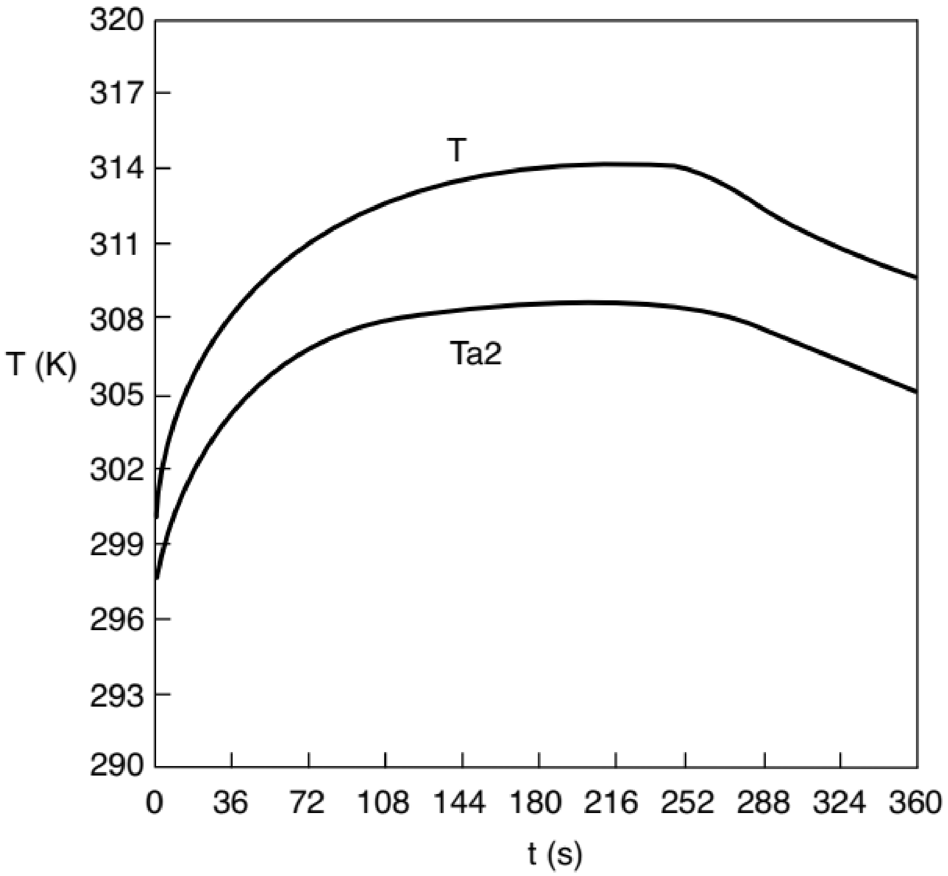
19 rc = -ra

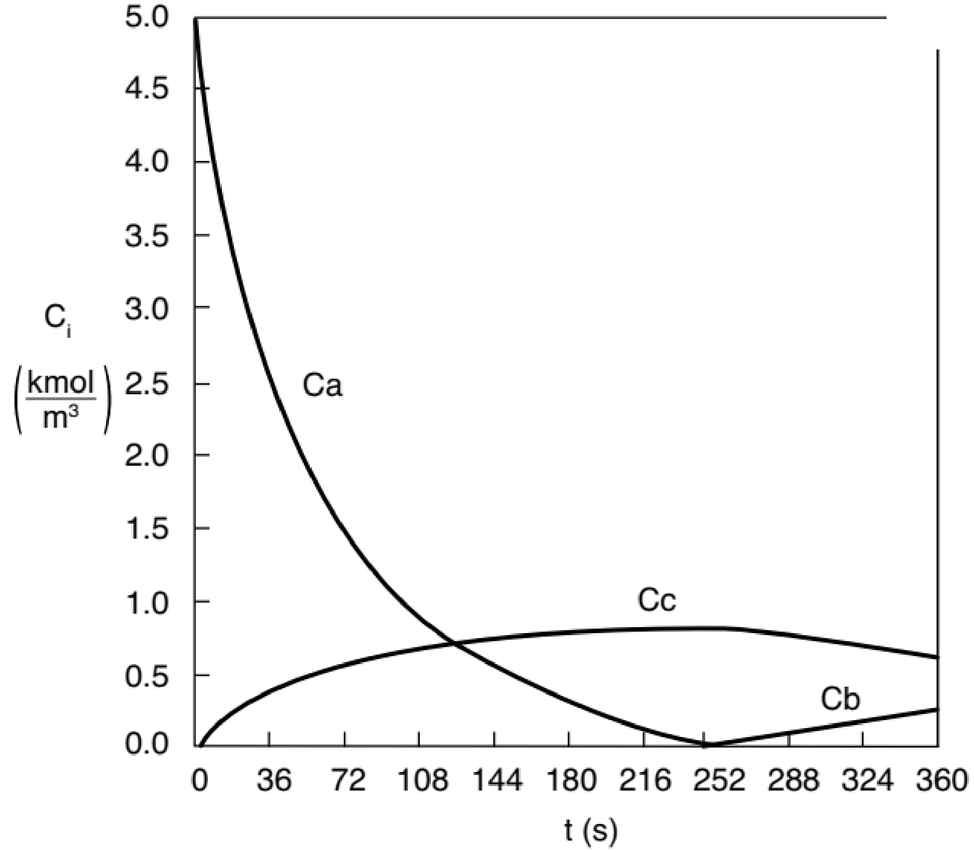
```
20 Nd = V*Cd
21 rate = -ra
22 NCp = cp*(Nb+Nc+Nd+Nw)+cpa*Na
23 Cpc = 18
24 Ta1 = 285
25 mc = 100
26 Qrs2 = -mc*Cpc*(Ta1-T)*(1-exp(-UA/mc/Cpc))
27 Ta2 = T-(T-Ta1)*exp(-UA/mc/Cpc)
28 Fw = Cw0*v0
29 Fb0 = Cb0*v0
30 Qrs1 = ((Fb0*cp)+(Fw*cp))*(T-T0)
31 Qgs = ra*V*dh
32 Qrs = Qrs1 + Qrs2
```

Calculated values of DEQ variables

	Variable	Initial value	Final value
1	Ca	5.	3.981E-13
2	Cb	0	0.2682927
3	Cb0	1.	1.
4	Cc	0	0.6097561
5	Cd	0	0.6097561
6	cp	7.524E+04	7.524E+04
7	cpa	1.707E+05	1.707E+05
8	Cpc	18.	18.
9	Cw0	55.	55.
10	dh	-7.908E+07	-7.908E+07
11	Fb0	0.004	0.004
12	Fw	0.22	0.22
13	k	2.379893	4.211077
14	Kc	8.943E+12	3.518E+12
15	mc	100.	100.

16	Na	1.	6.529E-13
17	Nb	0	0.44
18	Nc	0	1.
19	NCp	6.327E+05	6.605E+06
20	Nd	0	1.
21	Nw	6.14	85.34
22	Qgs	0	6.19E-07
23	Qrs	2.19E+04	1.993E+05
24	Qrs1	0	1.633E+05
25	Qrs2	2.19E+04	3.604E+04
26	ra	0	-4.773E-15
27	rate	0	4.773E-15
28	rb	0	-4.773E-15
29	rc	0	4.773E-15
30	t	0	360.
31	T	300.	309.6878
32	T0	300.	300.
33	Ta1	285.	285.
34	Ta2	297.1669	305.0248
35	UA	3000.	3000.
36	V	0.2	1.64
37	v0	0.004	0.004
38	Vi	0.2	0.2


T (K)
320
317
314
311
308
305
302
299
296
293
290
0
36
72
108
144
180
216
252
288
324
360
t (s)
T
Ta2


C_i
$\left(\frac{kmol}{m^3}\right)$
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
36
72
108
144
180
216
252
288
324
360
t (s)
Ca
Cc
Cb

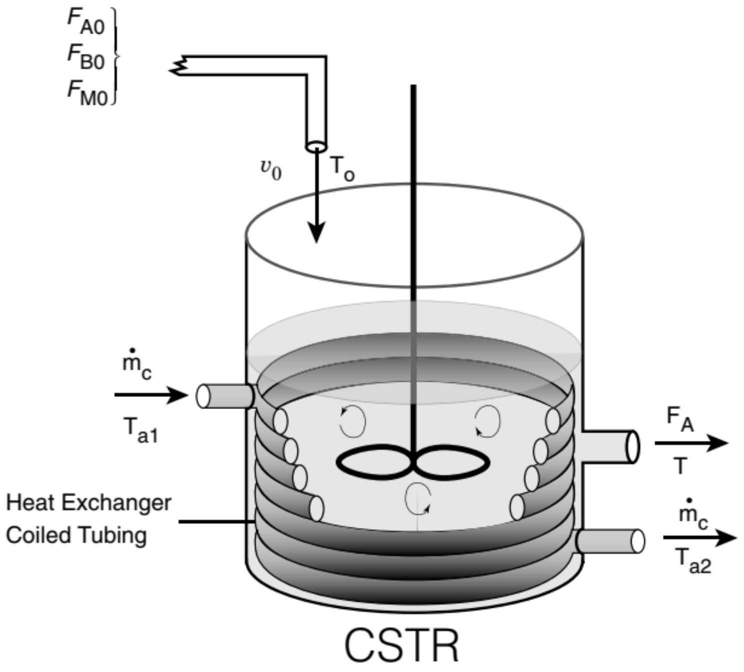
Topic 16. Unsteady-State, Non-isothermal CSTR and PFR operation

This lecture

- ✓ Unsteady Operation of a CSTR
- ✓ Non-isothermal Multiple Reactions

Unsteady Operation of a CSTR

The general transient mass balance is similar to that of a semi-batch reactor where there is variation in volume, as well as, concentration with time.



$$A + B \longrightarrow C$$

$$\frac{dN_A}{dt} = F_{Ao} - F_A + r_A V$$

$$\frac{dN_B}{dt} = F_{Bo} - F_B + r_B V$$

$$\frac{dN_C}{dt} = F_{Co} - F_C + r_C V$$

$$\frac{dC_i}{dt} = \frac{\nu_{in}}{V} C_{i\,in} - \frac{\nu_{out}}{V} C_{i\,out} + r_i$$

The rate of disappearance of A is $$r_{\mathrm{A}}V = \frac{dN_{\mathrm{A}}}{dt} = \frac{d(C_{\mathrm{A}}V)}{dt} = \frac{VdC_{\mathrm{A}}}{dt} + C_{\mathrm{A}}\frac{dV}{dt}$$

and $$\frac{dN_A}{dt} = F_{Ao} - F_A + r_A V$$

Combine the above equations: ➡ $$\frac{dC_{\mathrm{A}}}{dt} = r_{\mathrm{A}} + \frac{(C_{\mathrm{A0}} - C_{\mathrm{A}})v_0}{V}$$

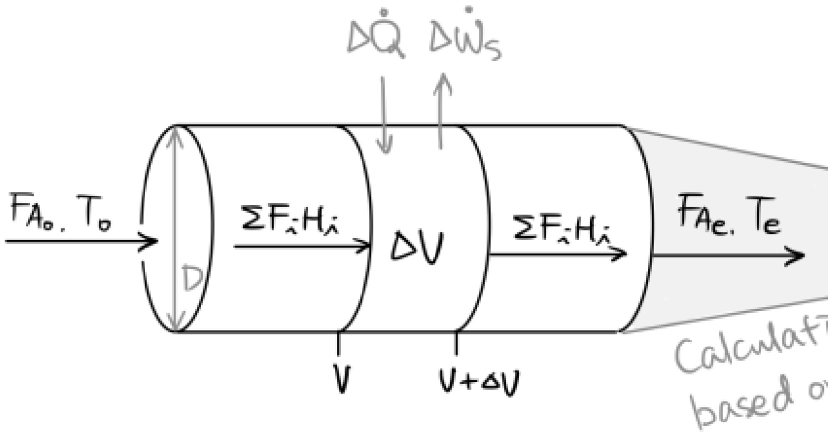
Similarly for component B: $$\frac{dC_{\mathrm{B}}}{dt} = r_{\mathrm{B}} + \frac{(C_{\mathrm{B0}} - C_{\mathrm{B}})v_0}{V}$$

And for C: ($F_{Co} = 0$) $$\frac{dC_{\mathrm{C}}}{dt} = r_{\mathrm{C}} + \frac{-C_{\mathrm{C}}v_0}{V}$$

Energy Balance:

$$\frac{dT}{dt}=\frac{\dot{Q}_{\mathrm{gs}}-\dot{Q}_{\mathrm{rs}}}{NC_{\mathrm{P}}}\qquad\left\{\begin{array}{l}\dot{Q}_{\mathrm{gs}}=\left(r_{\mathrm{A}}V\right)\left(\Delta H_{\mathrm{Rx}}\right)\\[2ex] \dot{Q}_{\mathrm{rs}}=\overbrace{F_{\mathrm{A0}}\sum\Theta_{\mathrm{i}}C_{\mathrm{P_i}}\left(T-T_0\right)}^{Q_{\mathrm{rs1}}}+\overbrace{\dot{m}_{\mathrm{c}}C_{\mathrm{P_c}}\left(T-T_{\mathrm{a1}}\right)\left[1-\exp\left[\frac{-UA}{\dot{m}_{\mathrm{c}}C_{\mathrm{P_c}}}\right]\right]}^{Q_{\mathrm{rs2}}}\end{array}\right.$$

Unsteady Operation of a PFR



The general transient mass balance is similar to that of a semi-batch reactor where there is variation in volume, as well as, concentration with time.

$$A + B \longrightarrow C$$

$$\frac{dN_A}{dt} = F_{Ao} - F_A + r_A V$$

$$\frac{dN_B}{dt} = F_{Bo} - F_B + r_B V$$

$$\frac{dN_C}{dt} = F_{Co} - F_C + r_C V$$

$$\frac{dC_i}{dt} = \frac{\nu_{in}}{V} C_{i\,in} - \frac{\nu_{out}}{V} C_{i\,out} + r_i$$

Energy Balance:

$$\frac{\partial E_{sys}}{\partial t} = \Delta\dot{Q} - \Delta\dot{w}_s - \left[\sum F_i H_i\,|_{V+\Delta V} - \sum F_i H_i\,|_V\right]$$

$$\hat{E}_{\text{sys}} = \sum_{i=1}^{m} N_i E_i = \sum_{i=1}^{m} N_i U_i = \left[\sum_{i=1}^{m} N_i (H_i - PV_i)\right]_{\text{sys}}$$

$$E_{sys} = \sum N_i H_i - P \sum N_i V_i = \sum C_i H_i \Delta V - P\Delta V$$

$$N_i = C_i \Delta V$$

$$\frac{\partial E_{sys}}{\partial t} = \Delta V\left[\sum C_i \frac{\partial H_i}{\partial t} + \sum \frac{\partial C_i}{\partial t} H_i - \frac{\partial P}{\partial t}\right]$$

$$\left[\sum C_i \frac{\partial H_i}{\partial t} + \sum \frac{\partial C_i}{\partial t} H_i - \frac{\partial P}{\partial t}\right] = \frac{\Delta\dot{Q}}{\Delta V} - \frac{\Delta\dot{w}_s}{\Delta V} - \frac{\left[\sum F_i H_i|_{V+\Delta V} - \sum F_i H_i|_V\right]}{\Delta V}$$

Rearrange, $\Delta V \rightarrow 0$

$$\frac{\partial \dot{Q}}{\partial V} - \frac{\partial \dot{w}_s}{\partial V} - \sum F_i \frac{\partial H_i}{\partial V} - \sum H_i \left(\frac{\partial F_i}{\partial V} + \frac{\partial C_i}{\partial t} \right) = \sum C_i \frac{\partial H_i}{\partial t} - \frac{\partial P}{\partial t}$$

Unsteady-state mole balance for PFR

$$\frac{\partial N_i}{\partial t} = r_i \Delta V + F_i|_V - F_i|_{V+\Delta V}$$

⇨

$$\frac{\partial C_i}{\partial t} = r_i - \frac{\partial F_i}{\partial V}$$

⇨

$$r_i = \frac{\partial C_i}{\partial t} + \frac{\partial F_i}{\partial V}$$

Substitute in the energy equation

$$\frac{\partial \dot{Q}}{\partial V} - \frac{\partial \dot{w}_s}{\partial V} - \sum F_i \frac{\partial H_i}{\partial V} - \sum H_i (r_i) = \sum C_i \frac{\partial H_i}{\partial t} - \frac{\partial P}{\partial t}$$

Write the energy balance in term of the key component, for example (*A*)

$$\frac{\partial \dot{Q}}{\partial V} - \frac{\partial \dot{w}_s}{\partial V} - \sum F_i \frac{\partial H_i}{\partial V} - \sum H_i(\nu_i r_A) = \sum C_i \frac{\partial H_i}{\partial t} - \frac{\partial P}{\partial t} \qquad \text{where } \boxed{r_i = \nu_i(-r_A)}$$

Assumption: No variation in shaft work and pressure with time ⇒

$$\boxed{\frac{\partial \dot{Q}}{\partial V} - \sum F_i \frac{\partial H_i}{\partial V} - \sum H_i(-\nu_i r_A) = \sum C_i \frac{\partial H_i}{\partial t}}$$

A. Co-current Flow

$$\boxed{\frac{\partial T_a}{\partial V} = \frac{Ua(T - T_a)}{\dot{m}C_p} = f(T, T_a)}$$

B. Counter-current Flow

$$\boxed{\frac{\partial T_a}{\partial V} = \frac{Ua(T_a - T)}{\dot{m}C_p} = f(T, T_a)}$$

$$\frac{\partial \dot{Q}}{\partial V}-\sum F_i\frac{\partial H_i}{\partial V}-\sum H_i(-\nu_i r_A)=\sum C_i\frac{\partial H_i}{\partial t}$$

But $\frac{\partial H_i}{\partial V}=C_{pi}\frac{\partial T}{\partial V}$ and $-\sum H_i(-\nu_i r_A)=(-r_A)(\Delta H_R)$

⇒

$$\boxed{Ua(T_a-\mathrm{T})-\left[\sum F_i\,C_{pi}\right]\frac{\partial T}{\partial V}+(-r_A)(-\Delta H_R)=\left[\sum C_i\,C_{pi}\right]\frac{\partial T}{\partial t}}$$

Co-current Flow

$$\boxed{\frac{\partial T_a}{\partial V}=\frac{Ua(T-T_a)}{\dot{m}C_p}=f(T,T_a)}$$

Counter-current Flow

$$\boxed{\frac{\partial T_a}{\partial V}=\frac{Ua(T_a-T)}{\dot{m}C_p}=f(T,T_a)}$$

Either of these equation must be coupled with design and rate equations

$$\frac{\partial C_i}{\partial t}=\nu_i r_A-\frac{\partial F_i}{\partial t}$$

and

$$r_A=f(C_i)$$

If the system is under steady state condition, these energy equations

$$Ua(T_a - \mathrm{T}) - \left[\sum F_i\, C_{pi}\right]\frac{\partial T}{\partial V} + (-r_A)(-\Delta H_R) = \left[\sum C_i\, C_{pi}\right]\frac{\partial T}{\partial t}$$

Reduce to

$$\boxed{\frac{dT}{dV} = \frac{Ua(T_a - \mathrm{T}) + \left[-\Delta H_{Rx}^{o}(T_R) - \left(\int_{T_R}^{T} \Delta C_p\, dT\right)\right](-r_A)}{F_{A0}\left(\sum_{i=1}^{n} \theta_i C_{pi} + X\, \Delta C_p\right)} = f(X, T, T_a)}$$

And the unsteady state design equation

$$\frac{\partial C_i}{\partial t} = \nu_i r_A - \frac{\partial F_i}{\partial t} \qquad \text{and} \qquad r_A = f(C_i)$$

Reduces to

$$0 = \nu_i r_A - \frac{\partial F_i}{\partial t} \qquad \text{or} \qquad \frac{\partial F_i}{\partial t} = \nu_i r_A = r_i$$

$$r_A = f(C_i) \qquad\qquad r_i = f(C_i)$$

Non-isothermal Multiple Reactions for Batch and semi-batch reactors

$$\boxed{\frac{dT}{dt}=\frac{\dot{m}_c C_{\mathrm{P}_c}(T_{a1}-T)[1-\exp(-UA/\dot{m}_c C_{\mathrm{P}_c})]+\sum_{i=1}^{q} r_{ij}\ V\ \Delta H_{\mathrm{Rx}ij}(T)-\sum_{j=1}^{m} F_{j0}C_{\mathrm{P}j}\left(T-T_0\right)}{\sum_{j=1}^{m} N_{j0}C_{\mathrm{P}j}}}$$

For large coolant
flow rates

$$\boxed{\frac{dT}{dt}=\frac{V\sum_{i=1}^{q} r_{ij}\ \Delta H_{\mathrm{Rx}ij}-UA(T-T_a)-\sum_{j=1}^{m} F_{j0}C_{\mathrm{P}_j}(T-T_0)}{\sum_{j=1}^{m} N_j C_{\mathrm{P}_j}}}$$