# Advanced Reactor Design

## Week 2

## Models for Nonideal Reactors

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# Introduction

- This presentation covers models for nonideal reactors with a focus on residence time distribution (RTD) and reactor flow behavior.

# Topics to be Addressed

- - Residence Time Distribution (RTD)
- - Nonideal Flow Patterns
- - Models for Mixing
- - Calculation of Exit Conversion
- - Reactor Performance Assessment

# Objectives

- - Understand the principles of nonideal flow in reactors
- - Learn how to use RTD for analyzing reactor performance
- - Apply mathematical models for mixing and conversion calculation
- - Compare different reactor modeling approaches

# Some Guidelines

RTD
Model
Kinetic Data

→

Exit Concentration
Exit Conversion

1.The model must be mathematically tractable.

The equations used to describe a chemical reactor should be able to be solved without an inordinate expenditure of human or computer time.

2.The model must realistically describe the characteristics of the nonideal reactor:

The phenomena occurring in the nonideal reactor must be reasonably described physically, chemically, and mathematically.

3.The model must not have more than two adjustable parameters.

This constraint is used because an expression with more than two adjustable parameters can be fitted to a great variety of experimental data, and the modeling process in this circumstance is nothing more than an exercise in curve fitting.

A one-parameter model is, of course, superior to a two-parameter model if the one-parameter model is sufficiently realistic.

To fair, however, in complex systems (e.g., internal diffusion and conduction, mass transfer limitations) where other parameters may be measured independently, then more than two parameters are quite acceptable.

# Nonideal Flow & Reactor Design

- So far, the reactors we have considered ideal flow patterns
  - Residence time of all molecules are identical
  - Perfectly mixed CSTRs & batch reactors
  - No radial diffusion in a PFR/PBR

- **Goal: mathematically describe non-ideal flow and solve design problems for reactors with nonideal flow**
  - Identify possible deviations
  - Measurement of residence time distribution
  - Models for mixing
  - Calculation of exit conversion in real reactors

# One-Parameter Models

~Tanks-in-series model

modeling tubular reactors as a series of identically sized CSTRs

a parameter is the number of tanks, n

~Dispersion model

a modification of the ideal reactor by imposing axial dispersion on plug flow

a parameter is the dispersion coefficient

## Two-Parameter Models

Using a combination of ideal reactors to model the real reactor

We could model the real reactor as two ideal PBRs in parallel with the two parameter being the fluid that channels, $v_b$, and the reactor dead volume, $V_D$. The reactor volume is $V=V_D+V_S$ with $v_0=v_b+v_S$.

Considering a packed bed reactor with channeling

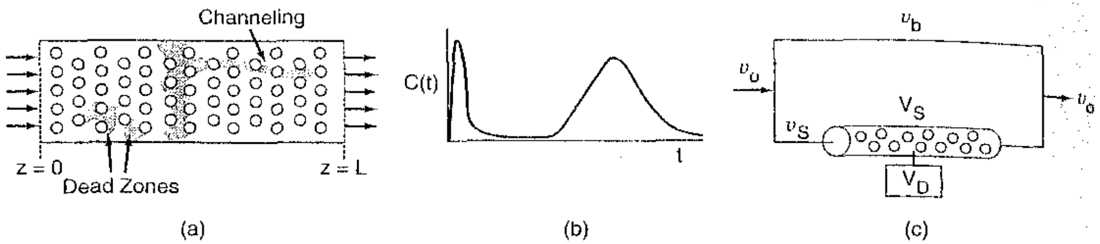
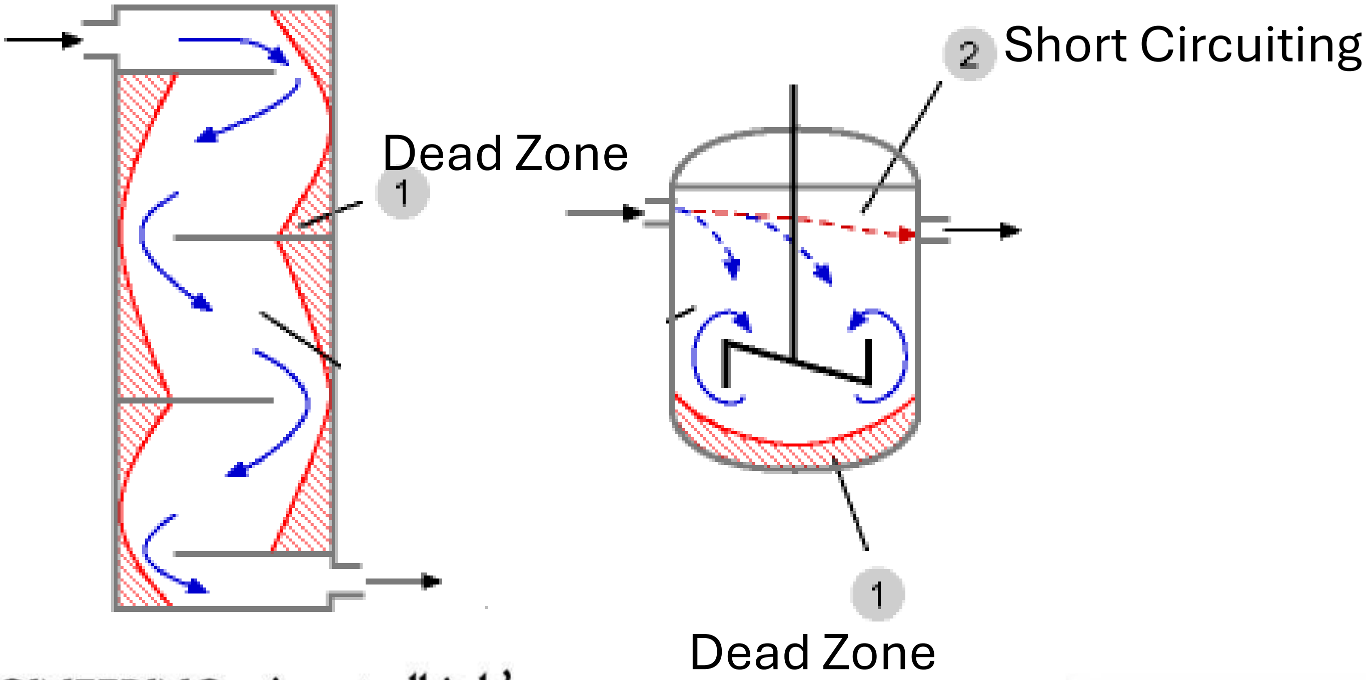


**Figure 14-1** (a) Real system; (b) outlet for a pulse input; (c) model system.

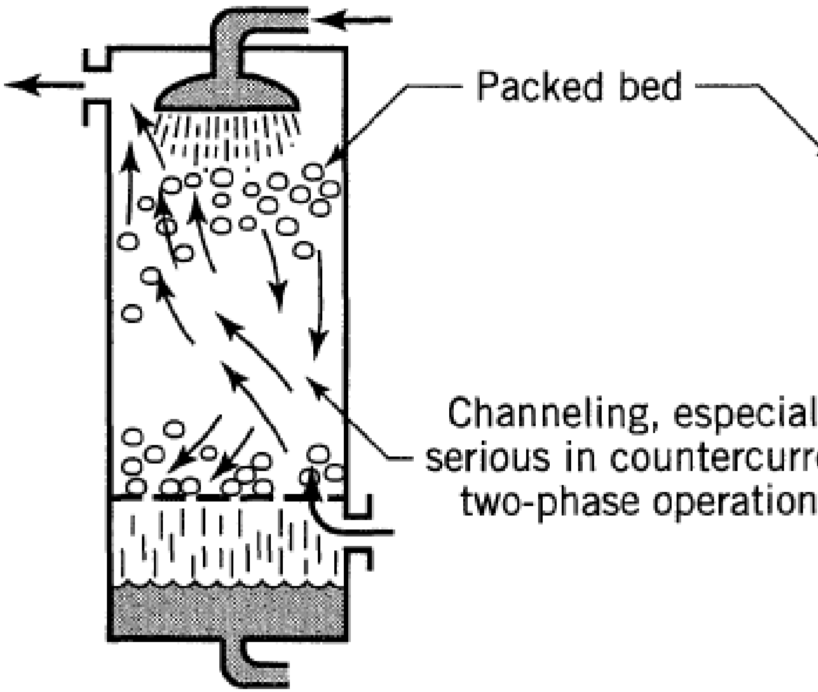
# Nonideal Flow in a CSTR

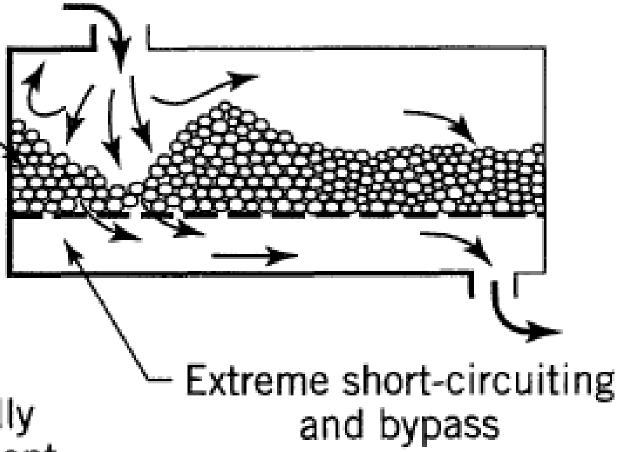
- Ideal CSTR: uniform reactant concentration throughout the vessel
- Real stirred tank
    - Relatively high reactant concentration at the feed entrance
    - Relatively low concentration in the stagnant regions, called dead zones (usually corners and behind baffles)

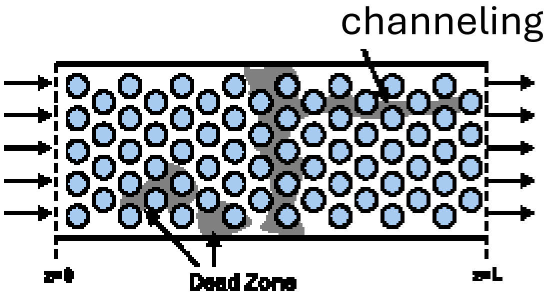


# Nonideal Flow in a PBR

- **Ideal plug flow reactor**: all reactant and product molecules at any given axial position move at same rate in the direction of the bulk fluid flow
- **Real plug flow reactor**: fluid velocity profiles, turbulent mixing, & molecular diffusion cause molecules to move with changing speeds and in different directions







# Residence Time Distribution (RTD)

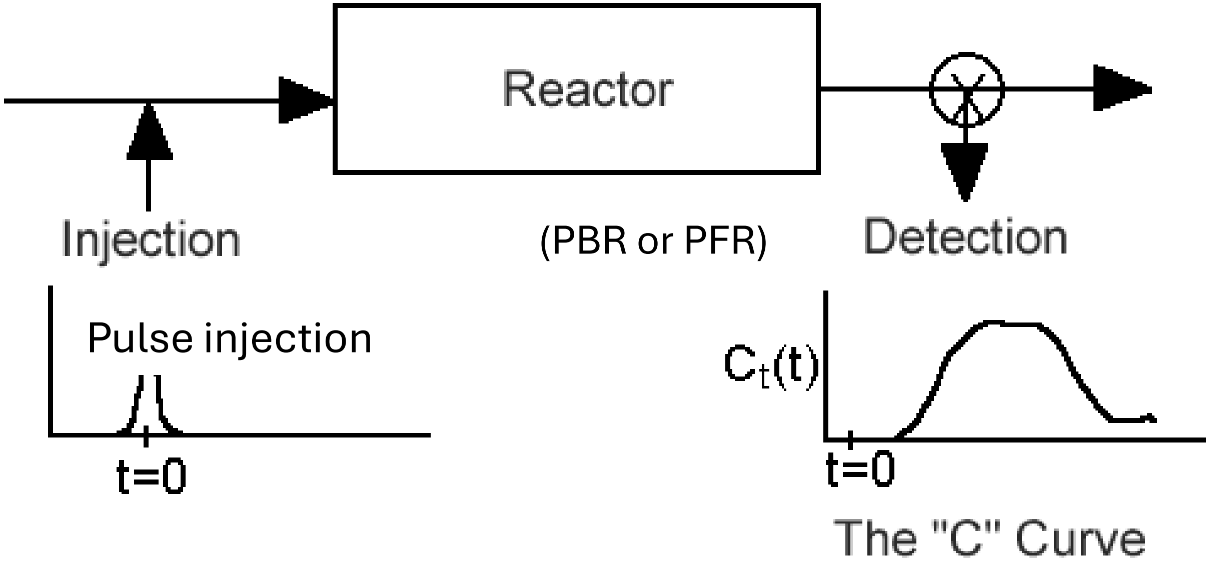
Flow through a reactor is characterized by:

1. The amount of time molecules spend in the reactor, called the RTD
2. Quality of mixing

RTD ≡ E(t) ≡ “residence time distribution” function

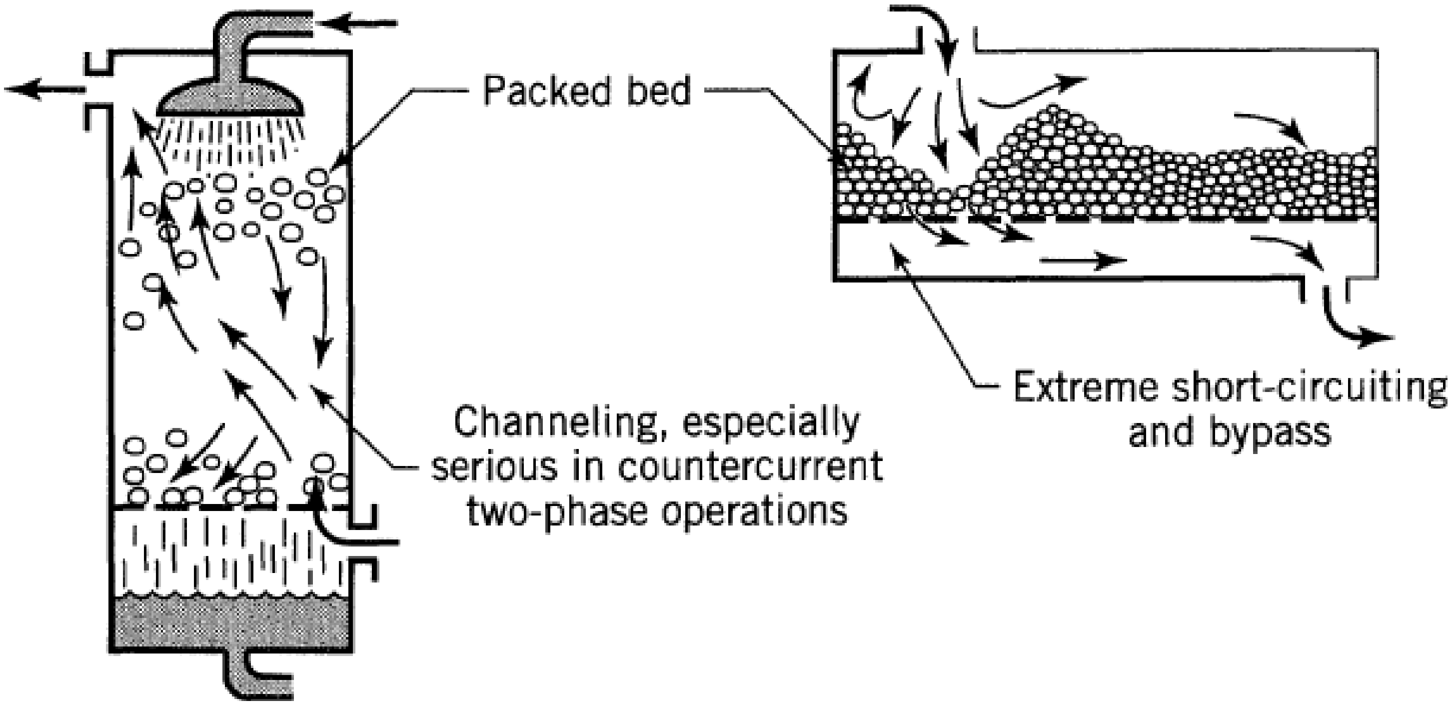
- RTD is measured experimentally by injecting an inert “tracer” at t=0 and measuring the tracer concentration C(t) at the exit as a function of time
- Tracer should be easy to detect & have physical properties similar to the reactant

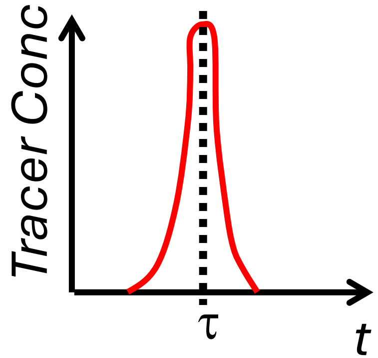
## Measurement of RTD



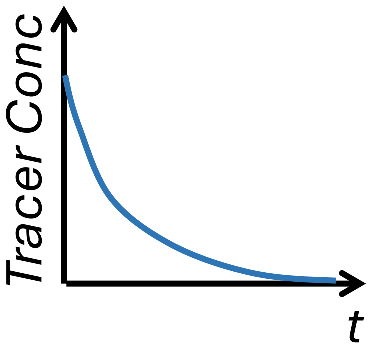
This plot would have the same shape as the pulse injection if the reactor had perfect plug flow

# RTD Profiles & Cum RTD Function F(t)

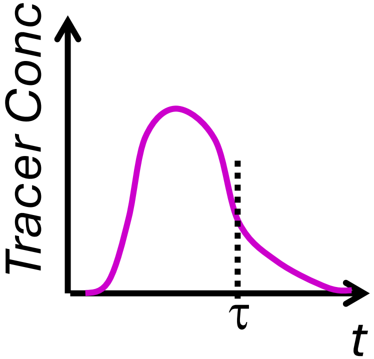




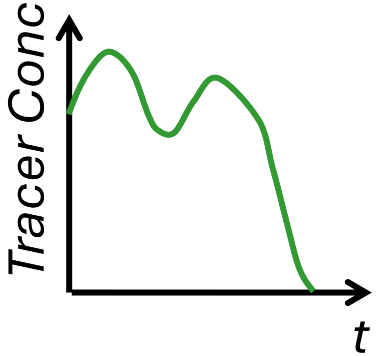
Nearly ideal PFR



Nearly ideal CSTR

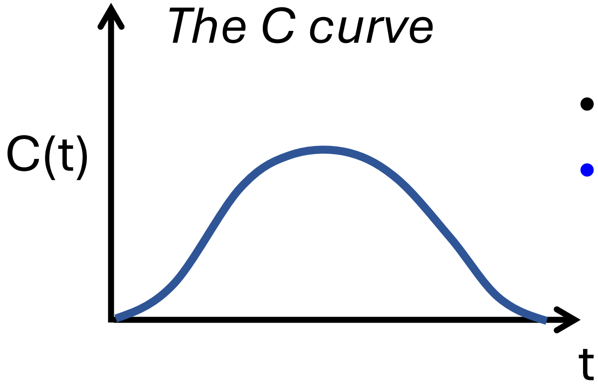


PBR w/ channeling & dead zones



CSTR with dead zones

# Calculation of RTD



- RTD ≡ E(t) ≡ “residence time distribution” function
- RTD describes the amount of time molecules have spent in the reactor

$$E(t)=\frac{C(t)}{\int_0^\infty C(t)dt}=\frac{\text{tracer concentration at reactor exit between time t and t+}\Delta\text{t}}{\text{sum of tracer concentration at exit for an infinite time}}$$

Fraction of material leaving the reactor that has resided in the reactor for a time between $t_1$ & $t_2$ $=\int_{t_1}^{t_2} E(t)dt$

$$\int_0^\infty E(t)dt=1$$

E(t)=0 for t<0 since no fluid can exit before it enters

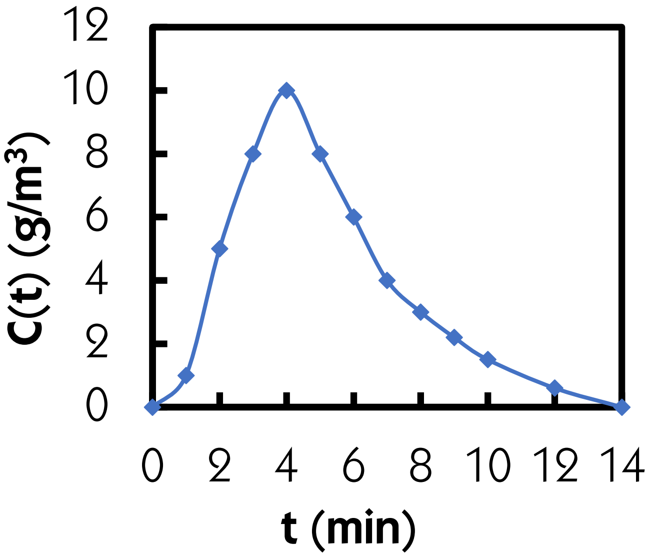
E(t)≥0 for t>0 since mass fractions are always positive

Fraction of fluid element in the exit stream with age less than $t_1$ is: $\int_0^{t_1} E(t)dt$

A pulse of tracer was injected into a reactor, and the effluent concentration as a function of time is in the graph below. Construct a figure of C(t) & E(t) and calculate the fraction of material that spent between 3 & 6 min in the reactor

| **t min** | **0** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **14** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C g/m$^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |

Plot C vs time:



Tabulate E(t): divide C(t) by the total area under the C(t) curve, which must be numerically evaluated

$$\int_0^{\infty} C(t)dt = \int_0^{10} C(t)dt + \int_{10}^{14} C(t)dt$$

$$\int_{X_0}^{X_N} f(x)dx = \frac{\Delta t}{3}\left(f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_4 \ldots + 4f_{N-1} + f_N\right)$$

$$\int_0^{10} C(t)dt = \frac{1}{3}\left[\begin{array}{l} 0+4(1)+2(5)+4(8)+2(10)+4(8) \\ +2(6)+4(4)+2(3)+4(2.2)+1.5 \end{array}\right]$$

$$\rightarrow \int_0^{10} C(t)dt = 47.4\,\frac{g\cdot min}{m^3}$$

A pulse of tracer was injected into a reactor, and the effluent concentration as a function of time is in the graph below. Construct a figure of C(t) & E(t) and calculate the fraction of material that spent between 3 & 6 min in the reactor

| **t min** | **0** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **14** |
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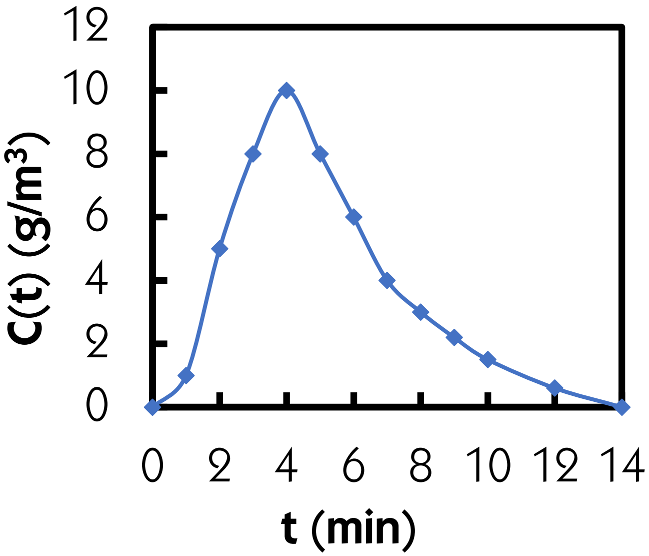


Tabulate E(t): divide C(t) by the total area under the C(t) curve, which must be numerically evaluated

$$\int_0^\infty C(t)dt = \int_0^{10} C(t)dt + \int_{10}^{14} C(t)dt$$

$$\int_{x_0}^{x_2} f(x)dx = \frac{\Delta t}{3}\left(f_0 + 4f_1 + f_2\right)$$

$$\int_{10}^{14} C(t)dt = \frac{2}{3}\left[1.5 + 4(0.6) + 0\right] = 2.6$$

$$\rightarrow \int_0^\infty C(t)dt = 47.4\frac{g\cdot min}{m^3} + 2.6\frac{g\cdot min}{m^3} = 50\frac{g\cdot min}{m^3}$$

A pulse of tracer was injected into a reactor, and the effluent concentration as a function of time is in the graph below. Construct a figure of C(t) & E(t) and calculate the fraction of material that spent

| t<br>min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C<br>$g/m^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

$$\int_0^\infty C(t)\,dt = 50\,\frac{g\cdot min}{m^3}$$

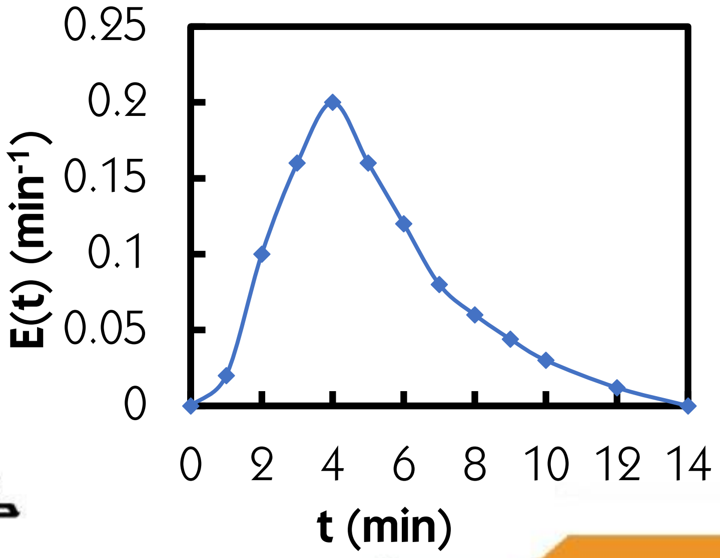
Plot E vs time:

Tabulate E(t): divide C(t) by the total area under the C(t) curve:

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt}$$

$$E(t_0) = \frac{0}{50} = 0 \qquad E(t_1) = \frac{1}{50} = 0.02$$

$$E(t_2) = \frac{5}{50} = 0.1 \qquad E(t_3) = \frac{8}{50} = 0.16$$

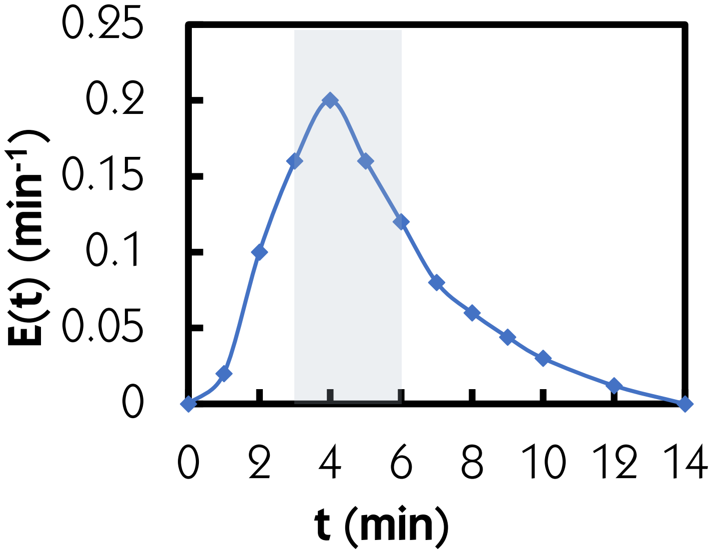


A pulse of tracer was injected into a reactor, and the effluent concentration as a function of time is in the graph below.

Construct a figure of C(t) & E(t) and calculate the fraction of material that spent between 3 & 6 min in the reactor

| t<br>min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C<br>g/m$^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

E vs time:



Fraction of material that spent between 3 & 6 min in reactor = area under E(t) curve between 3 & 6 min

Evaluate numerically:

$$\int_{X_0}^{X_3} f(x)dx = \frac{3}{8}\Delta t\left(f_0 + 3f_1 + 3f_2 + f_3\right)$$

$$\int_3^6 E(t) = \frac{3}{8}(1)\left(0.16 + 3(0.2) + 3(0.16) + 0.12\right)$$

$$\rightarrow \int_3^6 E(t) = 0.51$$

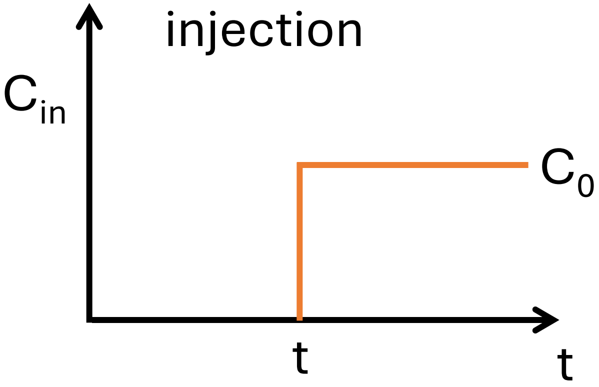
# Step-Input to Determine E(t)

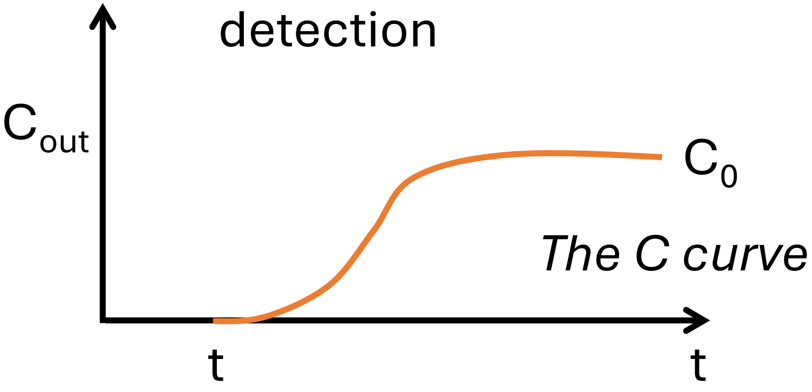
Disadvantages of pulse input:

- Injection must be done in a very short time
- Can be inaccurate when the c-curve has a long tail
- Amount of tracer used must be known

Alternatively, E(t) can be determined using a step input:

- Conc. of tracer is kept constant until outlet conc. = inlet conc.



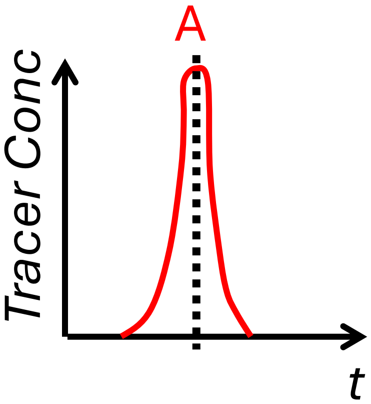


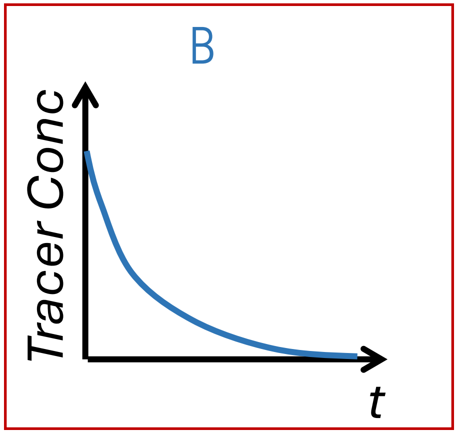
$$C_{out} = C_0 \int_0^t E(t)\,dt$$

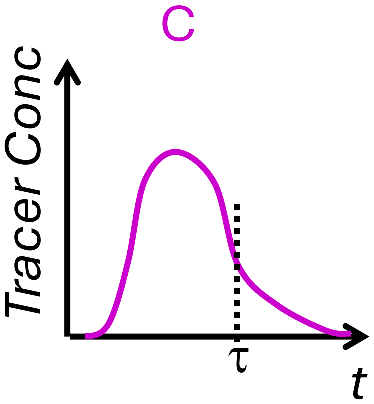
$$E(t) = \frac{d}{dt}\left(\frac{C(t)}{C_0}\right)_{step}$$

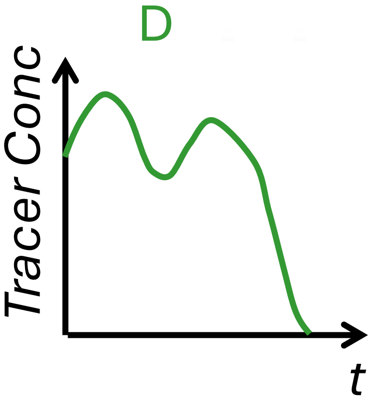
# Questions

1. Which of the following graphs would you expect to see if a pulse tracer test were performed on an ideal CSTR?

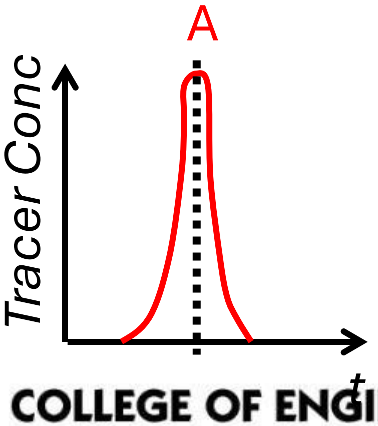


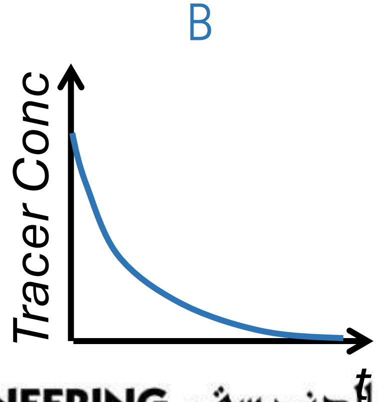


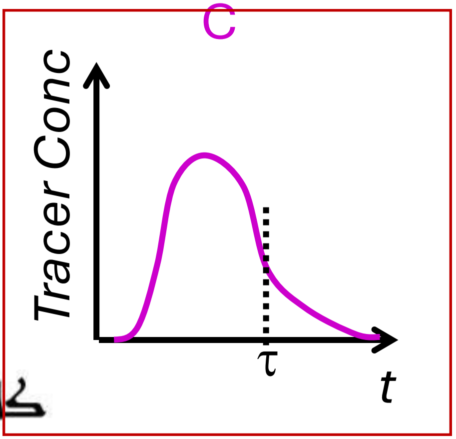


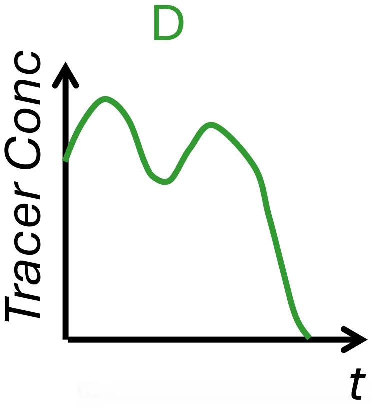


2. Which of the following graphs would you expect to see if a pulse tracer test were performed on a PBR that had dead zones?





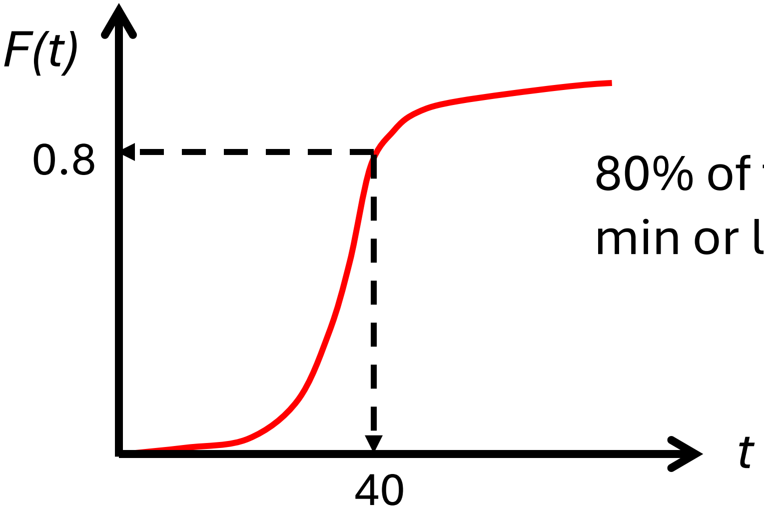




# Cumulative RTD Function F(t)

F(t) = fraction of effluent that has been in the reactor for less than time t

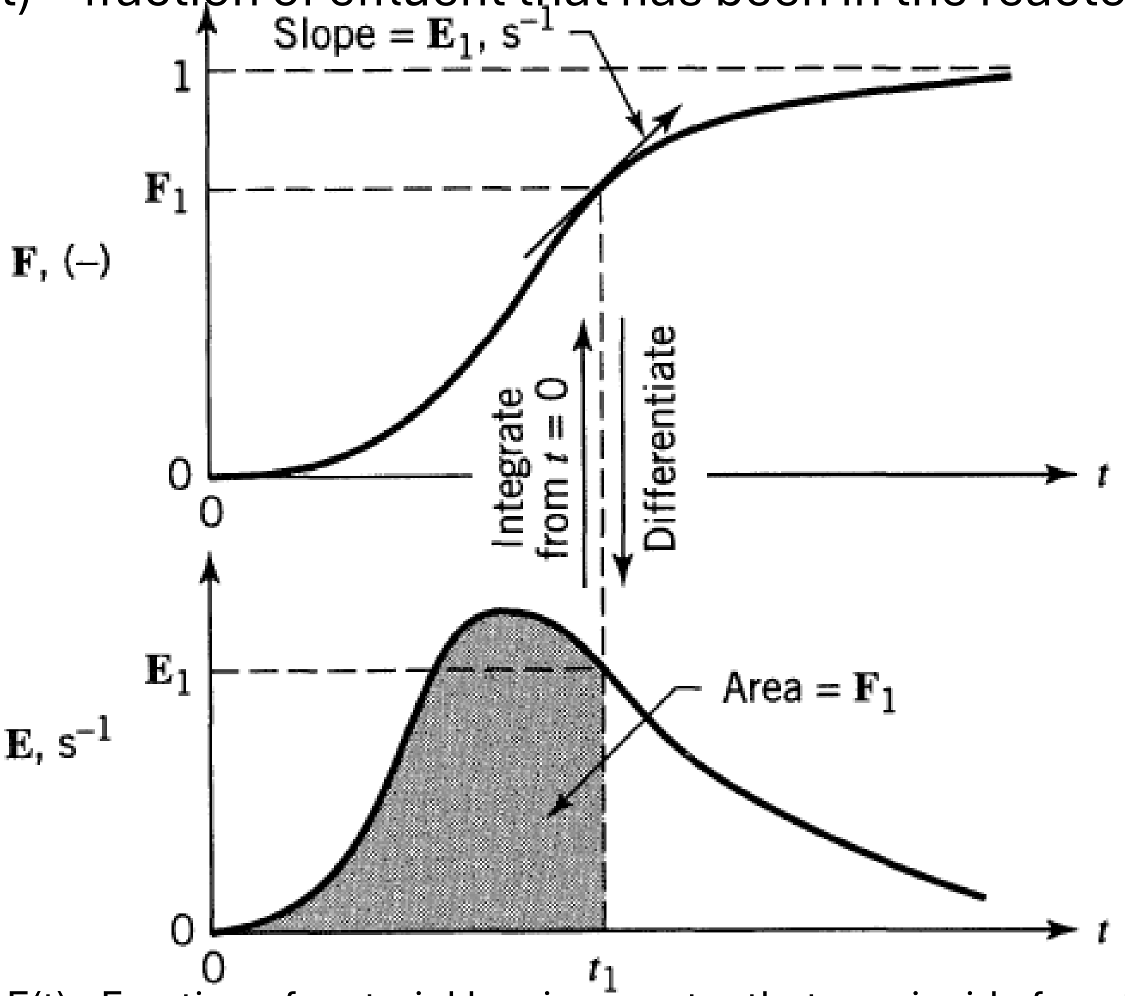
$$F(t)=\int_0^t E(t)\,dt \qquad \begin{array}{l} F(t)=0 \text{ when } t<0 \\ F(t)\geq 0 \text{ when } t\geq 0 \\ F(\infty)=1 \end{array} \qquad 1-F(t)=\int_t^\infty E(t)\,dt$$



80% of the molecules spend 40 min or less in the reactor

# Relationship between E & F Curves

F(t) = fraction of effluent that has been in the reactor for less than time t

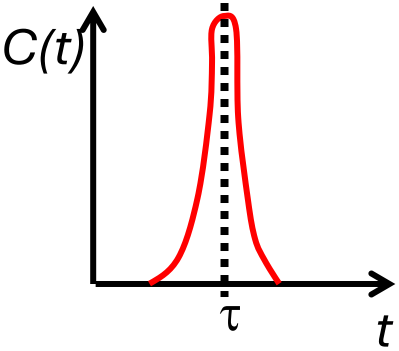


$$F(t) = \int_0^t E(t)\,dt$$

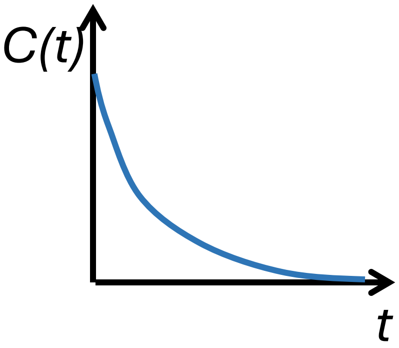
$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt}$$

E(t)= Fraction of material leaving reactor that was inside for a time between $t_1$ & $t_2$

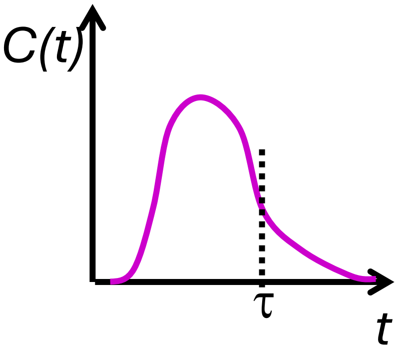
# Boundary Conditions for the Cum RTD Function F(t)



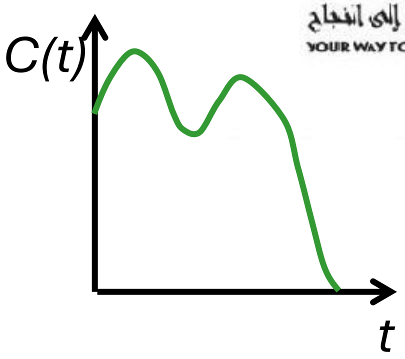
Nearly ideal PFR



Nearly ideal CSTR



PBR with channeling & dead zones



CSTR with dead zones

$$F(t)=\int_0^t E(t)\,dt$$

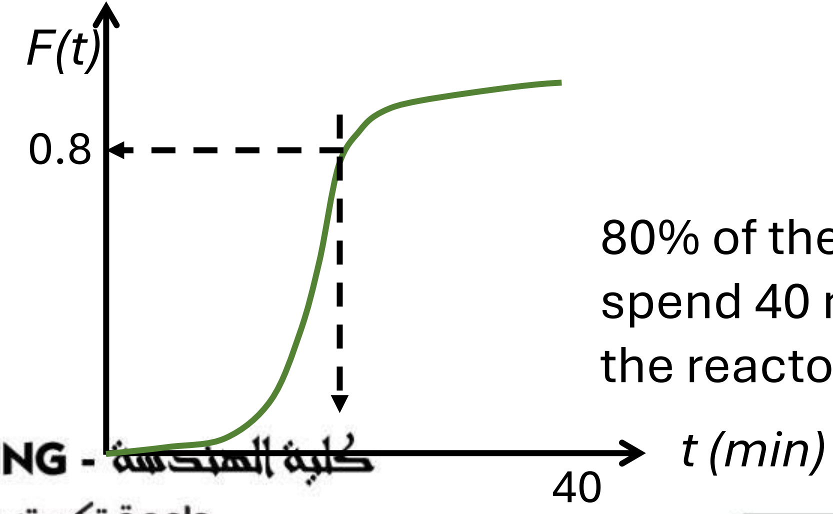
F(t)=fraction of effluent in the reactor less for than time t

$$F(t)=0 \text{ when } t<0$$

$$F(t)\geq 0 \text{ when } t\geq 0$$

$$F(\infty)=1$$

$$1-F(t)=\int_t^\infty E(t)\,dt$$



80% of the molecules spend 40 min or less in the reactor

# Mean Residence Time, $t_m$

- For an ideal reactor, the space time $\tau$ is defined as $V/\upsilon_0$
- The mean residence time $t_m$ is equal to $\tau$ in either ideal or nonideal reactors

$$t_m = \frac{\int_0^\infty tE(t)dt}{\int_0^\infty E(t)dt} = \int_0^\infty tE(t)dt = \tau \qquad \frac{V}{\upsilon_0} = \tau = t_m$$

By calculating $t_m$, the reactor V can be determined from a tracer experiment

The spread of the distribution (variance): $\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)dt$

Space time $\tau$ and mean residence time $t_m$ would be equal if the following two conditions are satisfied:

- No density change
- No backmixing

In practical reactors the above two may not be valid, hence there will be a difference between them

# RTD in Ideal Reactors

All the molecules leaving a PFR have spent ~ the same amount of time in the PFR, so the residence time distribution function is:

$$E(t) = \delta(t-\tau) \quad \text{where } \tau = V/\upsilon_0$$

The Dirac delta function satisfies:

$$\delta(x) = \begin{cases} \infty & \text{when } x = 0 \\ 0 & \text{when } x \neq 0 \end{cases} \qquad \int_{-\infty}^{\infty} \delta(x)\,dx = 1 \qquad \int_{-\infty}^{\infty} g(x)\,\delta(x-\tau)\,dx = g(\tau)$$

Zero everywhere but one point

...but =1 over the entire interval

$$t_m = \int_0^{\infty} t\,\delta(t-\tau)\,dt = \tau$$

# Significance of Mixing

- RTD provides information on how long material has been in the reactor
- RTD does not provide information about the exchange of matter within the reactor (i.e., mixing)!

- For a 1st order reaction:

$$\frac{dX}{dt} = k(1 - X)$$

- Concentration does not affect the rate of conversion, so RTD is sufficient to predict conversion
- But concentration does affect conversion in higher order reactions, so we need to know the degree of mixing in the reactor

- Macromixing: produces a distribution of residence times without specifying how molecules of different age encounter each other and are distributed inside of the reactor

- Micromixing: describes how molecules of different residence time encounter each other in the reactor

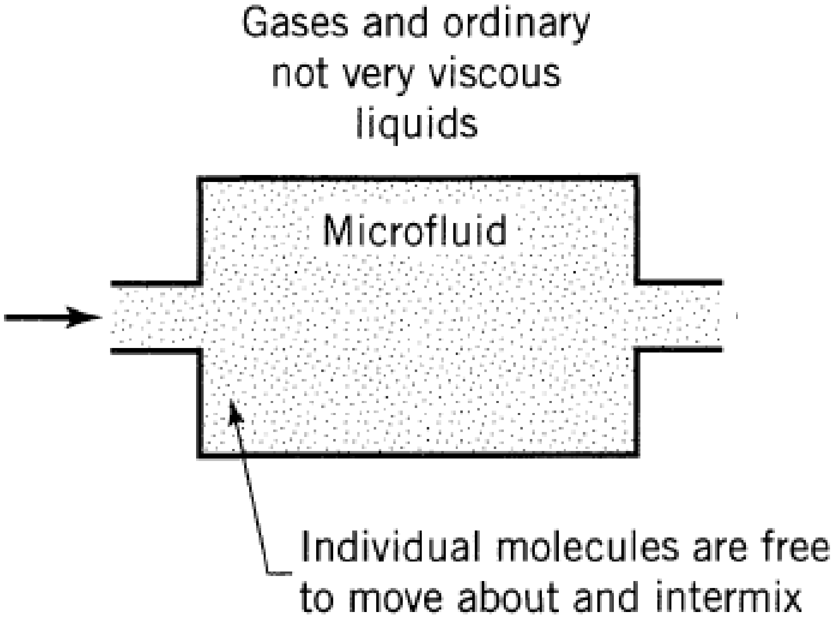
# Quality of Mixing

- RTDs alone are not sufficient to determine reactor performance
- Quality of mixing is also required

Goal: use RTD and micromixing models to predict conversion in real reactors

## 2 Extremes of Fluid Mixing

Maximum mixedness: molecules are free to move anywhere, like a microfluid. This is the extreme case early mixing



# Quality of Mixing

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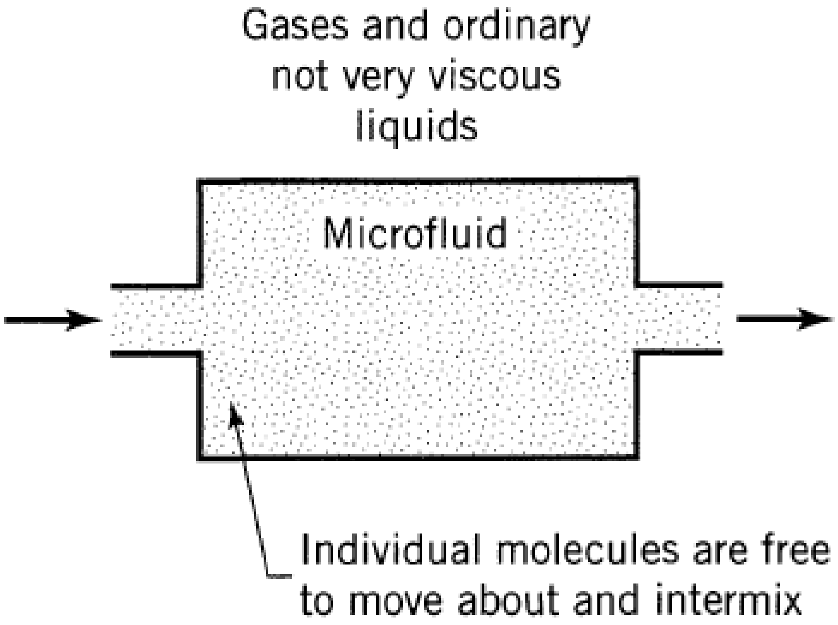
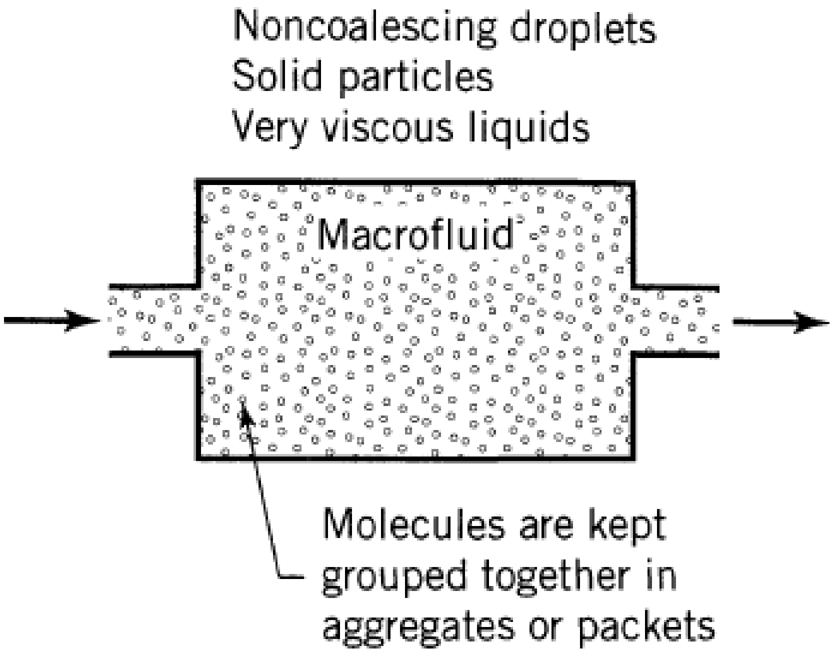
Goal: use RTD and micromixing models to predict conversion in real reactors

## 2 Extremes of Fluid Mixing

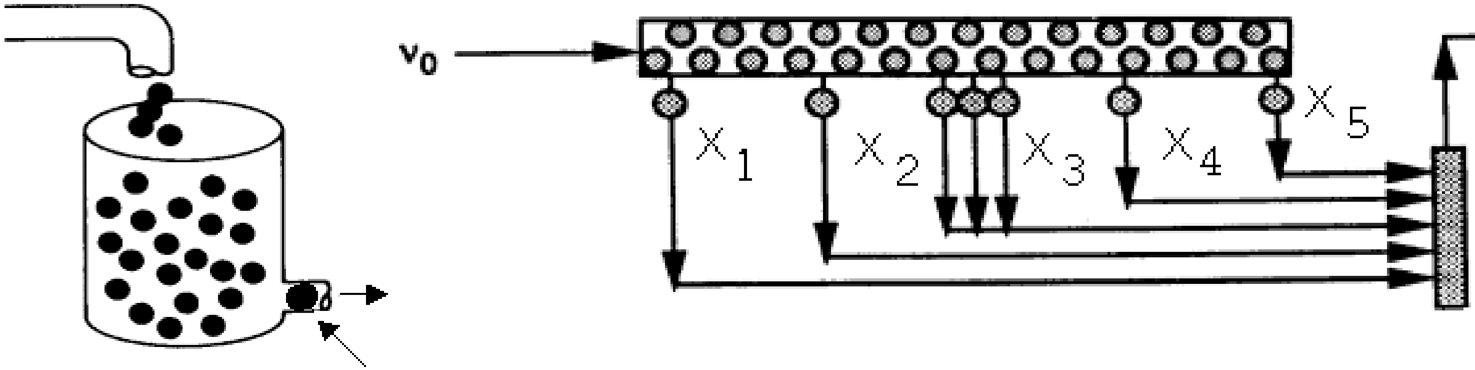
Maximum mixedness: molecules are free to move anywhere, like a microfluid. This is the extreme case of early mixing

Complete segregation: molecules of a given age do not mix with other globules. This is the extreme case of late mixing





# Complete Segregation Model



Mixing of different 'age groups' at the last possible moment

- Flow is visualized in the form of globules
- Each globule consists of molecules of the same residence time
- Different globules have different residence times
- No interaction/mixing between different globules

The mean conversion is the average conversion of the various globules in the exit stream:

$$\bar{X}_A = \sum_j \boxed{X_A\left(t_j\right)}\boxed{E\left(t_j\right)}\Delta t$$

Conversion achieved after spending time $t_j$ in the reactor

Fraction of globules that spend between $t_j$ and $t_j + \Delta t$ in the reactor

$$\xrightarrow{\Delta t \to 0} \bar{X}_A = \int_0^\infty X_A(t)E(t)dt$$

$X_A(t)$ is from the ***batch reactor*** design equation

# Complete Segregation Example

First order reaction, A→Products

Batch reactor design equation:

$$N_{A0}\frac{dX_A}{dt}=-r_AV \quad \rightarrow N_{A0}\frac{dX_A}{dt}=kC_AV$$

$$\rightarrow N_{A0}\frac{dX_A}{dt}=kC_{A0}\left(1-X_A\right)V \quad \rightarrow N_{A0}\frac{dX_A}{dt}=kN_{A0}\left(1-X_A\right)$$

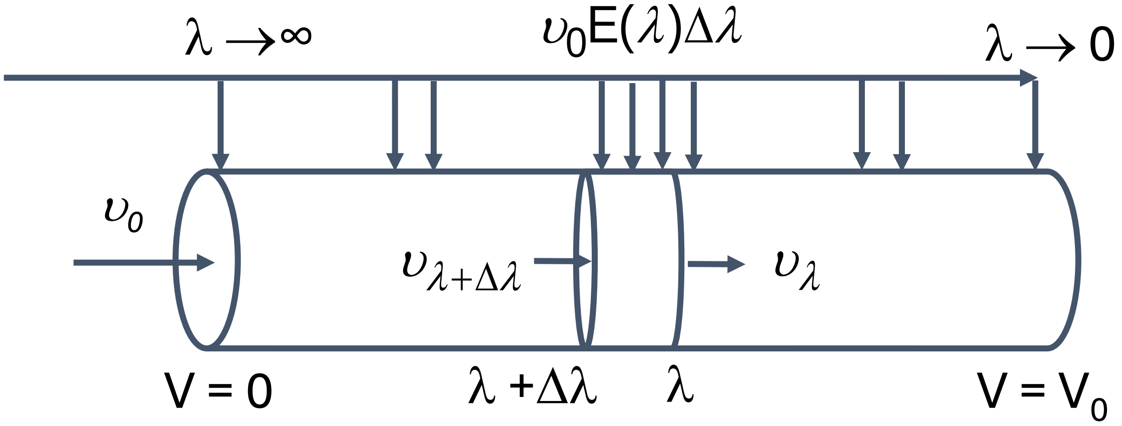
$$\rightarrow \frac{dX_A}{dt}=k\left(1-X_A\right) \quad \rightarrow \boxed{X_A\left(t\right)=1-e^{-kt}}$$

To compute conversion for a reaction with a 1st order rxn and complete segregation, insert E(t) from tracer experiment and $X_A(t)$ from batch reactor design equation into:

$$\bar{X}_A=\int_0^\infty X_A\left(t\right)E\left(t\right)dt$$ & integrate

# Maximum Mixedness Model

In a PFR: as soon as the fluid enters the reactor, it is completely mixed radially with the other fluid already in the reactor. Like a PFR with side entrances, where each entrance port creates a new residence time:



$\lambda$: time it takes for fluid to move from a particular point to end of the reactor

$\upsilon(\lambda)$: volumetric flow rate at $\lambda$, = flow that entered at $\lambda+\Delta\lambda$ plus what entered through the sides

$\upsilon_0 E(\lambda)\Delta\lambda$: Volumetric flow rate of fluid fed into side ports of reactor in interval between $\lambda + \Delta\lambda$ & $\lambda$

Volumetric flow rate of fluid fed to reactor at $\lambda$: $\upsilon(\lambda) = \upsilon_0 \int_\lambda^\infty E(\lambda)\,d\lambda = \upsilon_0\left[1 - \boxed{F(\lambda)}\right]$

Volume of fluid with life expectancy between $\lambda + \Delta\lambda$ & $\lambda$:

fraction of effluent in reactor for less than time t

$$\Delta V = \upsilon_0\left[1 - F(\lambda)\right]\Delta\lambda$$

# Maximum Mixedness & Polymath

**Mole balance on A gives:**

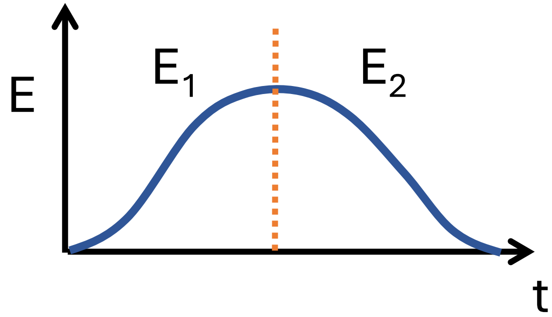
$$\frac{dX_A}{d\lambda} = \frac{r_A}{C_{A0}} + \frac{\boxed{E(\lambda)}}{1-\boxed{F(\lambda)}} X_A$$

residence time distribution function

fraction of effluent in reactor for less than time t

- E(t) must be specified
  - Often it is an expression that fits the experimental data
  - 2 curves, one on the increasing side, and a second for the decreasing side
  - Use the IF function to specify which E is used when

**See section 13.8 in book**



Also need to replace λ because Polymath cannot calculate as λ gets smaller

$$z = \bar{T} - \lambda \quad \text{where } \bar{T} \text{ is the longest time measured}$$

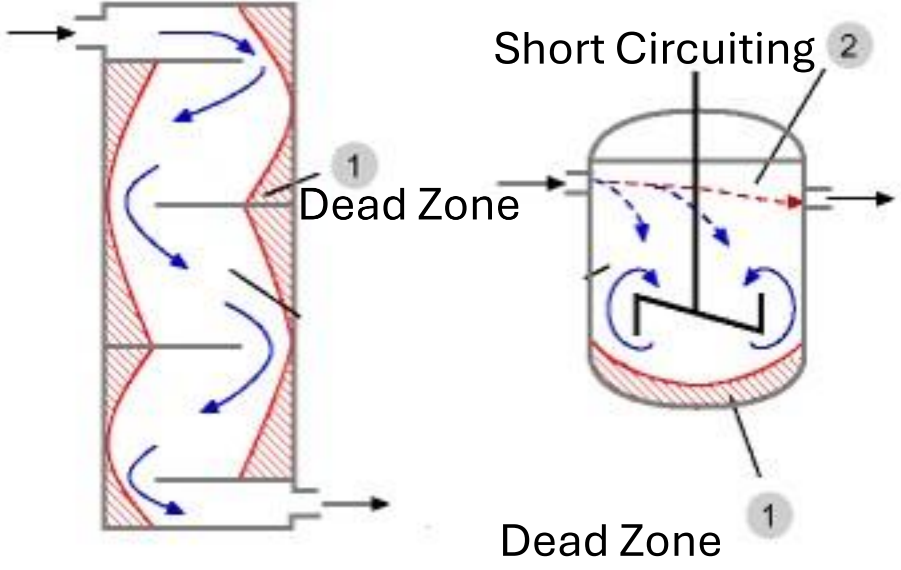
$$\frac{dX_A}{dz} = -\frac{r_A}{C_{A0}} - \frac{E(\bar{T}-z)}{1-F(\bar{T}-z)} X_A$$

Note that the sign on each term changes

# Review: Nonideal Flow & Reactor Design

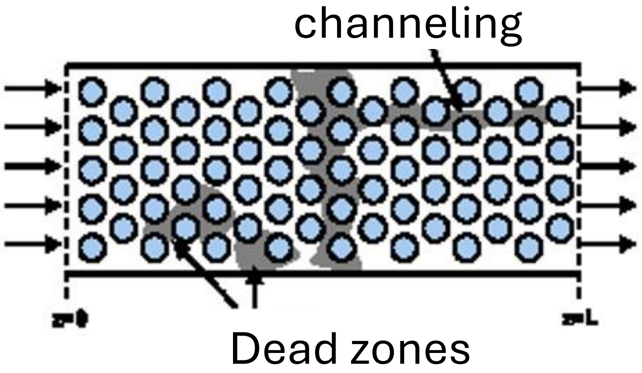
Real CSTRs

- Relatively high reactant conc at entrance
- Relatively low conc in stagnant regions, called dead zones (corners & behind baffles)



Real PBRs

- fluid velocity profiles, turbulent mixing, & molecular diffusion cause molecules to move at varying speeds & directions



Goal: mathematically describe non-ideal flow and solve design problems for reactors with nonideal flow

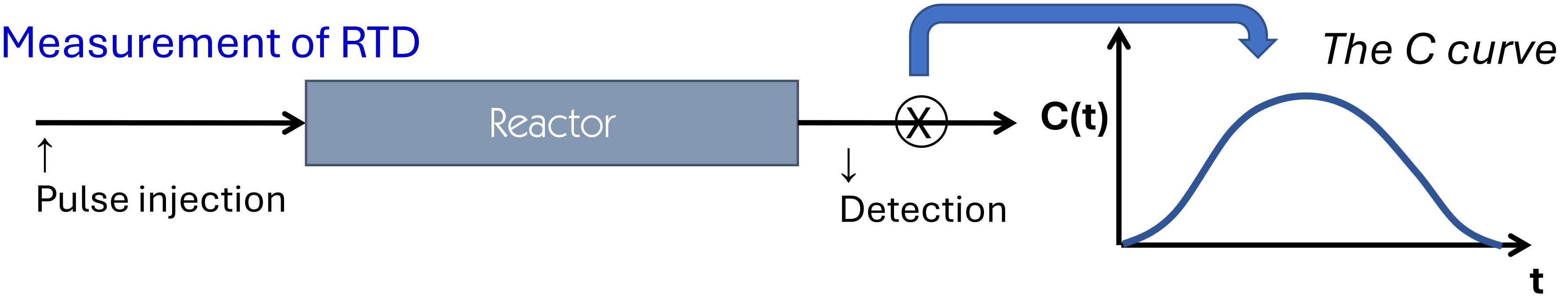
# Residence Time Distribution (RTD)

RTD ≡ E(t) ≡ “residence time distribution” function

RTD describes the amount of time molecules have spent in the reactor

RTD is experimentally determined by injecting an inert “tracer” at t=0 and measuring the tracer concentration C(t) at exit as a function of time

## Measurement of RTD



$$E(t)=\frac{C(t)}{\int_0^\infty C(t)dt}=\frac{\text{tracer conc at exit between t \& t+}\Delta\text{t}}{\text{sum of tracer conc at exit for infinite time}}$$

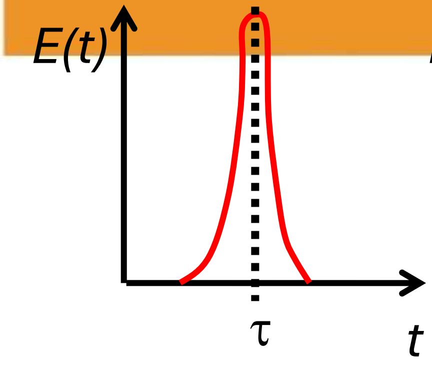
$$\int_0^\infty E(t)dt=1$$

E(t)=0 for t<0 since no fluid can exit before it enters

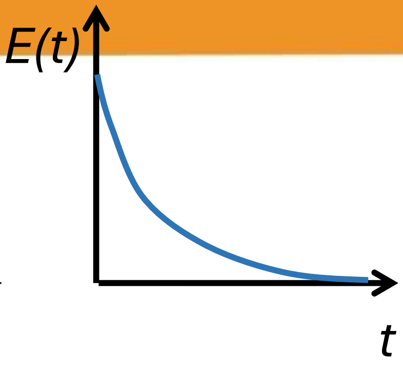
E(t)≥0 for t>0 since mass fractions are always positive

Fraction of material leaving reactor that has been inside reactor for a time between $t_1$ & $t_2$ $=\int_{t_1}^{t_2}E(t)dt$

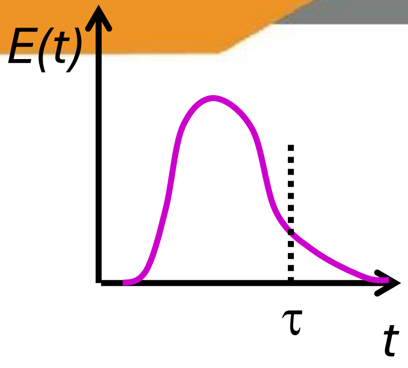
Nice multiple choice question



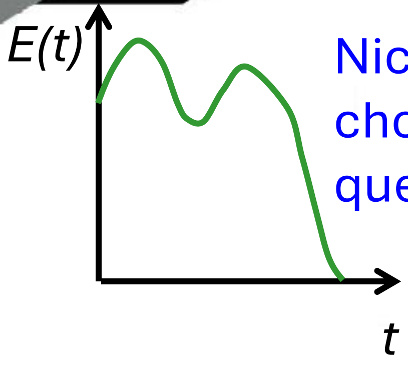
Nearly ideal PFR



Nearly ideal CSTR



PBR with dead zones



CSTR with dead zones

The fraction of the exit stream that has resided in the reactor for a period of time shorter than a given value *t*:

*F(t)* is a cumulative distribution function

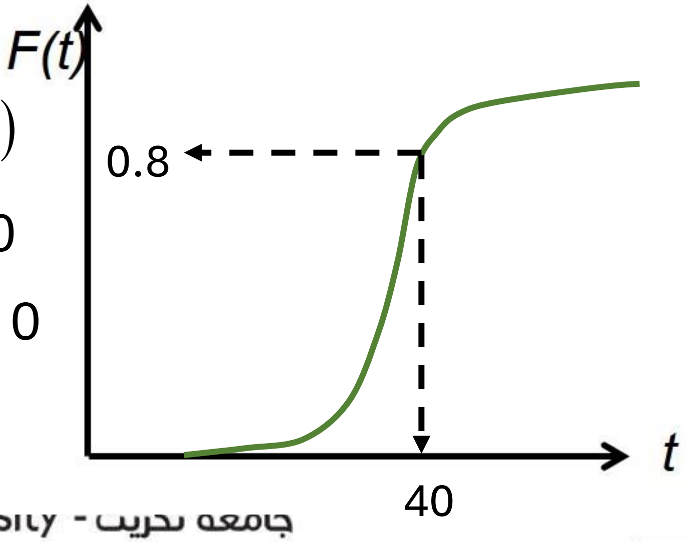
$$\int_0^t E(t)dt = F(t)$$

$$\int_t^\infty E(t)dt = 1 - F(t)$$

$$F(t) = 0 \text{ when } t<0$$

$$F(t) \geq 0 \text{ when } t \geq 0$$

$$F(\infty) = 1$$



80% of the molecules spend 40 min or less in the reactor

# Review: Mean Residence Time, $t_m$

- For an ideal reactor, the space time $\tau$ is defined as $V/\upsilon_0$
- The mean residence time $t_m$ is equal to $\tau$ in either ideal or nonideal-reactors

$$t_m = \frac{\int_0^\infty tE(t)dt}{\int_0^\infty E(t)dt} = \int_0^\infty tE(t)dt = \tau \qquad \frac{V}{\upsilon_0} = \tau = t_m$$

By calculating $t_m$, the reactor V can be determined from a tracer experiment

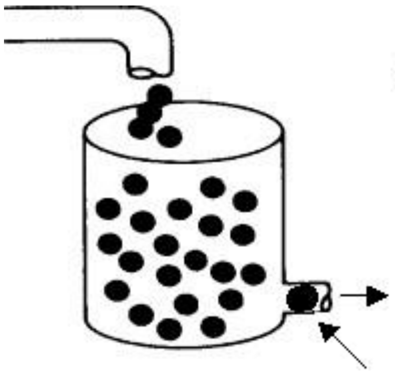
The spread of the distribution (variance): $\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)dt$

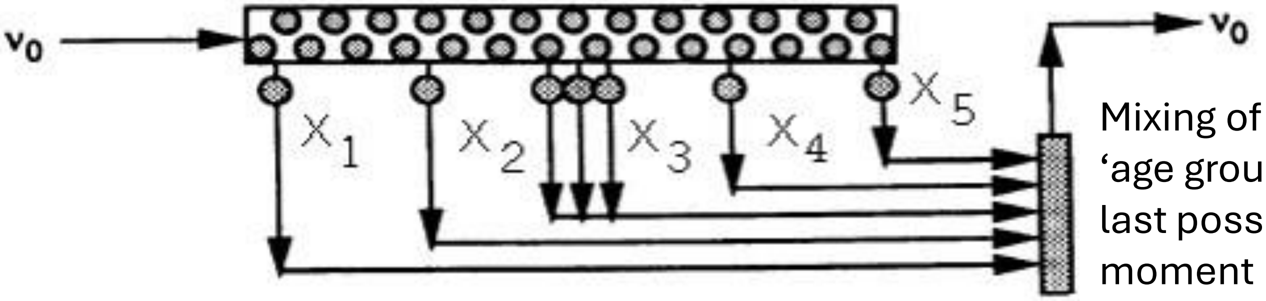
Space time $\tau$ and mean residence time $t_m$ would be equal if the following two conditions are satisfied:

- No density change
- No backmixing

In practical reactors the above two may not be valid, hence there will be a difference between them

# Review: Complete Segregation Model





Mixing of different 'age groups' at the last possible moment

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$X_A(t)$ is from the ***batch reactor*** design equation

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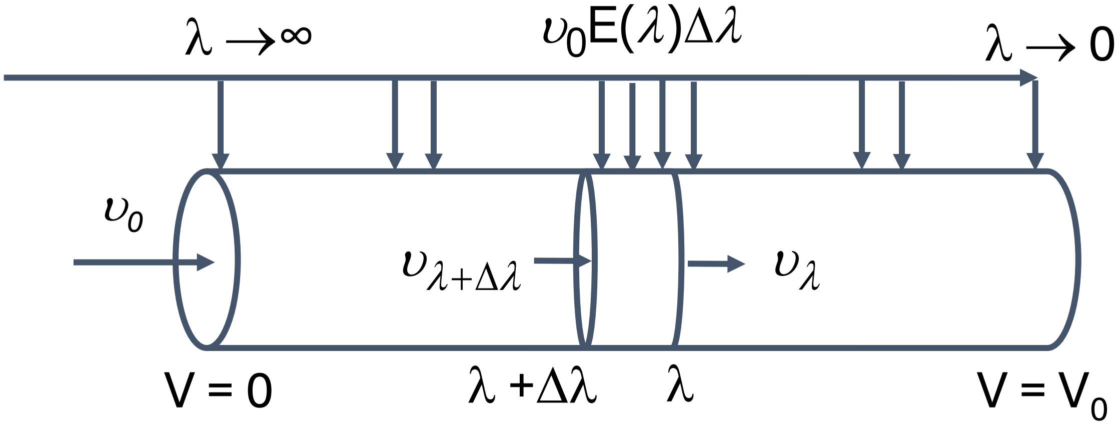

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Volumetric flow rate of fluid fed to reactor at $\lambda$: $\upsilon(\lambda) = \upsilon_0 \int_\lambda^\infty E(\lambda)d\lambda = \upsilon_0\left[1-\boxed{F(\lambda)}\right]$

fraction of effluent that in reactor for less than time t

Volume of fluid with life expectancy between $\lambda + \Delta\lambda$ & $\lambda$:

$$\Delta V = \upsilon_0\left[1-F(\lambda)\right]\Delta\lambda$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for (1) an ideal PFR and (2) for the complete segregation model.

$C_{A0}=C_{B0}=0.0313$ mol/L & k=176 $L^2/mol^2\cdot$min at 320K

| **t min** | **0** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **14** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C $g/m^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for (1) an ideal PFR and (2) for the complete segregation model.

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| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

Start with PFR design eq & see how far can we get:

$$\frac{dX_A}{dV}=\frac{-r_A}{F_{A0}}\rightarrow\frac{dX_A}{dV}=\frac{kC_AC_B^2}{C_{A0}\upsilon_0}\qquad C_A=C_{A0}(1-X_A)\qquad C_B=C_{B0}(1-X_A)$$

$$\rightarrow\frac{dX_A}{dV}=\frac{k\cancel{C_{A0}}C_{B0}^2(1-X_A)^3}{\cancel{C_{A0}}\upsilon_0}$$

Get like terms together & integrate

$$\rightarrow\int_0^{X_A}\frac{dX_A}{(1-X_A)^3}=\int_0^V\frac{kC_{B0}^2}{\upsilon_0}dV$$

$$\rightarrow\left.\frac{1}{2(1-X_A)^2}\right]_0^{X_A}=\frac{kC_{B0}^2}{\upsilon_0}V\rightarrow\frac{1}{(1-X_A)^2}-1=2kC_{B0}^2\tau\rightarrow X_A=1-\sqrt{\frac{1}{2kC_{B0}^2\tau+1}}$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for (1) an ideal PFR and (2) for the complete segregation model.

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| t*E(t) | 0 | 0.02 | 0.2 | 0.48 | 0.8 | 0.8 | 0.72 | 0.56 | 0.48 | 0.396 | 0.3 | 0.144 | 0 |

$$\boxed{X_A=1-\sqrt{\frac{1}{2kC_{B0}{}^2\tau+1}}}$$

How do we determine τ?

For an ideal reactor, $\tau = t_m$

$$t_m=\int_0^\infty tE(t)dt$$

Use numerical method to determine $t_m$:

$$t_m=\int_0^\infty tE(t)dt=\int_0^{10} tE(t)dt+\int_{10}^{14} tE(t)dt$$

$$\int_0^{10} tE(t)dt=\frac{1}{3}\begin{bmatrix}0+4(0.02)+2(0.2)+4(0.48)+2(0.8)+4(0.8)\\+2(0.72)+4(0.56)+2(0.48)+4(0.396)+0.3\end{bmatrix}=4.57$$

$$\int_{10}^{14} tE(t)dt=\frac{2}{3}\left[0.3+4(0.144)+0\right]=0.584$$

$$\rightarrow t_m=4.57+0.584=5.15\,\text{min}$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for (1) an ideal PFR and (2) for the complete segregation model.

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| t*E(t) | 0 | 0.02 | 0.2 | 0.48 | 0.8 | 0.8 | 0.72 | 0.56 | 0.48 | 0.396 | 0.3 | 0.144 | 0 |

$$\boxed{X_A=1-\sqrt{\frac{1}{2kC_{B0}{}^2\tau+1}}}$$

For an ideal PFR reactor, $\tau = t_m$

$$t_m=\int_0^\infty tE(t)dt$$

$$t_m=5.15\,\text{min}=\tau$$

$$X_{A,PFR}=1-\sqrt{\frac{1}{2\left(176\frac{L^2}{mol^2\cdot min}\right)\left(0.0313\frac{mol}{L}\right)^2(5.15\,\text{min})+1}}$$

$$X_{A,PFR}=0.40$$

For a pulse tracer expt, the effluent concentration C in the table below. The irreversible, liquid-phase, nonelementary rxn A+(t) & RTD function E(t) are given B→C+D, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model. $C_{A0}=C_{B0}=0.0313$ mol/L & $k=176\ L^2/mol^2\cdot min$ at 320K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
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Segregation model: $\bar{X}_A = \int_0^\infty X_A(t)E(t)dt$ $X_A(t)$ is from ***batch reactor*** design eq

Numerical method

1. Solve batch reactor design equation to determine eq for $X_A$
2. Determine $X_A$ for each time
3. Use numerical methods to determine $\bar{X}_A$

Polymath Method

1. Use batch reactor design equation to find eq for $X_A$
2. Use Polymath polynomial curve fitting to find equation for E(t)
3. Use Polymath to determine $\bar{X}_A$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

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Batch design eq:

$$N_{A0}=C_{A0}V$$

$$N_{A0}\frac{dX_A}{dt}=-r_AV \rightarrow N_{A0}\frac{dX_A}{dt}=kC_{A0}C_{B0}^2(1-X_A)^3V \rightarrow \frac{dX_A}{dt}=kC_{B0}^2(1-X_A)^3$$

Stoichiometry:

$$-r_A=kC_AC_B^2$$

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

$$C_B=C_{B0}(1-X_A)$$

$$\rightarrow \int_0^{X_A}\frac{dX_A}{(1-X_A)^3}=\int_0^t kC_{B0}^2dt \rightarrow \left.\frac{1}{2(1-X_A)^2}\right]_0^{X_A}=kC_{B0}^2t$$

$$\rightarrow \frac{1}{(1-X_A)^2}-1=2kC_{B0}^2t$$

$$\rightarrow X_A=1-\sqrt{\frac{1}{1+2kC_{B0}^2t}}$$

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
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| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |
| $X_A$ | | | | | | | | | | | | | |

Segregation model:

$$\bar{X}_A=\int_0^{\infty}X_A(t)E(t)dt$$

Numerical method

$$X_A=1-\sqrt{\frac{1}{1+2kC_{B0}{}^2t}}=1-\sqrt{\frac{1}{1+0.3429\,\text{min}^{-1}t}}$$

Plug in each t & solve

$$X_{A(0)}=1-\sqrt{\frac{1}{1+0.3429\,\text{min}^{-1}(0)}}=0$$

$$X_{A(1)}=1-\sqrt{\frac{1}{1+0.3429\,\text{min}^{-1}(1\text{min})}}=0.137$$

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| $X_A$ | 0 | 0.137 | 0.23 | 0.298 | 0.35 | 0.39 | 0.428 | 0.458 | 0.483 | 0.505 | 0.525 | 0.558 | 0.585 |

Segregation model:

$$\bar{X}_A=\int_0^\infty X_A(t)E(t)dt \qquad X_A=1-\sqrt{\frac{1}{1+2kC_{B0}{}^2t}}=1-\sqrt{\frac{1}{1+0.3429\,\text{min}^{-1}t}}$$

Numerical method

$$\bar{X}_A=\int_0^\infty X_A(t)E(t)dt=\int_0^{10} X_A(t)E(t)dt+\int_{10}^{14} X_A(t)E(t)dt$$

$$\int_0^{10} X_A(t)E(t)dt=\frac{1}{3}\begin{bmatrix}0+4(0.137)(0.02)+2(0.23)(0.1)+4(0.298)(0.16)\\+2(0.35)(0.2)+4(0.39)(0.16)+2(0.428)(0.12)+4(0.458)(0.08)\\+2(0.483)(0.06)+4(0.505)(0.044)+0.525(0.03)\end{bmatrix}$$

$$\int_0^{10} X_A(t)E(t)dt=0.35$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & $k=176$ L²/mol²·min at 320K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C g/m³ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |
| $X_A$ | 0 | 0.137 | 0.23 | 0.298 | 0.35 | 0.39 | 0.428 | 0.458 | 0.483 | 0.505 | 0.525 | 0.558 | 0.585 |

Segregation model:

$$\bar{X}_A=\int_0^\infty X_A(t)E(t)dt \qquad X_A=1-\sqrt{\frac{1}{1+2kC_{B0}{}^2t}}=1-\sqrt{\frac{1}{1+0.3429\,\text{min}^{-1}t}}$$

Numerical method

$$\bar{X}_A=\int_0^\infty X_A(t)E(t)dt=0.35+\int_{10}^{14}X_A(t)E(t)dt$$

$$\int_{10}^{14}X_A(t)E(t)dt=\frac{2}{3}\left[(0.525)(0.03)+4(0.558)(0.012)+(0.585)0\right]=0.0425$$

$$\bar{X}_A=\int_0^\infty X_A(t)E(t)dt=0.35+0.04\rightarrow\bar{X}_A=0.39$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & k=176 L²/mol²·min at 320K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C g/m³ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |
| $X_A$ | 0 | 0.137 | 0.23 | 0.298 | 0.35 | 0.39 | 0.428 | 0.458 | 0.483 | 0.505 | 0.525 | 0.558 | 0.585 |

Alternative approach: segregation model by Polymath:

$$\bar{X}_A=\int_0^\infty X_A(t)E(t)dt$$

$$\boxed{\frac{d\bar{X}_A}{dt}=X_A(t)E(t)}$$

$$\boxed{X_A=1-\sqrt{\frac{1}{1+2kC_{B0}^2t}}}$$

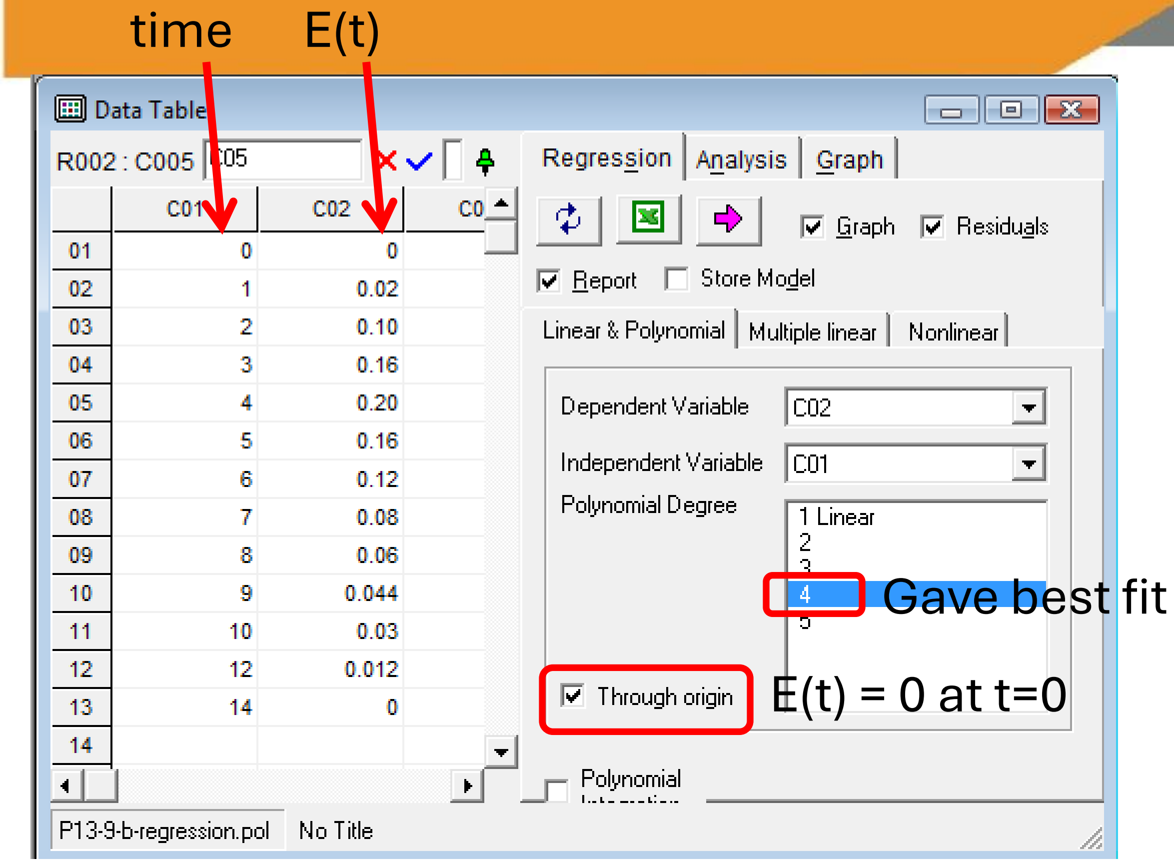
↓

Need an equation for E(t)

$\boxed{k=176}$

$\boxed{C_{B0}=0.0313}$

Use Polymath to fit the E(t) vs t data in the table to a polynomial



time

E(t)

Data Table

R002 : C005 | C05

|  | C01 | C02 |
|---|---|---|
| 01 | 0 | 0 |
| 02 | 1 | 0.02 |
| 03 | 2 | 0.10 |
| 04 | 3 | 0.16 |
| 05 | 4 | 0.20 |
| 06 | 5 | 0.16 |
| 07 | 6 | 0.12 |
| 08 | 7 | 0.08 |
| 09 | 8 | 0.06 |
| 10 | 9 | 0.044 |
| 11 | 10 | 0.03 |
| 12 | 12 | 0.012 |
| 13 | 14 | 0 |
| 14 |  |  |

Regression | Analysis | Graph

☑ Graph ☑ Residuals

☑ Report ☐ Store Model

Linear & Polynomial | Multiple linear | Nonlinear

Dependent Variable: C02

Independent Variable: C01

Polynomial Degree: 1 Linear, 2, 3, **4**, 5

4 — Gave best fit

☑ Through origin — $E(t) = 0$ at $t=0$

☐ Polynomial Integration

P13-9-b-regression.pol No Title

For the irreversible, liquid-phase, nonelementary rxn $A+B \rightarrow C+D$, $-r_A=kC_AC_B^2$ Calculate the $X_A$ using the complete segregation model using Polymath

Model: C02= a1*C01 + a2*C01^2 + a3*C01^3 + a4*C01^4

a1=0.0889237

a2= -0.0157181

a3= 0.0007926

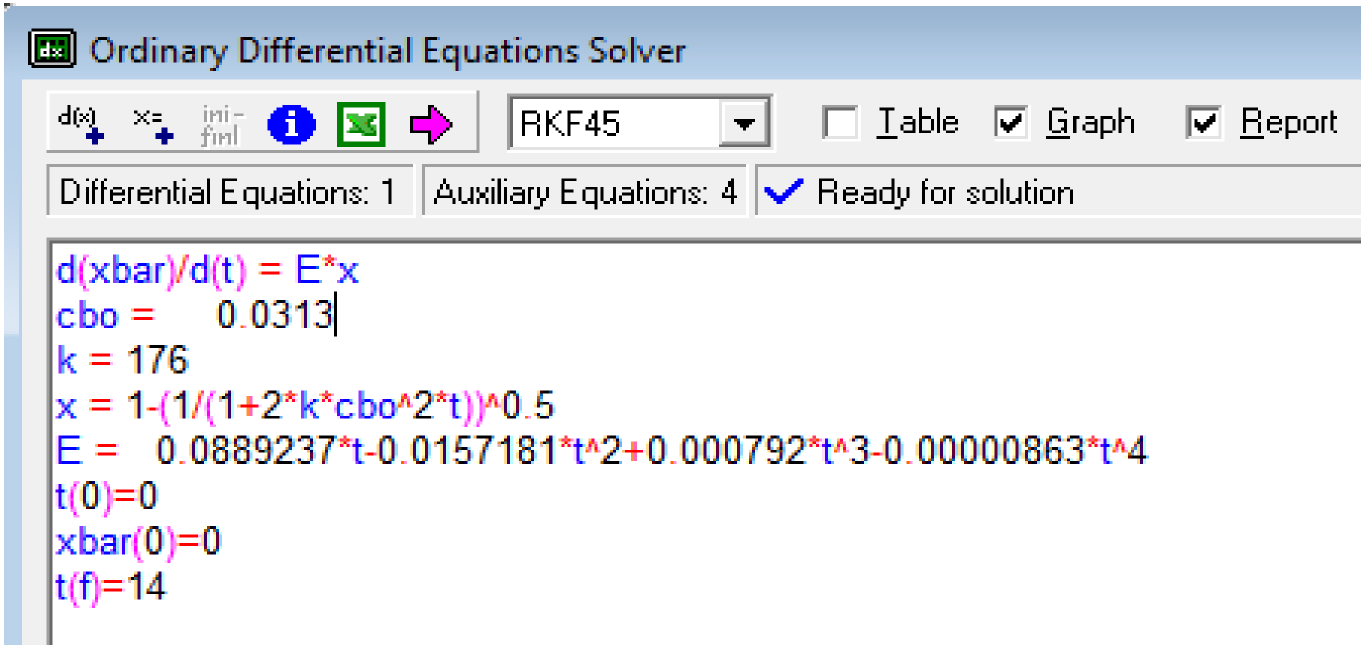
a4= -8.63E-06

Final Equation: $E= 0.0889237 t - 0.0157181 t^2 + 0.0007926 t^3 - 8.63E\text{-}6 t^4$

# Complete segregation model by Polymath

A+B→C+D

$-r_A=kC_AC_B^2$

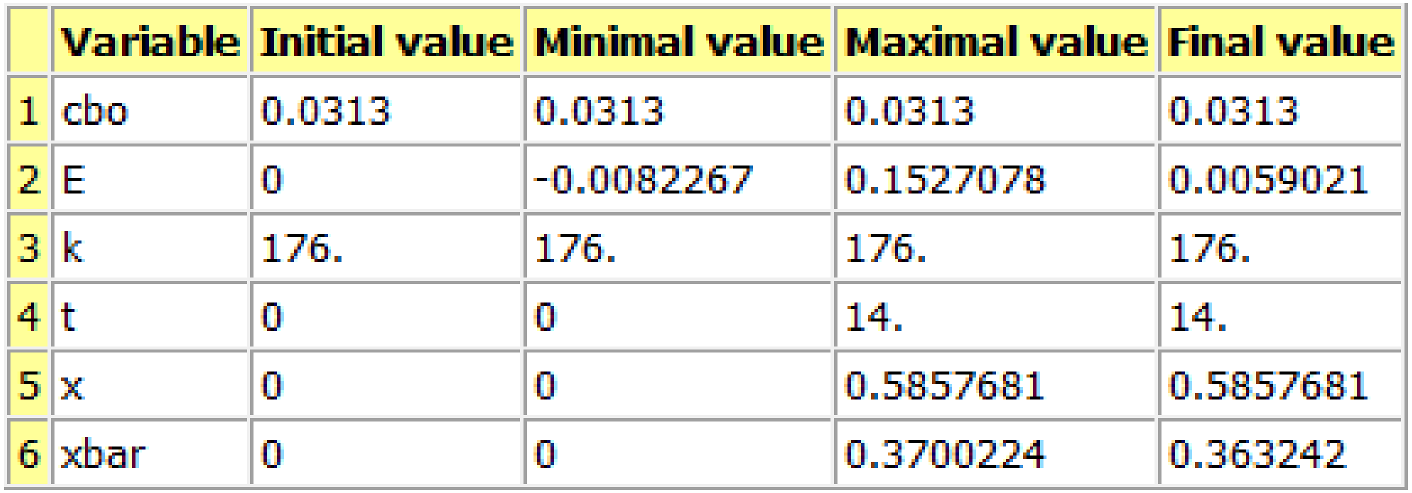


Ordinary Differential Equations Solver

RKF45 ☐ Table ☑ Graph ☑ Report

Differential Equations: 1 Auxiliary Equations: 4 ✓ Ready for solution

```
d(xbar)/d(t) = E*x
cbo =     0.0313
k = 176
x = 1-(1/(1+2*k*cbo^2*t))^0.5
E =   0.0889237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4
t(0)=0
xbar(0)=0
t(f)=14
```



|   | Variable | Initial value | Minimal value | Maximal value | Final value |
|---|---|---|---|---|---|
| 1 | cbo | 0.0313 | 0.0313 | 0.0313 | 0.0313 |
| 2 | E | 0 | -0.0082267 | 0.1527078 | 0.0059021 |
| 3 | k | 176. | 176. | 176. | 176. |
| 4 | t | 0 | 0 | 14. | 14. |
| 5 | x | 0 | 0 | 0.5857681 | 0.5857681 |
| 6 | xbar | 0 | 0 | 0.3700224 | 0.363242 |

$\overline{X}_A = 0.36$

**Segregation model by Polymath:**

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & k=176 $L^2/mol^2\cdot min$ at 320K

| **t min** | **0** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **14** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C $g/m^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

Maximum mixedness model:

$$\frac{dX_A}{d\lambda}=\frac{r_A}{C_{A0}}+\frac{E(\lambda)}{1-F(\lambda)}X_A \qquad \lambda\text{=time} \qquad \frac{dF}{d\lambda}=E$$

*F(λ)* is a cumulative distribution function

$$\boxed{-r_A=kC_{A0}C_{B0}^2(1-X_A)^3}\quad \boxed{C_{A0}=C_{B0}=0.0313\,mol/L}\quad \boxed{k=176\frac{L^2}{mol^2\cdot min}}$$

Polymath cannot solve because λ→0 (needs to increase)

Substitute λ **for** z, where $z=\bar{T}-\lambda$ where $\bar{T}$=longest time interval (14 min)

$$\boxed{\frac{dX_A}{dz}=-\left(\frac{r_A}{C_{A0}}+\frac{E(\bar{T}-z)}{1-F(\bar{T}-z)}X_A\right)}\quad \boxed{\frac{dF}{dz}=-E(\bar{T}-z)}$$

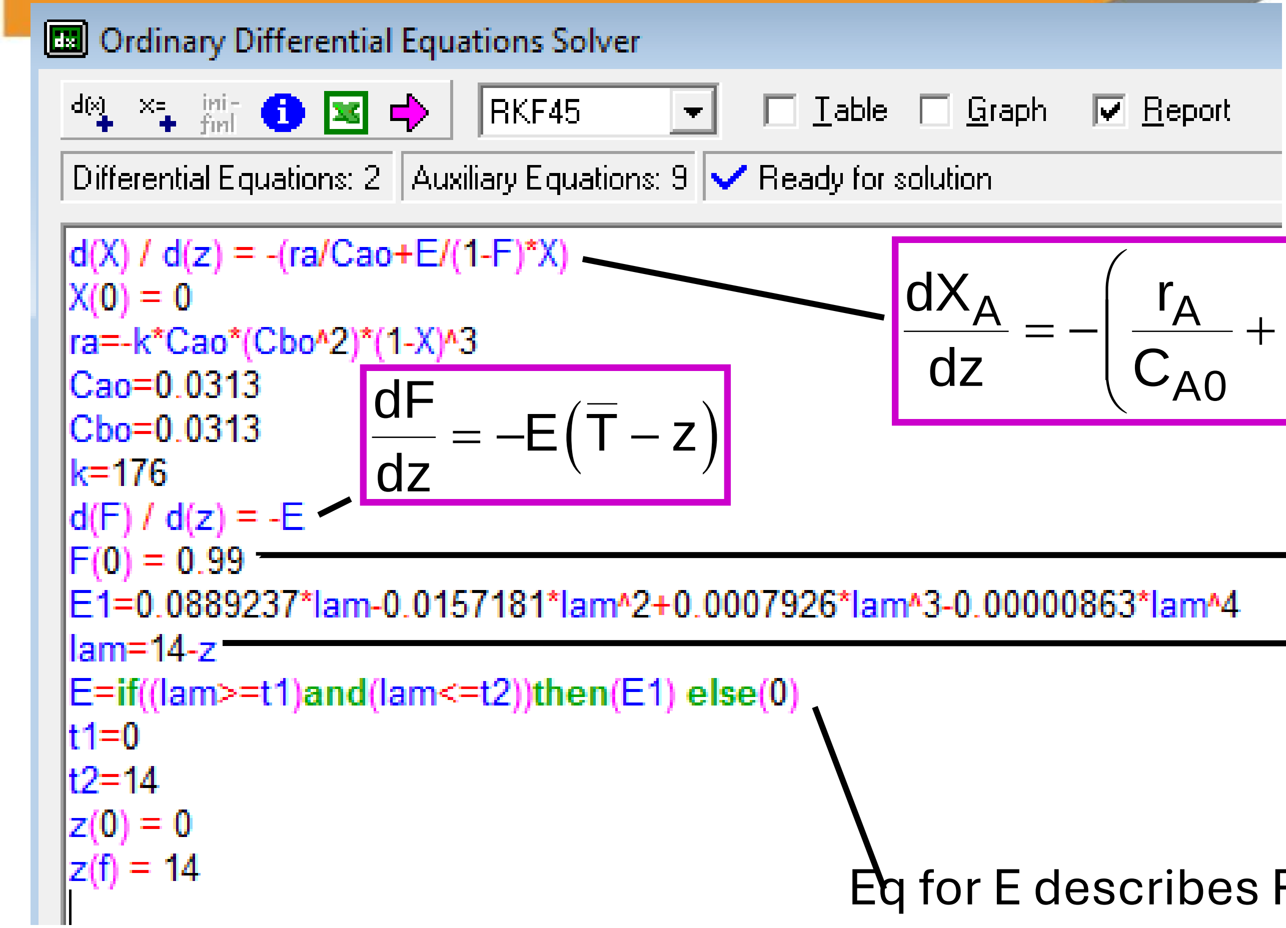
E must be in terms of $\bar{T}$-z. Since $\bar{T}$-z=λ & λ=t, simply substitute λ for t

$$\boxed{E(\lambda)=0.0889237*\lambda-0.0157181*\lambda^2+0.0007926*\lambda^3-8.63E\text{-}6*\lambda^4}$$

# Maximum Mixedness Model, nonelementary reaction

$A+B \rightarrow C+D$

$-r_A = kC_AC_B^2$



```
d(X) / d(z) = -(ra/Cao+E/(1-F)*X)
X(0) = 0
ra=-k*Cao*(Cbo^2)*(1-X)^3
Cao=0.0313
Cbo=0.0313
k=176
d(F) / d(z) = -E
F(0) = 0.99
E1=0.0889237*lam-0.0157181*lam^2+0.0007926*lam^3-0.00000863*lam^4
lam=14-z
E=if((lam>=t1)and(lam<=t2))then(E1) else(0)
t1=0
t2=14
z(0) = 0
z(f) = 14
```

$$\boxed{\frac{dX_A}{dz} = -\left(\frac{r_A}{C_{A0}} + \frac{E(\overline{T}-z)}{1-F(\overline{T}-z)}X_A\right)}$$

$$\boxed{\frac{dF}{dz} = -E(\overline{T}-z)}$$

Denominator cannot = 0

$$z = \overline{T} - \lambda \rightarrow \lambda = \overline{T} - z$$

Eq for E describes RTD function only on interval t= 0 to 14 minutes, otherwise E=0

$$X_{A,\text{ maximum mixedness}} = 0.347$$

For a pulse tracer expt, C(t) & E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $-r_A = kC_AC_B^2$ will be carried out in this reactor. Calculate the conversion for the complete segregation model under adiabatic conditions with $T_0$= 288K, $C_{A0}=C_{B0}$=0.0313 mol/L, k=176 $L^2/mol^2\cdot min$ at 320K, $\Delta H^\circ_{RX}$=-40000 cal/mol, E/R =3600K, $C_{PA}=C_{PB}$=20cal/mol·K & $C_{PC}=C_{PD}$=30 cal/mol·K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C g/m³ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

Polymath eqs for segregation model:

$$\boxed{\frac{d\bar{X}_A}{dt} = X_A(t)E(t)}$$

$$\boxed{\frac{dX_A}{dt} = kC_{B0}^2(1-X_A)^3}$$

$$\boxed{E(t) = 0.0889237 t - 0.0157181 t^2 + 0.0007926 t^3 - 8.63E\text{-}6 t^4}$$

Express k as function of T:

$$\boxed{k(T) = 176\frac{L^2}{mol^2\cdot min}\exp\left[3600K\left(\frac{1}{320K}-\frac{1}{T}\right)\right]}$$

Need equations from energy balance. For adiabatic operation:

$$T = \frac{\left[-\Delta H^\circ_{RX}(T_R)\right]X_A + \sum_{i=1}^{n}\Theta_iC_{p_i}T_0 + X_A\Delta C_PT_R}{\left[\sum_{i=1}^{n}\Theta_iC_{p_i} + X_A\Delta C_P\right]}$$

For a pulse tracer expt, C(t) & E(t) are given in the table below. The irreversible, liquid-phase, nonelementary rxn A+B→C+D, $-r_A=kC_AC_B^2$ will be carried out in this reactor. Calculate the conversion for the complete segregation model under adiabatic conditions with $T_0$= 288K, $C_{A0}=C_{B0}$=0.0313 mol/L, k=176 $L^2/mol^2\cdot min$ at 320K, $\Delta H^\circ_{RX}$=-40000 cal/mol, E/R =3600K, $C_{PA}=C_{PB}$=20cal/mol·K & $C_{PC}=C_{PD}$=30 cal/mol·K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C $g/m^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

Energy balance for adiabatic operation:

$$T=\frac{\left[-\Delta H^\circ_{RX}\left(T_R\right)\right]X_A+\sum_{i=1}^{n}\Theta_iC_{p_i}T_0+X_A\Delta C_P T_R}{\left[\sum_{i=1}^{n}\Theta_iC_{p_i}+X_A\Delta C_P\right]}$$

Not zero!

$$\sum_{i=1}^{n}\Theta_iC_{p_i}=C_{p_A}+C_{p_B}=40\frac{cal}{mol\cdot K}\qquad \Delta C_p=\left(30+30-20-20\right)\frac{cal}{mol\cdot K}=20\frac{cal}{mol\cdot K}$$

$$\rightarrow\boxed{T=\frac{1702\frac{cal}{mol}X_A+576\frac{cal}{mol}}{2\frac{cal}{mol\cdot K}+X_A\left(\frac{cal}{mol\cdot K}\right)}}$$

$$\boxed{\frac{d\bar{X}_A}{dt}=X_A\left(t\right)E\left(t\right)}\qquad\boxed{\frac{dX_A}{dt}=kC_{B0}^{\;2}\left(1-X_A\right)^3}$$

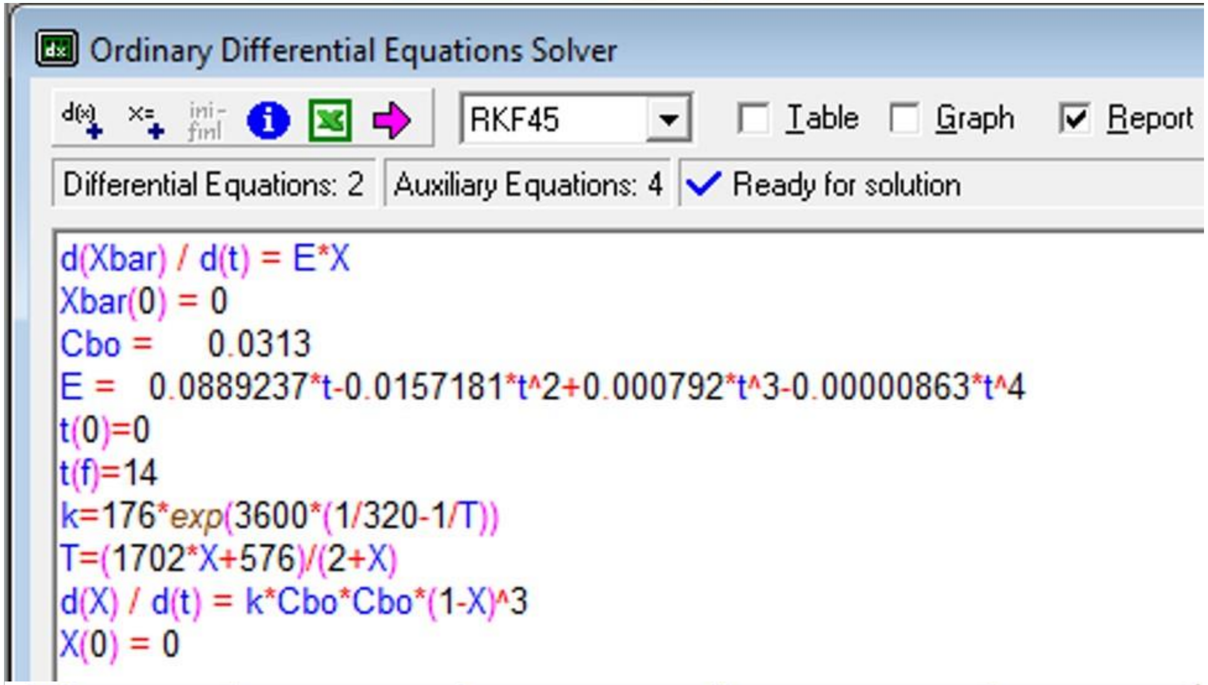
$$\boxed{k\left(T\right)=176\frac{L^2}{mol^2\cdot min}\exp\left[3600K\left(\frac{1}{320K}-\frac{1}{T}\right)\right]}$$

$E(t)= 0.0889237*t -0.0157181*t^2 + 0.0007926*t^3 - 8.63E-6*t^4$

# Segregation model, adiabatic operation, nonelementary reaction kinetics

$A+B \rightarrow C+D$

$-r_A=kC_AC_B^2$

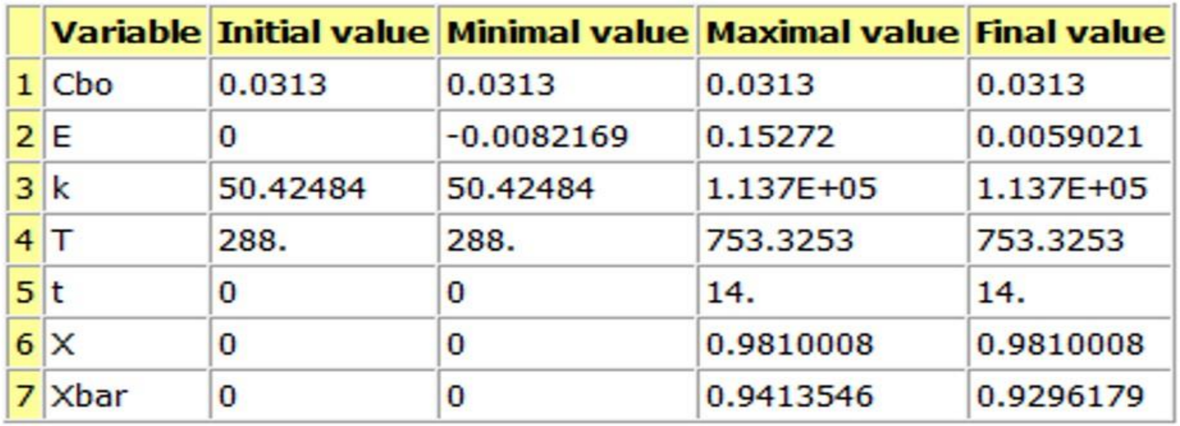


Differential Equations: 2

Auxiliary Equations: 4

✓ Ready for solution

```
d(Xbar) / d(t) = E*X
Xbar(0) = 0
Cbo =      0.0313
E =   0.0889237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4
t(0)=0
t(f)=14
k=176*exp(3600*(1/320-1/T))
T=(1702*X+576)/(2+X)
d(X) / d(t) = k*Cbo*Cbo*(1-X)^3
X(0) = 0
```



| | Variable | Initial value | Minimal value | Maximal value | Final value |
|---|---|---|---|---|---|
| 1 | Cbo | 0.0313 | 0.0313 | 0.0313 | 0.0313 |
| 2 | E | 0 | -0.0082169 | 0.15272 | 0.0059021 |
| 3 | k | 50.42484 | 50.42484 | 1.137E+05 | 1.137E+05 |
| 4 | T | 288. | 288. | 753.3253 | 753.3253 |
| 5 | t | 0 | 0 | 14. | 14. |
| 6 | X | 0 | 0 | 0.9810008 | 0.9810008 |
| 7 | Xbar | 0 | 0 | 0.9413546 | 0.9296179 |

$$\overline{X}_A = 0.93$$

The following slides show how the same problem would be solved and the solutions would differ if the reaction rate was still $-r_A=kC_AC_B^2$ but the reaction was instead elementary: $A+\underline{2B}\rightarrow C+D$

These slides may be provided as an extra example problem that the students may study on there own if time does not permit doing it in class.

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn $A+\underline{2B}\rightarrow C+D$, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model. $C_{A0}=C_{B0}=0.0313$ mol/L & $k=176\ L^2/mol^2\cdot min$ at 320K

| **t min** | **0** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **12** | **14** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C g/m$^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

Start with PFR design eq & see how far can we get:

$$\frac{dX_A}{dV}=\frac{-r_A}{F_{A0}}\rightarrow\frac{dX_A}{dV}=\frac{kC_AC_B^2}{C_{A0}\upsilon_0}\rightarrow\frac{dX_A}{d\tau}=\frac{kC_AC_B^2}{C_{A0}}$$

$$C_A=C_{A0}(1-X_A)\qquad \nu_b=\frac{b}{a}=\frac{2}{1}\rightarrow C_B=C_{B0}(1-2X_A)$$

$$\rightarrow\frac{dX_A}{d\tau}=\frac{k\cancel{C_{A0}}C_{B0}^2(1-X_A)(1-2X_A)^2}{\cancel{C_{A0}}}\rightarrow\boxed{\frac{dX_A}{d\tau}=kC_{B0}^2(1-X_A)(1-2X_A)^2}$$

Could solve with Polymath if we knew the value of $\tau$

$\boxed{C_{B0}=0.0313}$ $\boxed{k=0.0313}$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn $A+2B \rightarrow C+D$, $-r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & $k=176$ L²/mol²·min at 320K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C g/m³ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |
| t*E(t) | 0 | 0.02 | 0.2 | 0.48 | 0.8 | 0.8 | 0.72 | 0.56 | 0.48 | 0.396 | 0.3 | 0.144 | 0 |

$$\boxed{\frac{dX_A}{d\tau}=kC_{B0}^2(1-X_A)(1-2X_A)^2}$$

How do we determine τ?

For an ideal reactor, $\tau = t_m$

$$t_m=\int_0^\infty tE(t)dt$$

Use numerical method to determine $t_m$:

$$t_m=\int_0^\infty tE(t)dt=\int_0^{10} tE(t)dt+\int_{10}^{14} tE(t)dt$$

$$\int_0^{10} tE(t)dt=\frac{1}{3}\begin{bmatrix}0+4(0.02)+2(0.2)+4(0.48)+2(0.8)+4(0.8)\\ +2(0.72)+4(0.56)+2(0.48)+4(0.396)+0.3\end{bmatrix}=4.57$$

$$\int_{10}^{14} tE(t)dt=\frac{2}{3}[0.3+4(0.144)+0]=0.584$$

$$\rightarrow t_m=4.57+0.584=5.15\,\text{min}$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn A+2B→C+D, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

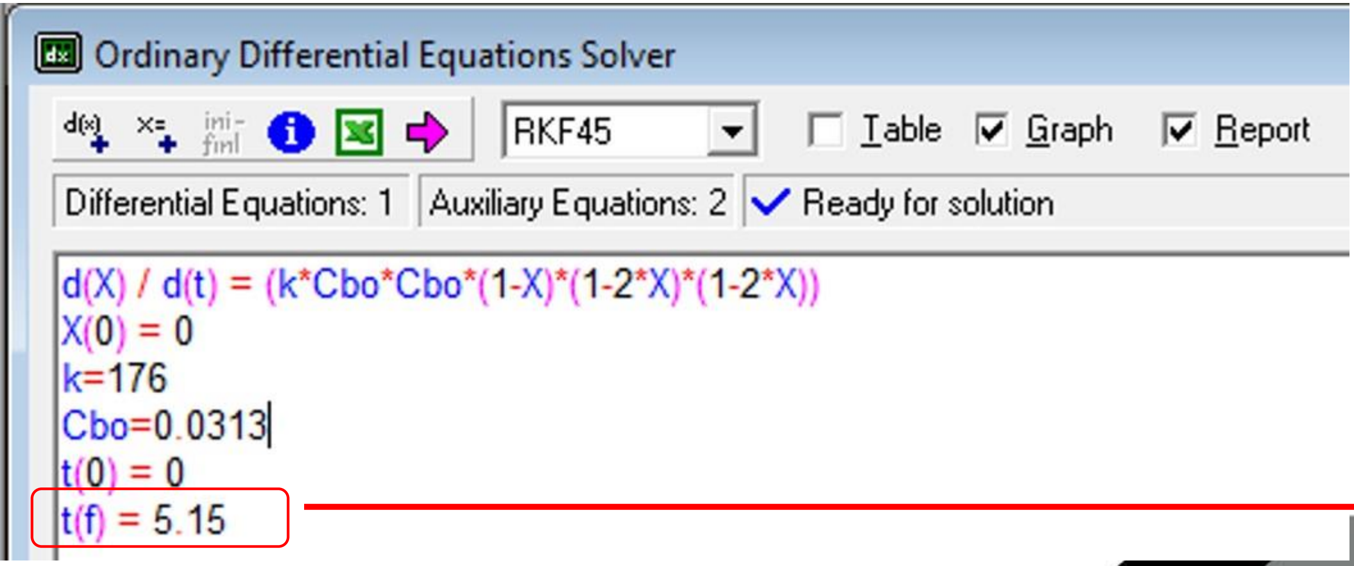
$C_{A0}=C_{B0}$=0.0313 mol/L & k=176 L²/mol²·min at 320K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C g/m³ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |
| t*E(t) | 0 | 0.02 | 0.2 | 0.48 | 0.8 | 0.8 | 0.72 | 0.56 | 0.48 | 0.396 | 0.3 | 0.144 | 0 |

$$\boxed{\frac{dX_A}{d\tau} = kC_{B0}^2(1-X_A)(1-2X_A)^2}$$

For an ideal reactor, $\tau = t_m$

$$t_m = \int_0^\infty tE(t)dt$$



```
d(X) / d(t) = (k*Cbo*Cbo*(1-X)*(1-2*X)*(1-2*X))
X(0) = 0
k=176
Cbo=0.0313
t(0) = 0
t(f) = 5.15
```

$$t_m = 5.15\,\text{min} = \tau$$

Final $X_A$ corresponds to $\tau$=5.15 min

$$X_{A,PFR} = 0.29$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn $A+\underline{2B}\rightarrow C+D$, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & $k=176$ $L^2/mol^2\cdot min$ at 320K

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| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C $g/m^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

Segregation model with Polymath:

$$\bar{X}_A=\int_0^\infty X_A(t)E(t)dt \quad \boxed{\rightarrow \frac{d\bar{X}_A}{dt}=X_A(t)E(t)}$$

$X_A(t)$ is from ***batch reactor*** design eq

Batch reactor design eq:

$$N_{A0}\frac{dX_A}{dt}=-r_AV \rightarrow \cancel{N_{A0}}\frac{dX_A}{dt}=k\cancel{C_{A0}}C_{B0}^2(1-X_A)(1-2X_A)^2\cancel{V}$$

$$N_{A0}=C_{A0}V$$

Stoichiometry:

$$\rightarrow \boxed{\frac{dX_A}{dt}=kC_{B0}^2(1-X_A)(1-2X_A)^2}$$

$$-r_A=kC_AC_B^2$$

$$C_B=C_{B0}(1-2X_A)$$

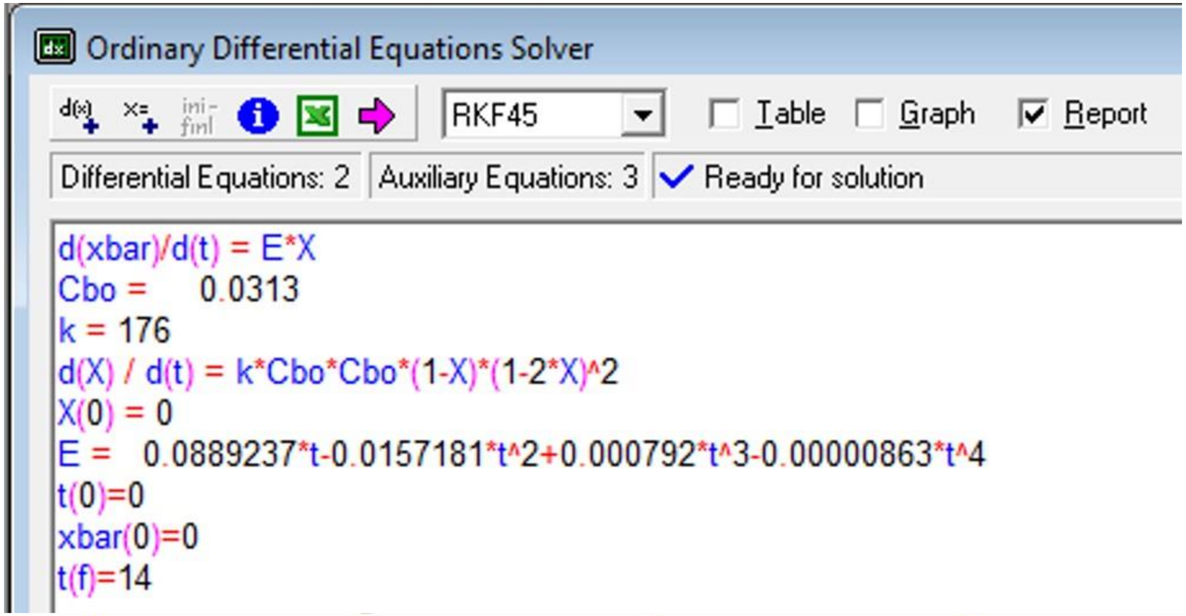
$$C_A=C_{A0}(1-X_A)$$

$\boxed{k=176}$ $\boxed{C_{B0}=0.0313}$

Best-fit polynomial line for E(t) vs t calculated by Polymath (slide 19)

$$\boxed{E(t)=0.0889237*t-0.0157181*t^2+0.0007926*t^3-8.63E\text{-}6*t^4}$$

# Segregation model, isothermal operation, elementary rxn: A+<u>2B</u>→C+D



RKF45

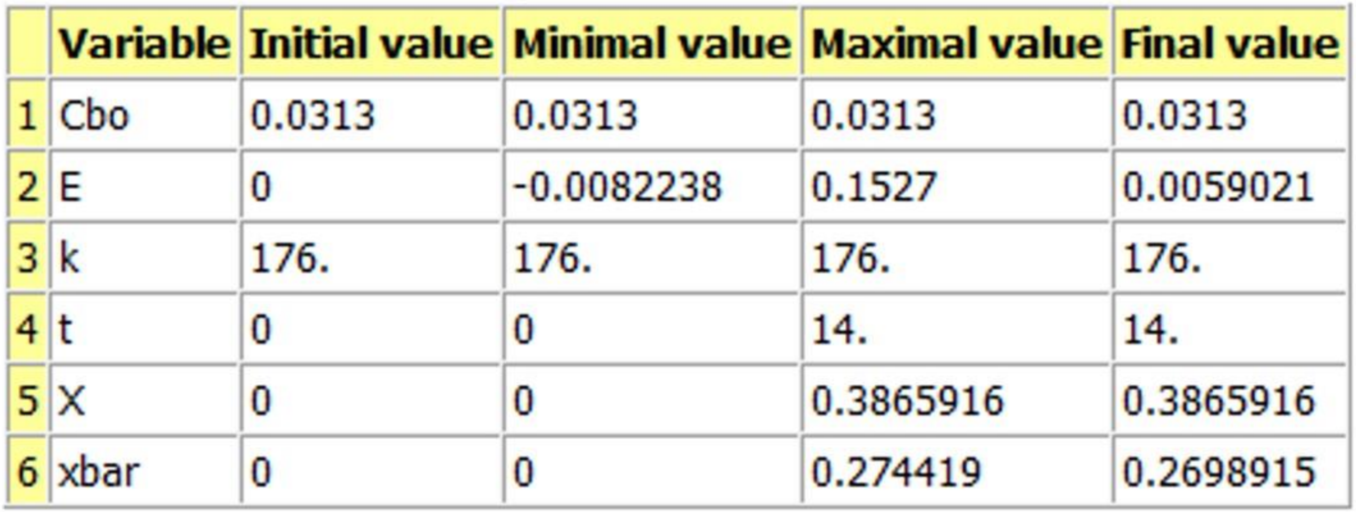
☐ Table ☐ Graph ☑ Report

Differential Equations: 2

Auxiliary Equations: 3

✓ Ready for solution

```
d(xbar)/d(t) = E*X
Cbo =     0.0313
k = 176
d(X) / d(t) = k*Cbo*Cbo*(1-X)*(1-2*X)^2
X(0) = 0
E =  0.0889237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4
t(0)=0
xbar(0)=0
t(f)=14
```



|  | Variable | Initial value | Minimal value | Maximal value | Final value |
|---|---|---|---|---|---|
| 1 | Cbo | 0.0313 | 0.0313 | 0.0313 | 0.0313 |
| 2 | E | 0 | -0.0082238 | 0.1527 | 0.0059021 |
| 3 | k | 176. | 176. | 176. | 176. |
| 4 | t | 0 | 0 | 14. | 14. |
| 5 | X | 0 | 0 | 0.3865916 | 0.3865916 |
| 6 | xbar | 0 | 0 | 0.274419 | 0.2698915 |

$$X_{A,seg} = 0.27$$

For a pulse tracer expt, the effluent concentration C(t) & RTD function E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn $A+\underline{2B}\rightarrow C+D$, $r_A=kC_AC_B^2$ will be carried out isothermally at 320K in this reactor. Calculate the conversion for an ideal PFR, the complete segregation model and maximum mixedness model.

$C_{A0}=C_{B0}=0.0313$ mol/L & k=176 $L^2/mol^2\cdot min$ at 320K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C $g/m^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

Maximum mixedness model:

$$\frac{dX_A}{d\lambda}=\frac{r_A}{C_{A0}}+\frac{E(\lambda)}{1-F(\lambda)}X_A \qquad \lambda\text{=time} \qquad \frac{dF}{d\lambda}=E$$

Polymath cannot solve because λ→0 (must increase)

$$\boxed{-r_A=kC_{A0}C_{B0}^2(1-X_A)(1-2X_A)^2}$$

$$\boxed{k=176\frac{L^2}{mol^2\cdot min}}$$

$$\boxed{C_{A0}=C_{B0}=0.0313\,mol/L}$$

Substitute λ **for** z, where $z=\bar{T}-\lambda$ where $\bar{T}$=longest time interval (14 min)

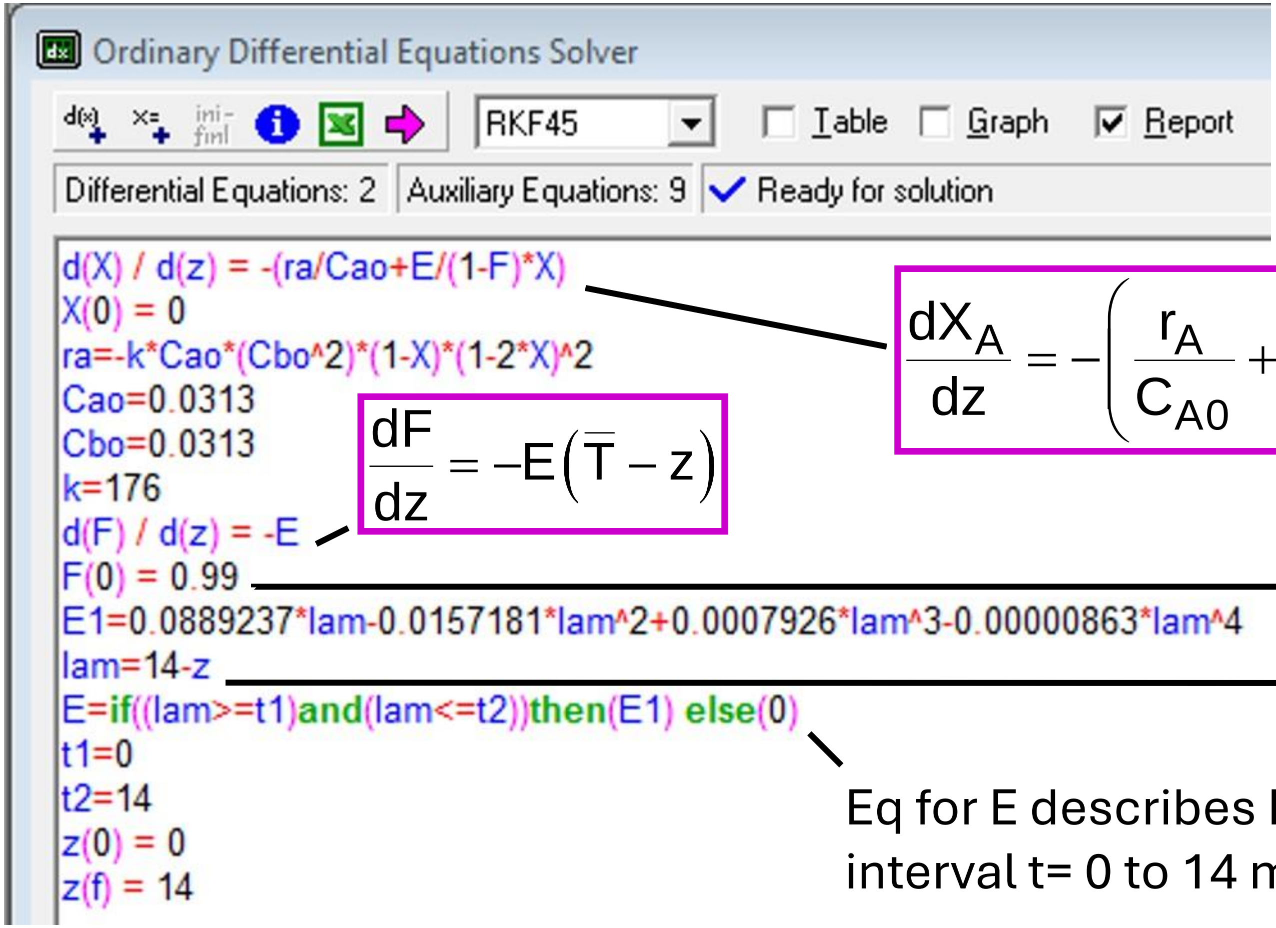
$$\boxed{\frac{dX_A}{dz}=-\left(\frac{r_A}{C_{A0}}+\frac{E(\bar{T}-z)}{1-F(\bar{T}-z)}X_A\right)}$$

$$\boxed{\frac{dF}{dz}=-E(\bar{T}-z)}$$

E must be in terms of $\bar{T}$-z. Since $\bar{T}$-z=λ & λ=t, simply substitute λ for t

$$\boxed{E(\lambda)=0.0889237*\lambda-0.0157181*\lambda^2+0.0007926*\lambda^3-8.63E\text{-}6*\lambda^4}$$

# Maximum Mixedness Model, elementary reaction A+2B→C+D, $-r_A=kC_AC_B^2$



RKF45 ☐ Table ☐ Graph ☑ Report

Differential Equations: 2 | Auxiliary Equations: 9 | ✓ Ready for solution

```
d(X) / d(z) = -(ra/Cao+E/(1-F)*X)
X(0) = 0
ra=-k*Cao*(Cbo^2)*(1-X)*(1-2*X)^2
Cao=0.0313
Cbo=0.0313
k=176
d(F) / d(z) = -E
F(0) = 0.99
E1=0.0889237*lam-0.0157181*lam^2+0.0007926*lam^3-0.00000863*lam^4
lam=14-z
E=if((lam>=t1)and(lam<=t2))then(E1) else(0)
t1=0
t2=14
z(0) = 0
z(f) = 14
```

$$\boxed{\frac{dX_A}{dz}=-\left(\frac{r_A}{C_{A0}}+\frac{E(\bar{T}-z)}{1-F(\bar{T}-z)}X_A\right)}$$

$$\boxed{\frac{dF}{dz}=-E(\bar{T}-z)}$$

Denominator cannot = 0

$$z=\bar{T}-\lambda \rightarrow \lambda=\bar{T}-z$$

Eq for E describes RTD function only on interval t= 0 to 14 minutes, otherwise E=0

$$X_{A,\text{ maximum mixedness}}=0.25$$

For a pulse tracer expt, C(t) & E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn A+2B→C+D, $-r_A=kC_AC_B^2$ will be carried out in this reactor. Calculate the conversion for the complete segregation model under adiabatic conditions with $T_0$= 288K, $C_{A0}=C_{B0}$=0.0313 mol/L, k=176 L²/mol²·min at 320K, $\Delta H°_{RX}$=-40000 cal/mol, E/R =3600K, $C_{PA}=C_{PB}$=20cal/mol·K & $C_{PC}=C_{PD}$=30 cal/mol·K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C g/m³ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

Polymath eqs for segregation model:

$$\boxed{\frac{d\bar{X}_A}{dt}=X_A(t)E(t)}\qquad\boxed{\frac{dX_A}{dt}=kC_{B0}^2(1-X_A)(1-2X_A)^2}$$

$$\boxed{E(t)=0.0889237*t-0.0157181*t^2+0.0007926*t^3-8.63E\text{-}6*t^4}$$

Express k as function of T:

$$\boxed{k(T)=176\frac{L^2}{mol^2\cdot min}\exp\left[3600K\left(\frac{1}{320K}-\frac{1}{T}\right)\right]}$$

Need equations from energy balance. For adiabatic operation:

$$T=\frac{\left[-\Delta H^{\circ}_{RX}(T_R)\right]X_A+\sum_{i=1}^{n}\Theta_iC_{p_i}T_0+X_A\Delta C_PT_R}{\left[\sum_{i=1}^{n}\Theta_iC_{p_i}+X_A\Delta C_P\right]}$$

For a pulse tracer expt, C(t) & E(t) are given in the table below. The irreversible, liquid-phase, elementary rxn A+2B→C+D, $-r_A=kC_AC_B^2$ will be carried out in this reactor. Calculate the conversion for the complete segregation model under adiabatic conditions with $T_0$= 288K, $C_{A0}=C_{B0}$=0.0313 mol/L, k=176 $L^2/mol^2\cdot min$ at 320K, $\Delta H°_{RX}$=-40000 cal/mol, E/R =3600K, $C_{PA}=C_{PB}$=20cal/mol·K & $C_{PC}=C_{PD}$=30 cal/mol·K

| t min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C $g/m^3$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| E(t) | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |

Adiabatic EB:

$$T=\frac{\left[-\Delta H^{\circ}{}_{RX}\left(T_R\right)\right]X_A+\sum_{i=1}^{n}\Theta_iC_{p_i}T_0+X_A\Delta C_PT_R}{\left[\sum_{i=1}^{n}\Theta_iC_{p_i}+X_A\Delta C_P\right]}$$

$$\Delta C_p=\left(30+30-2\left(20\right)-20\right)=0$$

$$\sum_{i=1}^{n}\Theta_iC_{p_i}=C_{pA}+C_{pB}=40\frac{cal}{mol\cdot K}$$

$$\boxed{T=288K+1000X_A}$$

$$\boxed{\frac{d\bar{X}_A}{dt}=X_A\left(t\right)E\left(t\right)}$$

$$\boxed{\frac{dX_A}{dt}=kC_{B0}{}^2\left(1-X_A\right)\left(1-2X_A\right)^2}$$

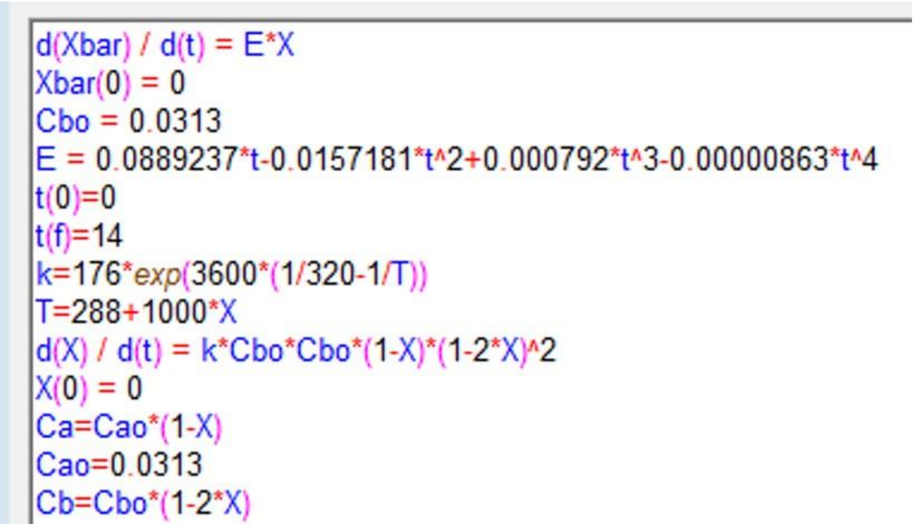
$$\boxed{k\left(T\right)=176\frac{L^2}{mol^2\cdot min}\exp\left[3600K\left(\frac{1}{320K}-\frac{1}{T}\right)\right]}$$

$$\boxed{E(t)=0.0889237*t-0.0157181*t^2+0.0007926*t^3-8.63E\text{-}6*t^4}$$

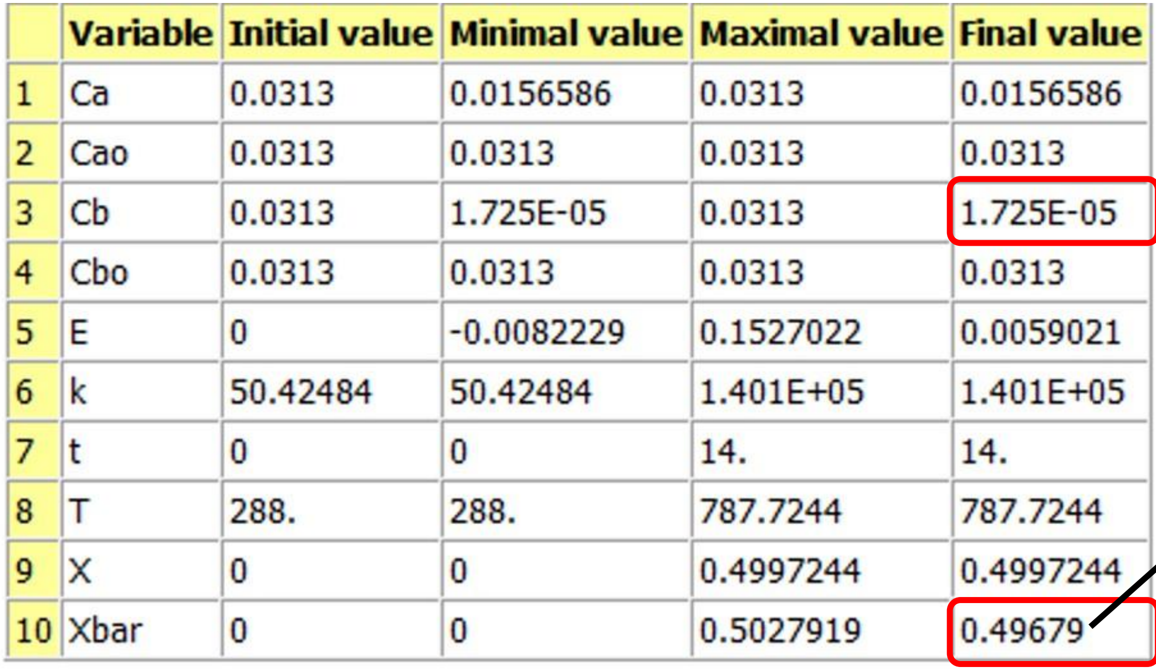
# Segregation model, adiabatic operation, elementary reaction kinetics

$A+\underline{2B}\rightarrow C+D$

$-r_A=kC_AC_B^2$



```
d(Xbar) / d(t) = E*X
Xbar(0) = 0
Cbo = 0.0313
E = 0.0889237*t-0.0157181*t^2+0.000792*t^3-0.00000863*t^4
t(0)=0
t(f)=14
k=176*exp(3600*(1/320-1/T))
T=288+1000*X
d(X) / d(t) = k*Cbo*Cbo*(1-X)*(1-2*X)^2
X(0) = 0
Ca=Cao*(1-X)
Cao=0.0313
Cb=Cbo*(1-2*X)
```



|  | Variable | Initial value | Minimal value | Maximal value | Final value |
|---|---|---|---|---|---|
| 1 | Ca | 0.0313 | 0.0156586 | 0.0313 | 0.0156586 |
| 2 | Cao | 0.0313 | 0.0313 | 0.0313 | 0.0313 |
| 3 | Cb | 0.0313 | 1.725E-05 | 0.0313 | 1.725E-05 |
| 4 | Cbo | 0.0313 | 0.0313 | 0.0313 | 0.0313 |
| 5 | E | 0 | -0.0082229 | 0.1527022 | 0.0059021 |
| 6 | k | 50.42484 | 50.42484 | 1.401E+05 | 1.401E+05 |
| 7 | t | 0 | 0 | 14. | 14. |
| 8 | T | 288. | 288. | 787.7244 | 787.7244 |
| 9 | X | 0 | 0 | 0.4997244 | 0.4997244 |
| 10 | Xbar | 0 | 0 | 0.5027919 | 0.49679 |

Because B is completely consumed by $X_A=0.5$

$\bar{X}_A = 0.50$

Why so much lower than before?

# Tanks-in-Series (T-I-S) Model

We are first going to develop the RTD equation for three tanks in series (Figure 14-2) and then generalize to n reactors in series to derive an equation that gives the number of tanks in series that best fits the RTD data.

Considering a tracer pulse injected into the first reactor of three equally sized CSTRs in series

$$V_1 \frac{dC_1}{dt} = -vC_1 \longrightarrow C_1 = C_0 e^{-vt/V_1} = C_0 e^{-t/\tau_1}$$

$$C_0 = N_0 / V_1 = \frac{v_0 \int_0^\infty C_3(t)dt}{V_1}$$

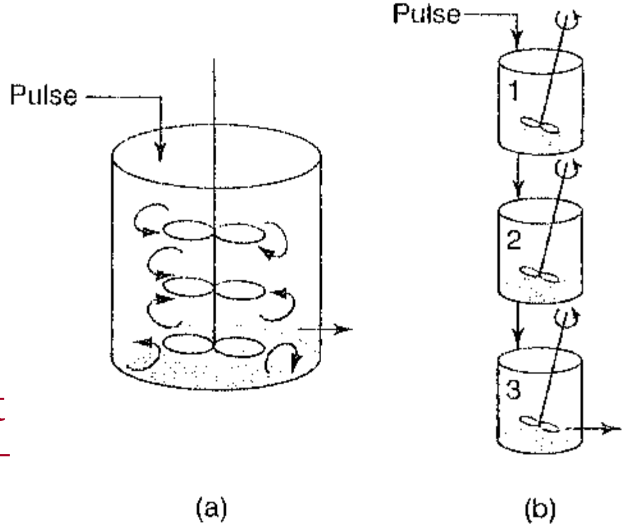


**Figure 14-2** Tanks in series: (a) real system, (b) model system.

$$v = v_0$$

$$V_1 = V_2 = V_i$$

$$\tau_1 = \tau_2 = \tau_i$$

$$\tau_i = \tau / n$$

$$V_i \frac{dC_2}{dt} = vC_1 - vC_2 \longrightarrow \frac{dC_2}{dt} + \frac{C_2}{\tau_i} = \frac{C_0}{\tau_i} e^{-t/\tau_i} \longrightarrow C_2 = \frac{C_0 t}{\tau_i} e^{-t/\tau_i} \longrightarrow C_3 = \frac{C_0 t^2}{2\tau_i^2} e^{-t/\tau_i}$$

$$\longrightarrow E(t) = \frac{C_3(t)}{\int_0^\infty C_3(t)dt} = \frac{C_0 t^2/(2\tau_i^2) e^{-t/\tau_i}}{\int_0^\infty \frac{C_0 t^2 e^{-t/\tau_i}}{2\tau_i^2} dt} = \frac{t^2}{2\tau_i^3} e^{-t/\tau_i} \longrightarrow E(t) = \frac{t^{n-1}}{(n-1)!\,\tau_i^n} e^{-t/\tau_i}$$

$$\tau_i = \tau / n \xrightarrow{\qquad} E(\Theta) = \tau E(t) = \frac{n(n\Theta)^{n-1}}{(n-1)!} e^{-n\Theta}$$

$n\to\infty$, the behavior of the system approaches that of a plug-flow reactor

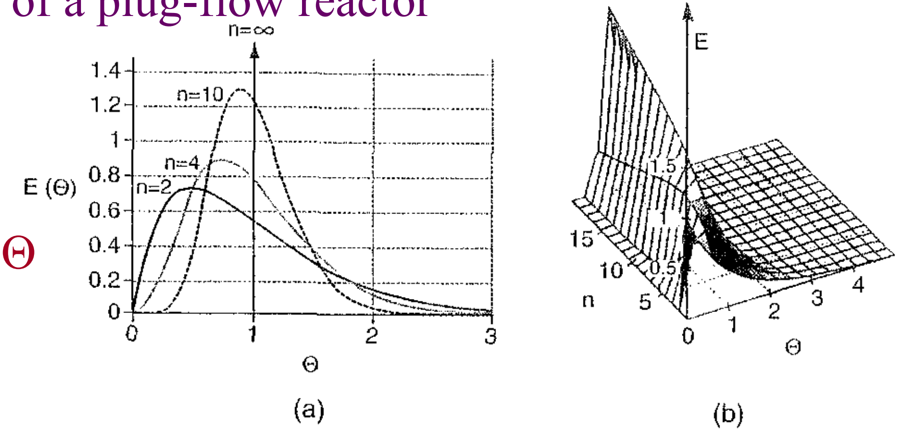


**Figure 14-3** Tanks-in-series response to a pulse tracer input for different numbers of tanks.

$$\sigma_\Theta^2 = \frac{\sigma^2}{\tau^2} = \int_0^\infty (\Theta-1)^2 E(\Theta)d\Theta$$

$$\bullet\bullet\bullet = \int_0^\infty \Theta^2 E(\Theta)d\Theta - 2\int_0^\infty \Theta E(\Theta)d\Theta + \int_0^\infty E(\Theta)d\Theta$$

$$\bullet\bullet\bullet = \int_0^\infty \Theta^2 E(\Theta)d\Theta - 1$$

$$\sigma_\Theta^2 = \int_0^\infty \Theta^2 E(\Theta)d\Theta - 1$$

$$\bullet\bullet\bullet = \int_0^\infty \Theta^2 \frac{n(n\Theta)^{n-1}}{(n-1)!} e^{-n\Theta} d\Theta - 1$$

$$\bullet\bullet\bullet = \frac{n^n}{(n-1)!}\int_0^\infty \Theta^{n+1} e^{-n\Theta} d\Theta - 1$$

$$\bullet\bullet\bullet = \frac{n^n}{(n-1)!}\left[\frac{(n+1)!}{n^{n+2}}\right] - 1 = \frac{1}{n}$$

$$\int_0^\infty E(\Theta)d\Theta = 1$$

$$\int_0^\infty \Theta E(\Theta)d\Theta = 1$$

$$\xrightarrow{\qquad} n = \frac{1}{\sigma_\Theta^2} = \frac{\tau^2}{\sigma^2}$$

# For a first order reaction,

$$X = 1 - \frac{1}{(1+\tau_i k)^n} \qquad \tau_i = \frac{V}{v_0 n}$$

n may be a noninteger.

# For reactions other than first order,

an integer number of reactors must be used.

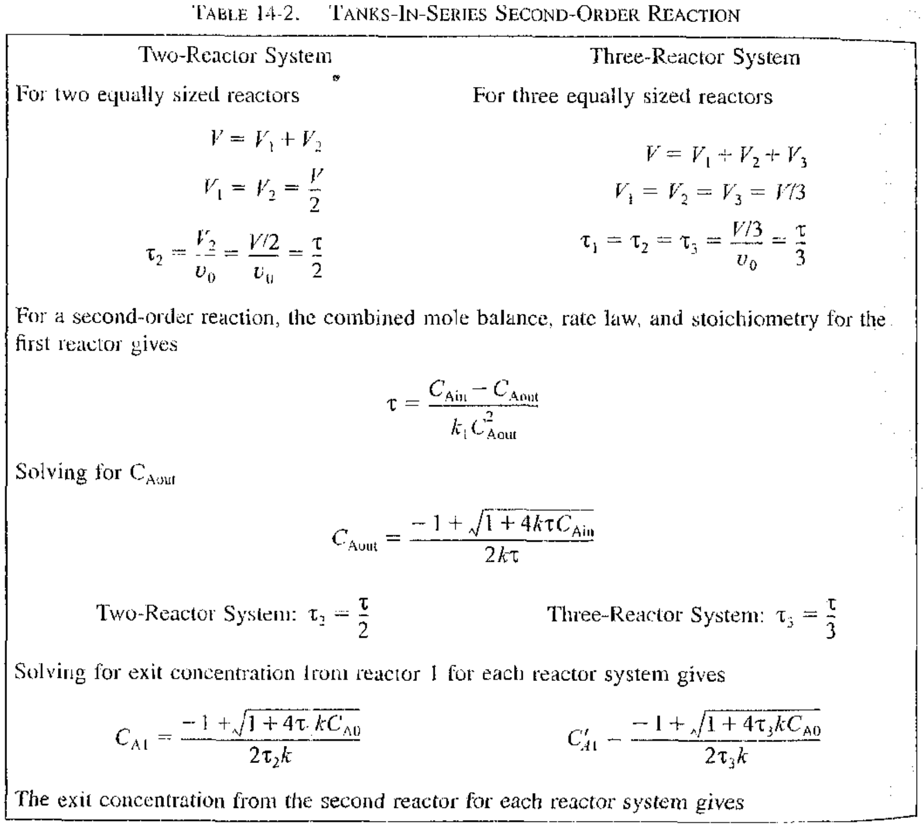


Table 14-2. Tanks-In-Series Second-Order Reaction

| Two-Reactor System | Three-Reactor System |
|---|---|
| For two equally sized reactors | For three equally sized reactors |
| $V = V_1 + V_2$ | $V = V_1 + V_2 + V_3$ |
| $V_1 = V_2 = \frac{V}{2}$ | $V_1 = V_2 = V_3 = V/3$ |
| $\tau_2 = \frac{V_2}{v_0} = \frac{V/2}{v_0} = \frac{\tau}{2}$ | $\tau_1 = \tau_2 = \tau_3 = \frac{V/3}{v_0} = \frac{\tau}{3}$ |

For a second-order reaction, the combined mole balance, rate law, and stoichiometry for the first reactor gives

$$\tau = \frac{C_{\text{Ain}} - C_{\text{Aout}}}{k_1 C_{\text{Aout}}^2}$$

Solving for $C_{\text{Aout}}$

$$C_{\text{Aout}} = \frac{-1 + \sqrt{1 + 4k\tau C_{\text{Ain}}}}{2k\tau}$$

Two-Reactor System: $\tau_2 = \frac{\tau}{2}$ Three-Reactor System: $\tau_3 = \frac{\tau}{3}$

Solving for exit concentration from reactor 1 for each reactor system gives

$$C_{A1} = \frac{-1 + \sqrt{1 + 4\tau\, kC_{A0}}}{2\tau_2 k} \qquad C'_{A1} = \frac{-1 + \sqrt{1 + 4\tau_3 kC_{A0}}}{2\tau_3 k}$$

The exit concentration from the second reactor for each reactor system gives

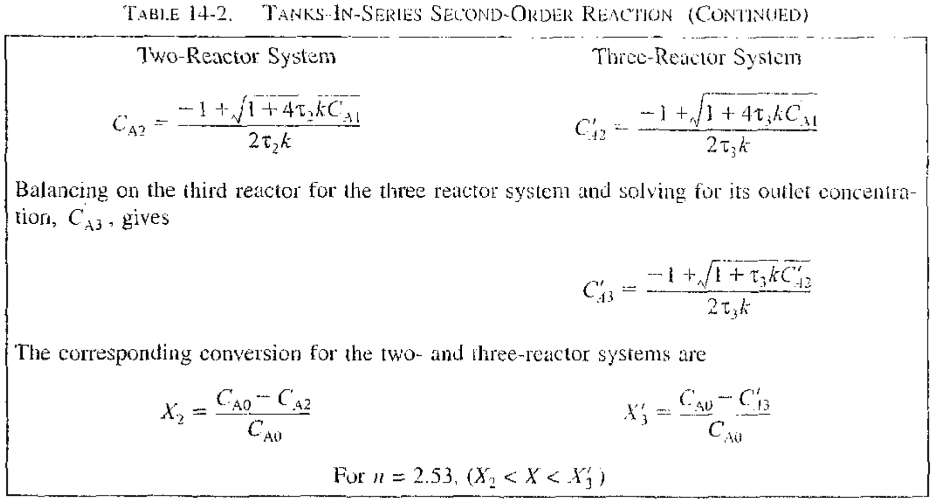


Table 14-2. Tanks-In-Series Second-Order Reaction (Continued)

| Two-Reactor System | Three-Reactor System |
|---|---|
| $C_{A2} = \frac{-1 + \sqrt{1 + 4\tau_2 kC_{A1}}}{2\tau_2 k}$ | $C'_{A2} = \frac{-1 + \sqrt{1 + 4\tau_3 kC_{A1}}}{2\tau_3 k}$ |

Balancing on the third reactor for the three reactor system and solving for its outlet concentration, $C'_{A3}$, gives

$$C'_{A3} = \frac{-1 + \sqrt{1 + \tau_3 kC'_{A2}}}{2\tau_3 k}$$

The corresponding conversion for the two- and three-reactor systems are

$$X_2 = \frac{C_{A0} - C_{A2}}{C_{A0}} \qquad X'_3 = \frac{C_{A0} - C'_{A3}}{C_{A0}}$$

For $n = 2.53$, $(X_2 < X < X'_3)$

# Example 2-1

Show that $X_{T\text{-}I\text{-}S}=X_{MM}$ for a first-order reaction

$$A \xrightarrow{k} B$$

Solution

For a first-order reaction,

$$X_{seg} = X_{MM}$$

Therefore we only need to show $X_{seg}=X_{T\text{-}I\text{-}S}$.

For a first-order reaction in a batch reactor the conversion is

$$X = 1 - e^{-kt}$$

Segregation model

$$\bar{X} = \int_0^\infty X(t)E(t)dt = \int_0^\infty (1-e^{-kt})E(t)dt = 1 - \int_0^\infty e^{-kt}E(t)dt$$

$$\xrightarrow{e^{-kt} = 1 - kt + \frac{k^2t^2}{2} + \text{error}} \bar{X} = \int_0^\infty \left( kt - \frac{k^2t^2}{2} \right) E(t)dt = k\int_0^\infty tE(t)dt - \frac{k^2}{2}\int_0^\infty t^2E(t)dt$$

$$\longrightarrow \quad \bar{X} = k\tau - \frac{k^2}{2}\int_0^\infty t^2 E(t)dt$$

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)dt$$

$$\bullet\bullet\bullet \quad = \int_0^\infty t^2 E(t)dt - 2\tau\int_0^\infty tE(t)dt + \tau^2\int_0^\infty E(t)dt \quad \longrightarrow \quad \int_0^\infty t^2 E(t)dt = \sigma^2 + \tau^2$$

$$\bullet\bullet\bullet \quad = \int_0^\infty t^2 E(t)dt - 2\tau^2 + \tau^2$$

$$\bullet\bullet\bullet \quad = \int_0^\infty t^2 E(t)dt - \tau^2$$

$$\longrightarrow \quad \bar{X} = k\tau - \frac{k^2}{2}(\sigma^2 + \tau^2)$$

Tanks in Series

$$X = 1 - \frac{1}{\left(1 + \frac{\tau}{n}k\right)^n} \quad \longrightarrow \quad X = 1 - \left(1 + \frac{\tau}{n}k\right)^{-n}$$

$$\bullet\bullet\bullet \quad = 1 - \left(1 - n\frac{\tau}{n}k + \frac{n(n+1)}{2}\frac{\tau^2 k^2}{n^2} + \text{error}\right)$$

$$\bullet\bullet\bullet \quad = k\tau - \frac{\tau^2 k^2}{2} - \frac{\tau^2 k^2}{2n} = k\tau - \frac{k^2}{2}\left(\tau^2 + \frac{\tau^2}{n}\right)$$

$$\xrightarrow{\sigma^2 = \frac{\tau^2}{n}} \quad X = k\tau - \frac{k^2}{2}(\tau^2 + \sigma^2) \quad \longrightarrow \quad X_{T-I-S} = X_{seg} = X_{MM}$$

# Dispersion Model

In addition to transport by bulk flow, $UA_cC$, every component in the mixture is transported through any cross section of the reactor at a rate equal to $[-D_aA_c(dC/dz)]$ resulting from molecular and convective diffusion.

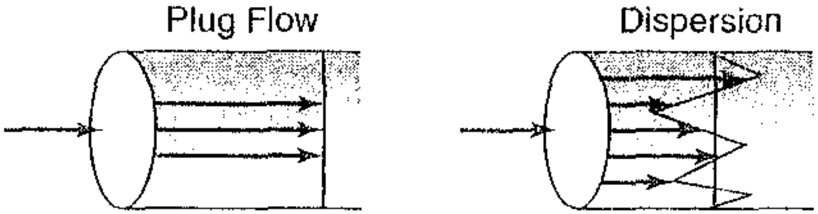


**Figure 14-4** Concentration profiles (a) without and (b) with dispersion.

By convective diffusion (i.e, dispersion) we mean either Aris-Taylor dispersion in laminar flow reactors or turbulent diffusion resulting from turbulent eddies.

Radial concentration profiles for plug flow (a) and a representative axial and radial profile for dispersive flow (b) are shown in Figure 14-1.

Some molecules will diffuse forward ahead of molar average velocity while others will lag behind.

Figure 14-5 presents how dispersion causes the pulse to broaden as it moves down the reactor and becomes less concentrated.

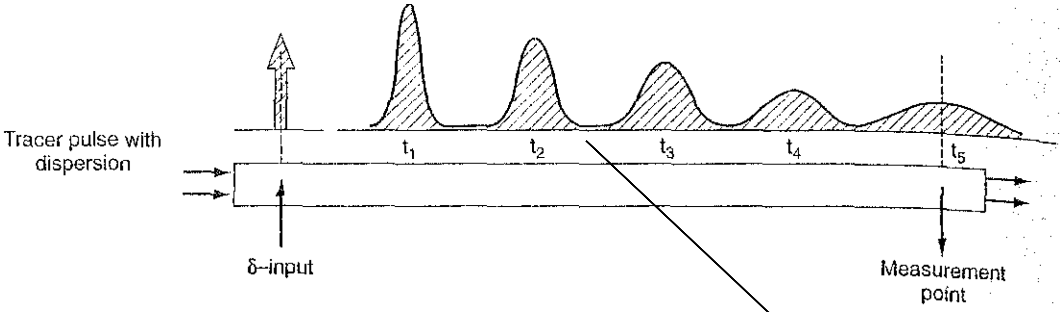


**Figure 14-5** Dispersion in a tubular reactor. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.)

The molar flow rate of tracer ($F_T$) by both convection and dispersion is

$$F_T = \left( -D_a \frac{\partial C_T}{\partial z} + UC_T \right) A_c$$

$D_a$ is the effective dispersion coefficient ($m^2/s$)

U is the superficial velocity (m/s)

There is a concentration gradient on both sides of the peak causing molecules to diffuse away from the peak and thus broaden the pulse. The pulse broadens as it moves through the reactor.

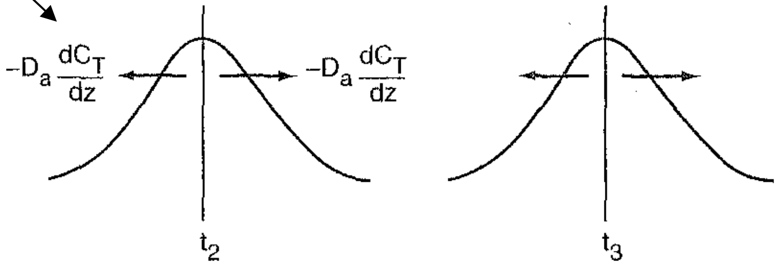


**Figure 14-6** Symetric concentration gradients causing the spreading by dispersion of a pulse input.

A mole balance on the inert tracer T gives

$$-\frac{\partial F_T}{\partial z} = A_c \frac{\partial C_T}{\partial t} \longrightarrow D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial (UC_T)}{\partial z} = \frac{\partial C_T}{\partial t} \longrightarrow C_T \text{ vs. } t$$

# Flow, Reaction, and Dispersion

## Balance Equations

A mole balance is taken on a particular component of the mixture (say, species A) over a short length Δz of a tubular reactor of cross section $A_c$, to arrive at

$$\left.\begin{array}{l} -\dfrac{1}{A_c}\dfrac{dF_A}{dz}+r_A=0 \\[2ex] \dfrac{F_A}{A_c}=-D_a\dfrac{dC_A}{dz}+UC_A \end{array}\right\} \longrightarrow \frac{D_a}{U}\frac{d^2C_A}{dz^2}-\frac{dC_A}{dz}+\frac{r_A}{U}=0$$

A second-order ordinary differential equation.

Nonlinear when $r_A$ is other than zero or fist order.

$$\xrightarrow{r_A=-kC_A}\frac{D_a}{U}\frac{d^2C_A}{dz^2}-\frac{dC_A}{dz}+\frac{-kC_A}{U}=0\xrightarrow{\psi=\frac{C_A}{C_{A0}},\ \lambda=\frac{z}{l}}\frac{1}{Pe_r}\frac{d^2\psi}{d\lambda^2}-\frac{d\psi}{d\lambda}-Da\cdot\psi=0$$

Da:Damkohler number
Pe:Peclet number

$$Da=\frac{\text{Rate of consumption of A by reaction}}{\text{Rate of transport of A by convection}}=k\tau$$

$l$ is the characteristic length

$$Pe=\frac{\text{Rate of transport by convection}}{\text{Rate of transport by diffusion or dispersion}}=\frac{Ul}{D_a}$$

$$Pe_r = \frac{UL}{D_a} \text{ reactor Peclet number}$$

$$Pe_f = \frac{Ud_p}{\phi D_a} \text{ (for packed bed)}, \ \frac{Ud_t}{D_a} \text{ (for empty tube) fluid Peclet number}$$

For open tubes

$Pe_r \sim 10^6$, $Pe_f \sim 10^4$

For packed beds

$Pe_r \sim 10^3$, $Pe_f \sim 10^1$

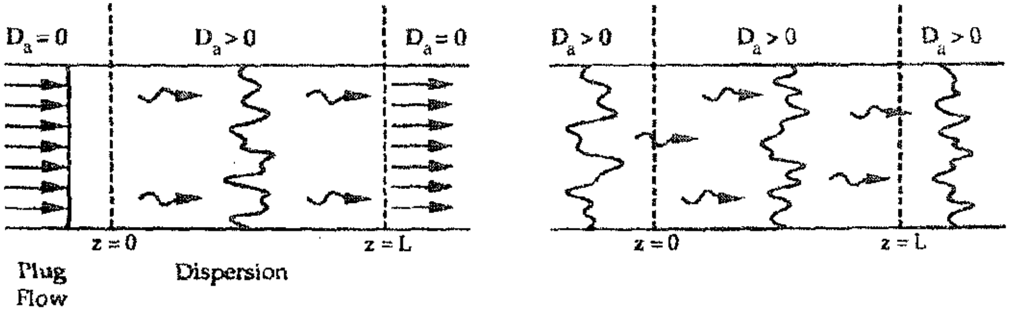
## Boundary Conditions

### closed-closed vessel

there is no dispersion or radial variation in concentration either upstream (closed) or downstream (closed) of the reaction section

### open-open vessel

dispersion occurs both upstream (open) and downstream (open) of the reaction section



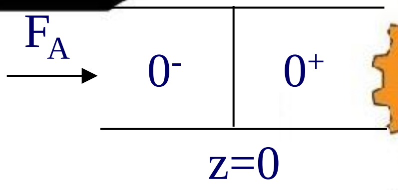
Closed-closed vessel Open-open vessel

**Figure 14-7** Types of boundary conditions.

A closed-open vessel boundary condition is one in which there is no dispersion in the entrance section but there is dispersion in the reaction and exit section.

# Closed-Closed Vessel Boundary Condition

## Danckwerts boundary conditions



At z=0

$$\left.\begin{aligned} F_A(0^-) &= F_A(0^+) \\ F_A &= -A_c D_a \frac{\partial C_A}{\partial z} + U A_c C_A \end{aligned}\right\} \longrightarrow U A_c C_A(0^-) = -A_c D_a \left(\frac{\partial C_A}{\partial z}\right)_{z=0^+} + U A_c C_A(0^+)$$

$$\xrightarrow{C_A(0^-) = C_{A0}} C_{A0} = -\frac{D_a}{U}\left(\frac{\partial C_A}{\partial z}\right)_{z=0^+} + C_A(0^+)$$

At z=L

$$C_A(L^-) = C_A(L^+)$$

$$\frac{\partial C_A}{\partial z} = 0$$

open-open vessel

$$\Big\downarrow$$

$$-\frac{D_a}{U}\left(\frac{\partial C_A}{\partial z}\right)_{z=0^-} + C_A(0^-) = -\frac{D_a}{U}\left(\frac{\partial C_A}{\partial z}\right)_{z=0^+} + C_A(0^+)$$

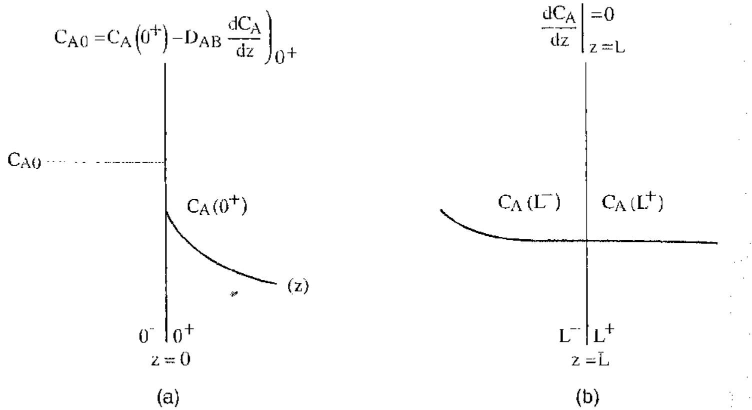


**Figure 14-8** Schematic of Danckwerts boundary conditions. (a) Entrance (b) Exit

# Back to the Solution for a Closed-Closed System

$$\frac{1}{Pe_r}\frac{d^2\psi}{d\lambda^2} - \frac{d\psi}{d\lambda} - Da\cdot\psi = 0$$

$$\text{At } \lambda = 0 \text{ then } 1 = -\frac{1}{Pe_r}\left(\frac{d\psi}{d\lambda}\right)_{0^+} + \psi(0^+)$$

$$\text{At } \lambda = 1 \text{ then } \frac{d\psi}{d\lambda} = 0$$

$$\longrightarrow \psi_L = \frac{C_{AL}}{C_{A0}} = 1 - X = \frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_r q/2) - (1-q)^2(-Pe_r q/2)} \quad q = \sqrt{1 + 4Da/Pe_r}$$

$$\longrightarrow X = 1 - \frac{4q\exp(Pe_r/2)}{(1+q)^2\exp(Pe_r q/2) - (1-q)^2(-Pe_r q/2)}$$

outside the limited case of a first-order reaction, a numerical solution of the equation is required, and because this is s split-boundary-value problem, an iterative technique is required.

## Finding $D_a$ and Peclet Number

1. Laminar flow with radial and axial molecular diffusion theory
2. Correlation from the literature for pipes and packed beds
3. Experimental tracer data

# Dispersion in a Tubular Reactor with Laminar Flow

The axial velocity varies in the radial direction according to the Hagen-Poiseuille equation:

$$u(r) = 2U\left[1-\left(\frac{r}{R}\right)^2\right]$$

U is the average velocity

$$E(t) = \begin{cases} 0 \bullet\bullet\bullet\bullet t & < \tau/2 \\ \dfrac{\tau^2}{2t^3} \bullet\bullet t & \geq \tau/2 \end{cases} \bullet\bullet\bullet$$

In arriving at this distribution E(t), it was assumed that there are no transfer of molecules in the radial direction between streamlines.

$$r = 0 \bullet\bullet\bullet\bullet\bullet\bullet u = 2U \bullet\bullet\bullet\bullet\bullet\bullet t = \tau/2$$

$$r = 3R/4 \bullet\bullet\bullet u = 7U/8 \bullet\bullet\bullet t = 8\tau/7 \bullet$$

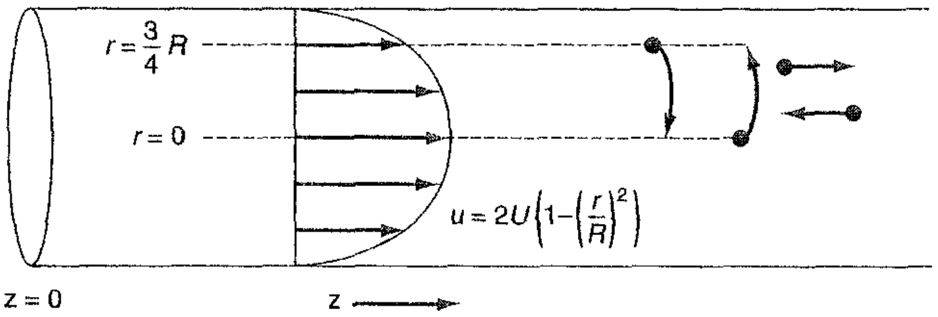


**Figure 14-9** Radial diffusion in laminar flow.

In addition to the molecules diffusing between streamlines, they can also move forward or backward relative to the average fluid velocity by molecular diffusion (Fick's law).

The convective-diffusion equation for solute (e.g., tracer) transport in both the axial and radial direction can be obtained.

$$\frac{\partial C}{\partial t} + u(r)\frac{\partial C}{\partial z} = D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + \frac{\partial^2 C}{\partial z^2}\right]$$

$$\xrightarrow{z^* = z - Ut} \left(\frac{\partial C}{\partial t}\right)_{z^*} + [u(r) - U]\frac{\partial C}{\partial z^*} = D_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + \frac{\partial^2 C}{\partial z^{*2}}\right]$$

$$\longrightarrow \bar{C}(z,t) = \frac{1}{\pi R^2}\int_0^R C(r,z,t)2\pi r\,dr$$

$$\frac{\partial \bar{C}}{\partial t} + U\frac{\partial \bar{C}}{\partial z^*} = D^*\frac{\partial^2 \bar{C}}{\partial z^{*2}}$$

D* is the Aris-Taylor dispersion coefficient

$$D^* = D_{AB} + \frac{U^2R^2}{48D_{AB}}$$

For laminar flow in a pipe

$$D_a \equiv D^*$$

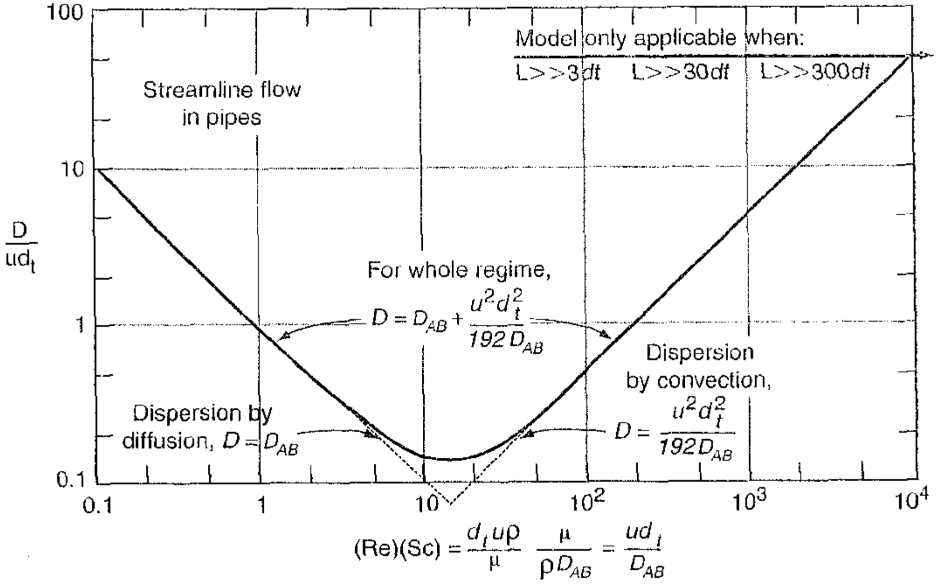


**Figure 14-10** Correlation for dispersion for streamline flow in pipes. (From O. Levenspiel, Chemical Reaction Engineering, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [Note: $D \equiv D_a$ and $D \equiv D_{AB}$]

# Correlations for $D_a$

## Dispersion for Laminar and Turbulent Flow in Pipes

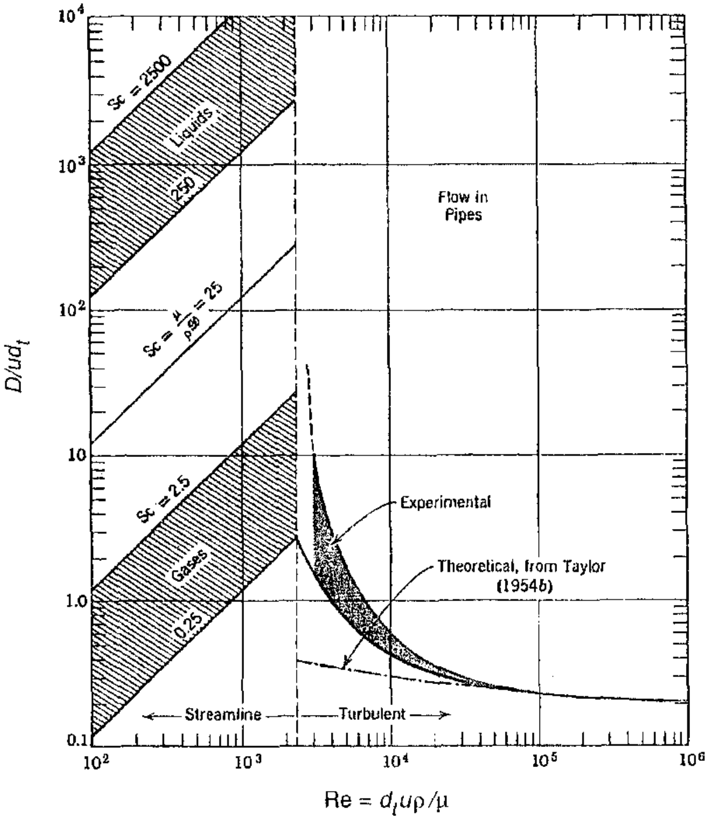


**Figure 14-11** Correlation for dispersion of fluids flowing in pipes. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$]

$d_t$ is the tube diameter

Sc is the Schmidt number

## Dispersion in Packed Beds

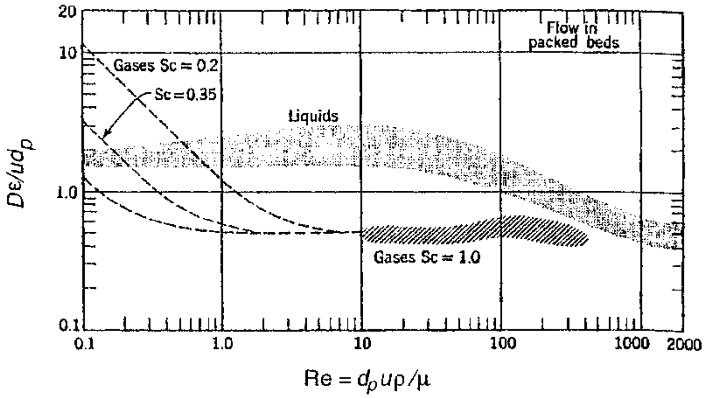


**Figure 14-12** Experimental findings on dispersion of fluids flowing with mean axial velocity $u$ in packed beds. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$]

$d_p$ is the particle diameter

$\varepsilon$ is the porosity

# Experimental Determination of $D_a$

$$D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial (U C_T)}{\partial z} = \frac{\partial C_T}{\partial t}$$

For the different types of boundary conditions at the reactor entrance and exit, to solve for the exit concentration as a function of dimensionless time ($\Theta = t/\tau$), and then relate $D_a$, $\sigma^2$, and $\tau$.

## Unsteady-State Tracer Balance

$$\xrightarrow{\psi = \frac{C_T}{C_{T0}},\ \lambda = \frac{z}{L},\ \Theta = \frac{tU}{L}} \quad \frac{1}{Pe_r}\frac{\partial^2 \psi}{\partial \lambda^2} - \frac{\partial \psi}{\partial \lambda} = \frac{\partial \Psi}{\partial \Theta}$$

Initial condition

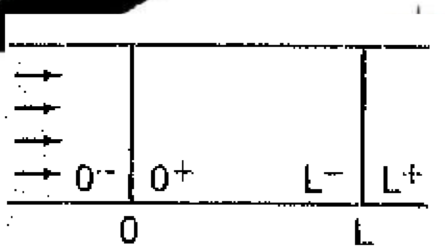
$$t > 0,\ z > 0,\ C_T(0^+, 0) = 0,\ \psi(0^+) = 0$$

Mass of tracer injected, M is

$$M = U A_C \int_0^\infty C_T(0^-, t)\,dt$$

For a pulse input, $C_{T0}$ is defined as the mass of tracer injected, M, divided by the vessel volume, V.

# Solution for a Closed-Closed System



At λ=0

$$C_{T0} = -\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=0^+} + C_T(0^+) \longrightarrow \left(-\frac{1}{Pe_r}\frac{\partial \psi}{\partial \lambda}\right)_{0^+} + \psi(0^+) = 1$$

At λ=1

$$\frac{\partial C_A}{\partial z} = 0 \longrightarrow \frac{\partial \psi}{\partial \lambda} = 0$$

$$\longrightarrow t_m = \tau \longrightarrow \frac{\sigma^2}{t_m^2} = \frac{1}{\tau^2}\int_0^\infty (t-\tau)^2 E(t)dt$$

$$\longrightarrow \frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}(1 - e^{-Pe_r})$$

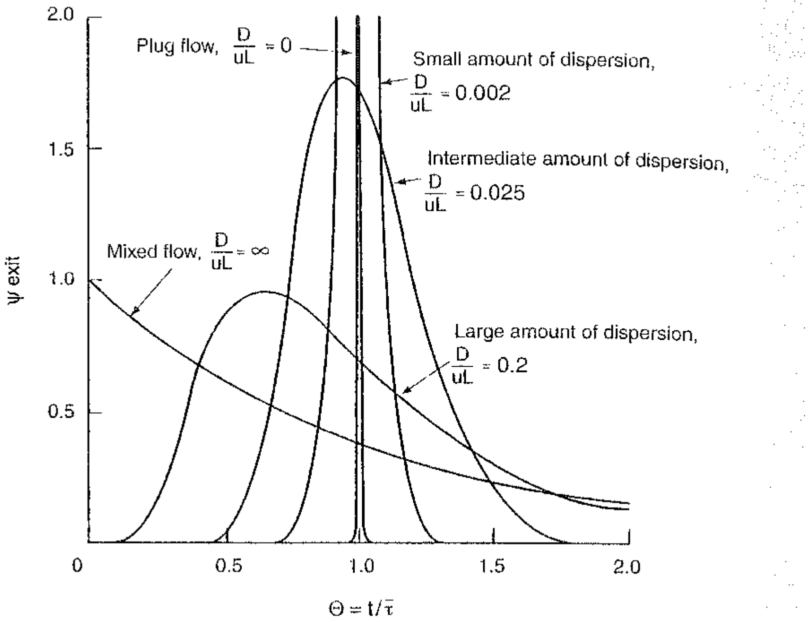


**Figure 14-13** *C* curves in closed vessels for various extents of back-mixing as predicted by the dispersion model. (From O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed. Copyright © 1972 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc. All rights reserved.) [*Note*: $D \equiv D_a$][10]

$$\text{RTD data} \longrightarrow \begin{matrix} t_m \\ \sigma^2 \end{matrix} \longrightarrow Pe_r \longrightarrow D_a$$

# Solution for a Open-Open System

At $\lambda$=0

$$-\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=0^-}+C_T(0^-,t)=-\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=0^+}+C_T(0^+,t) \qquad C_T(0^-,t)=C_T(0^+,t)$$

At $\lambda$=1

$$-\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=L^-}+C_T(L^-,t)=-\frac{D_a}{U}\left(\frac{\partial C_T}{\partial z}\right)_{z=L^+}+C_T(L^+,t) \qquad C_T(L^-,t)=C_T(L^+,t)$$

Consider the case when there is no variation in the dispersion coefficient for all z and an impulse of tracer is injected at z=0 at t=0.

For long tubes (Pe>100) in which the concentration gradient at ±∞ will be zero →

$$\psi(1,\Theta)=\frac{C_T(L,t)}{C_{T0}}=\frac{1}{2\sqrt{\pi\Theta/Pe_r}}\exp\left[\frac{-(1-\Theta)^2}{4\Theta/Pe_r}\right]$$

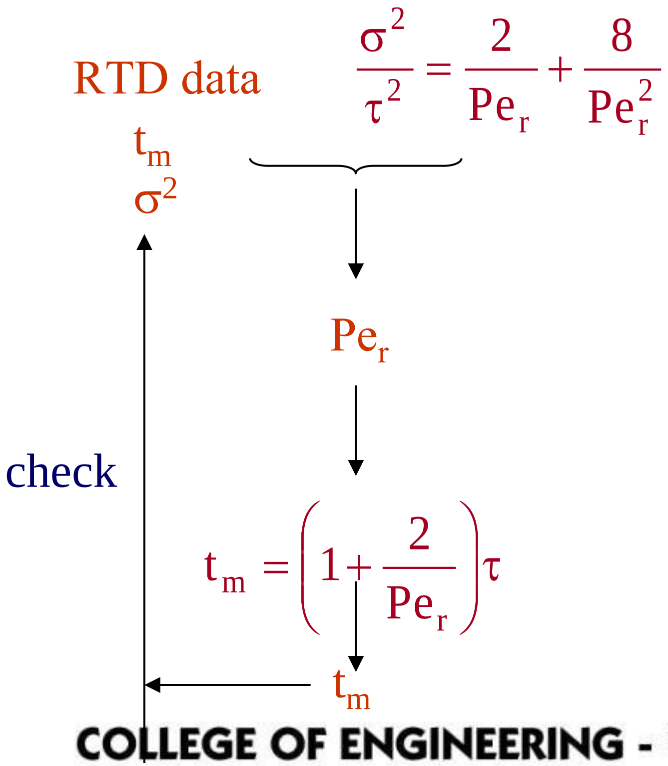
$$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau$$

τ is based on the volume between z=0 and z=L (i.e., reactor volume measured with a yardstick).

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}$$

The mean residence time for an open system is greater than that for a closed-system. The reason is that the molecules can diffuse back into the reactor after they exit.

## Case 1~space time τ is known



RTD data

$t_m$

$\sigma^2$

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}$$

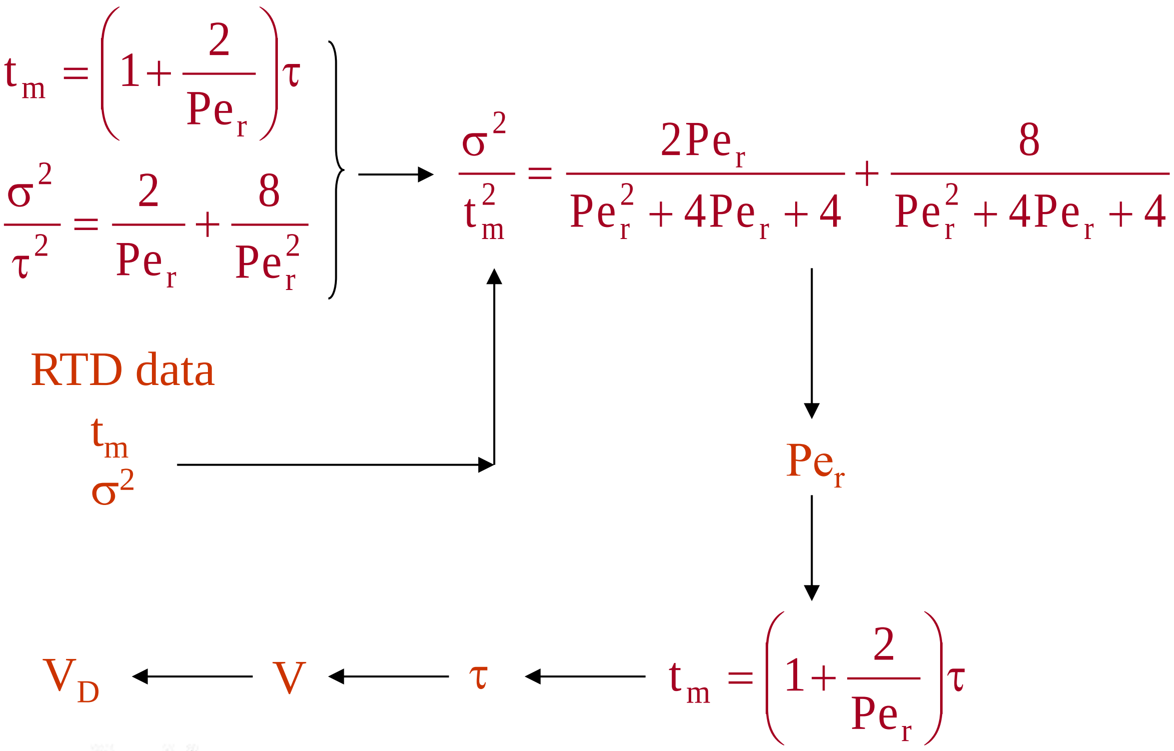
$Pe_r$

$$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau$$

$t_m$

check

## Case 2~space time τ is unknown



$$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau$$

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}$$

$$\frac{\sigma^2}{t_m^2} = \frac{2Pe_r}{Pe_r^2 + 4Pe_r + 4} + \frac{8}{Pe_r^2 + 4Pe_r + 4}$$

RTD data

$t_m$

$\sigma^2$

$Pe_r$

$$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau$$

$V_D \leftarrow V \leftarrow \tau$

# Sloppy Tracer Inputs

It is not always possible to inject a tracer pulse cleanly as an input to a system because it takes a finite time to inject the reactor.

When the injection does not approach a perfect input (Figure 14-14), the differences in the variances between the input and output tracer measurements are used to calculate the Peclet number:

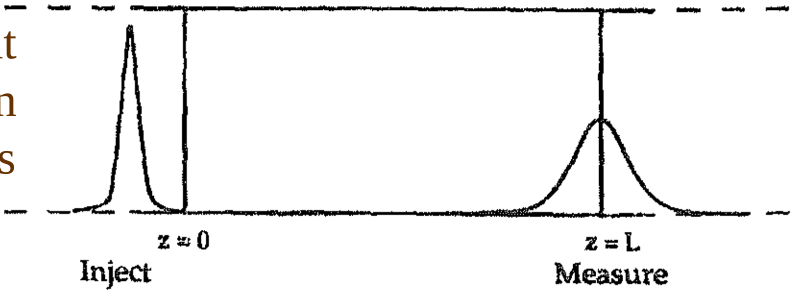


**Figure 14-14** Imperfect tracer input.

$$\Delta\sigma^2 = \sigma_{in}^2 - \sigma_{out}^2$$

$\sigma_{in}^2$ is the variance of the tracer measured at some point upstream (near the entrance)

$\sigma_{out}^2$ is the variance of the tracer measured at some point downstream (after the exit)

For an open-open system

$$\frac{\Delta\sigma^2}{t_m^2} = \frac{2}{Pe_r}$$

# Example 2-2

The first-order reaction

$$A \rightarrow B$$

is carried out in a 10-cm-diameter tubular reactor 6.36 m in length. The specific reaction rate is 0.25 min$^{-1}$. The results of a tracer test carried out this reactor are shown in Table E14-2.1.

Table E14-2.1. Effluent Tracer Concentration as a Function of Time

| $t$ (min) | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C$ (mg/L) | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |

Calculate conversion using (a) the closed vessel dispersion model, (b) PFR, (c) the tanks-in-series model, and (d) a single CSTR.

# Solution

(a)

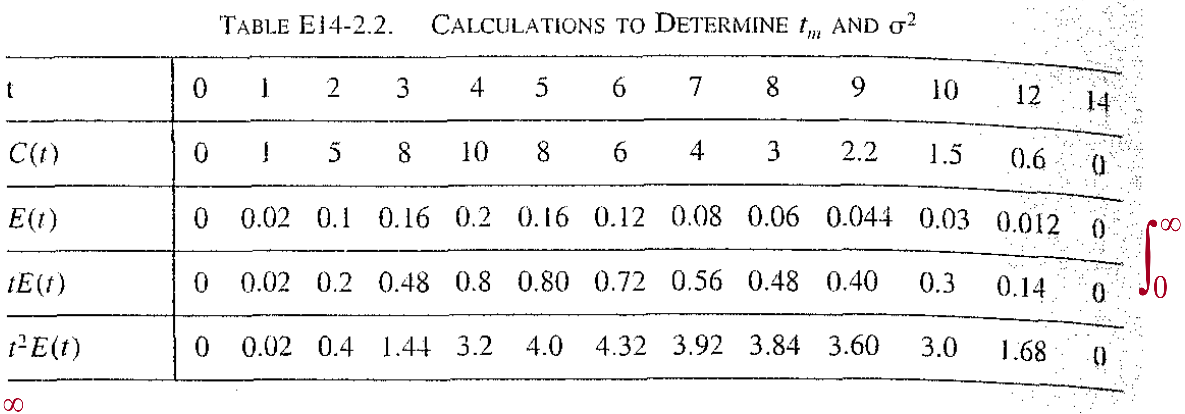


TABLE E14-2.2. CALCULATIONS TO DETERMINE $t_m$ AND $\sigma^2$

| $t$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C(t)$ | 0 | 1 | 5 | 8 | 10 | 8 | 6 | 4 | 3 | 2.2 | 1.5 | 0.6 | 0 |
| $E(t)$ | 0 | 0.02 | 0.1 | 0.16 | 0.2 | 0.16 | 0.12 | 0.08 | 0.06 | 0.044 | 0.03 | 0.012 | 0 |
| $tE(t)$ | 0 | 0.02 | 0.2 | 0.48 | 0.8 | 0.80 | 0.72 | 0.56 | 0.48 | 0.40 | 0.3 | 0.14 | 0 |
| $t^2E(t)$ | 0 | 0.02 | 0.4 | 1.44 | 3.2 | 4.0 | 4.32 | 3.92 | 3.84 | 3.60 | 3.0 | 1.68 | 0 |

$$\int_0^\infty C(t)dt = 50\,g\cdot\min$$

$$t_m = \int_0^\infty tE(t)dt = 5.15\,\min$$

$$\sigma^2 = \int_0^\infty (t-t_m)^2E(t)dt = \int_0^\infty t^2E(t)dt - t_m^2 = 32.63-(5.15)^2 = 6.10\,\min^2$$

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}(1-e^{-Pe_r}) \longrightarrow \frac{6.1}{(5.15)^2} = 0.23 = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}(1-e^{-Pe_r}) \longrightarrow Pe_r = 7.5$$

$$Da = \tau k = t_m k = (5.15\,\min)(0.25\,\min^{-1}) = 1.29 \longrightarrow$$

$$q = \sqrt{1+\frac{4Da}{Pe_r}} = \sqrt{1+\frac{4(1.29)}{7.5}} = 1.30$$

$$\longrightarrow X = 1 - \frac{4(1.30)\exp(7.5/2)}{(1+1.3)^2\exp(4.87)-(1-1.3)^2(-4.87)} = 0.68$$

$$\frac{Pe_r q}{2} = \frac{(7.5)(1.3)}{2} = 4.87$$

(b)

$$X = 1 - e^{-\tau k} = 1 - e^{-Da} = 1 - e^{-1.29} = 0.725$$

(c)

$$n = \frac{\tau^2}{\sigma^2} = \frac{(5.15)^2}{6.1} = 4.35$$

$$X = 1 - \frac{1}{\left(1 + \frac{\tau}{n} k\right)^n} = 1 - \frac{1}{(1 + 1.29/4.35)^{4.35}} = 0.677$$

(d)

$$X = \frac{\tau k}{1 + \tau k} = \frac{1.29}{1 + 1.29} = 0.563$$

PFR: X=72.5%

Dispersion: X=68.0%

Tanks in series: X=67.7%

Single CSTR: X=56.3%

# Tanks-in-Series Model Versus Dispersion Model

For first-order reactions, the two models can be applied with equal ease.

However, the tanks-in-series model is mathematically easier to use to obtain the effluent concentration and conversion for reaction orders other than one and for multiple reactions.

These two models are equivalent when the Peclet-Bodenstein number is related to the number of tanks in series, n, by the equation

$$Bo = 2(n-1) \longrightarrow n = \frac{Bo}{2} + 1$$

$Bo = UL/D_a$
U is the superficial velocity
L is the reactor length
$D_a$ is the dispersion coefficient

$$\left.\begin{aligned} n &= \frac{Bo}{2} + 1 = \frac{7.5}{2} + 1 = 4.75 \\ n &= \frac{\tau^2}{\sigma^2} = \frac{(5.15)^2}{6.1} = 4.35 \end{aligned}\right\} \longrightarrow$$

For reactions other than first order,

$X(n=4) < X < X(n=5)$

# Two-Parameter Models-Modeling Real Reactors with Combinations of Ideal Reactors

## Real CSTR Modeled Using Bypassing and Dead Space

A CSTR is believed to modeled as a combination of an ideal CSTR of volume $V_s$, a dead zone of volume $V_d$, and a bypass with a volumetric flow rate $v_b$ (Figure 14-15)

We have used a tracer experiment to evaluate the parameters of the model $V_s$ and $v_s$. Because the total volume and volumetric flow rate are known, once $V_s$ and $v_s$ are found, $v_b$ and $V_d$ can readily be calculated.

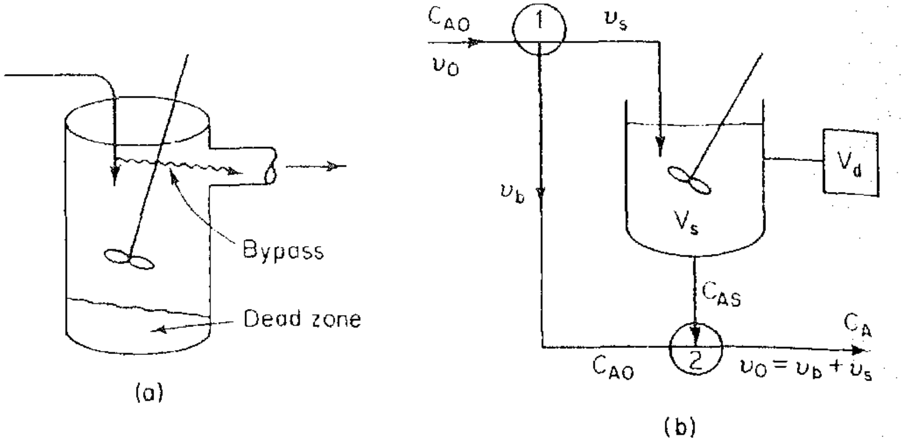
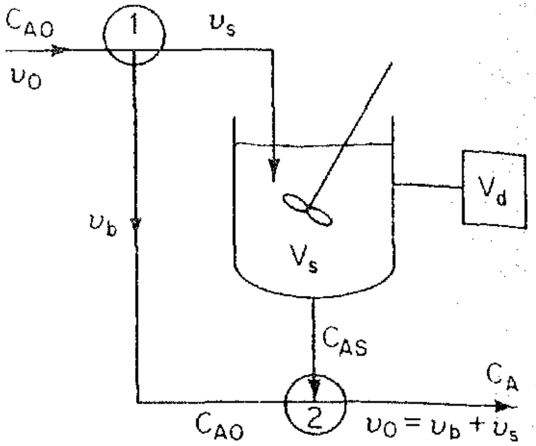


Figure 14-15 (a) Real system; (b) model system.

# Solving the Model System for $C_A$ and X



The bypass stream and effluent stream from the reaction volume are mixed at point 2.

Considering the first-order reaction

$$A \rightarrow B$$

From a balance on species A around point 2

$$\text{In} = \text{Out}$$

$$C_{A0}v_b + C_{As}v_s = C_A(v_b + v_s)$$

$$\longrightarrow C_A = \frac{C_{A0}v_b + C_{As}v_s}{v_b + v_s} = \frac{C_{A0}v_b + C_{As}v_s}{v_0}$$

$$\xrightarrow{\beta = \frac{v_b}{v_0}} C_A = \beta C_{A0} + (1-\beta)C_{As}$$

A mole balance on $V_s$ gives

$$v_s C_{A0} - v_s C_{As} - kC_{As}V_s = 0 \xrightarrow{\alpha = \frac{V_s}{V},\ \bullet\bullet\ \beta = \frac{v_b}{v_0}} C_{As} = \frac{C_{A0}(1-\beta)v_0}{(1-\beta)v_0 + \alpha Vk}$$

$$\longrightarrow \frac{C_A}{C_{A0}} = 1 - X = \beta + \frac{(1-\beta)^2}{(1-\beta) + \alpha\tau k} \longrightarrow$$

$\alpha = ?$

$\beta = ?$

evaluated with tracer experiments and RTD data

# Using a Tracer to Determine the Model Parameters in CSTR-with-Dead-Space-and-Bypass Model

We shall inject our tracer, T, as a positive step input. The unsteady-state balance on the nonreacting tracer T in the reactor volume $V_s$ is

$$\text{In} - \text{Out} = \text{accumulation}$$

$$v_s C_{T0} - v_s C_{Ts} = \frac{dN_{Ts}}{dt} = V_s \frac{dC_{Ts}}{dt}$$

$$\text{At} \bullet t < 0 \bullet\bullet C_T = 0$$

$$\text{At} \bullet t \geq 0 \bullet\bullet C_T = C_{T0}$$

$$V_s = \alpha V$$

$$v_b = \beta v_0$$

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

$$\longrightarrow \frac{C_{Ts}}{C_{T0}} = 1 - \exp\left[-\frac{1-\beta}{\alpha}\left(\frac{t}{\tau}\right)\right]$$

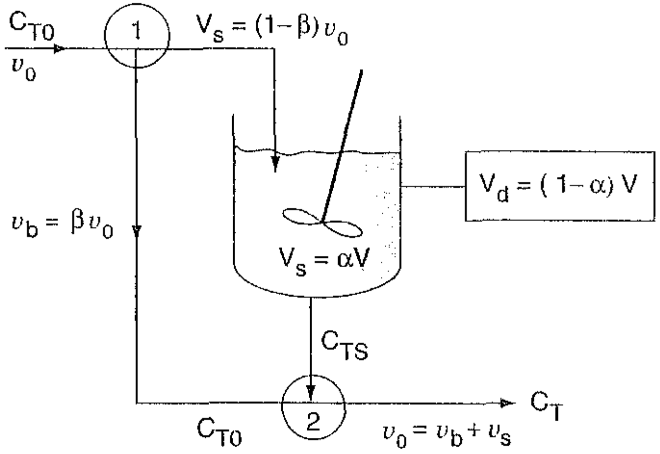


**Figure 14-16** Model system: CSTR with dead volume and bypassing.

A balance around junction point 2 gives

$$C_T = \frac{C_{T0} v_b + C_{Ts} v_s}{v_0} \longrightarrow C_T = \beta C_{T0} + (1-\beta) C_{Ts} \longrightarrow \frac{C_T}{C_{T0}} = 1 - (1-\beta)\exp\left[-\frac{1-\beta}{\alpha}\left(\frac{t}{\tau}\right)\right]$$

$$\longrightarrow \ln\left(\frac{C_{T0}}{C_{T0} - C_T}\right) = \ln\left(\frac{1}{1-\beta}\right) + \left(\frac{1-\beta}{\alpha}\right)\frac{t}{\tau} \longrightarrow \ln\left(\frac{C_{T0}}{C_{T0} - C_T}\right) \bullet \text{vs} . \bullet t \longrightarrow$$

$$\text{slope} = \frac{1-\beta}{\alpha\tau}$$

$$\text{intercept} = \ln\left(\frac{1}{1-\beta}\right)$$

# Example 2-3

The elementary reaction

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

is to be carried out in the CSTR shown schematically in Figure 14-15. There is both bypassing and a stagnant region in this reactor. The tracer output for this reactor is shown in Table E14-4.1. The measured reactor volume is 1.0 $m^3$ and the flow rate to the reactor is 0.1 $m^3$/min. The reaction rate constant is 0.28 $m^3$/kmol·min. The feed is equimolar in A and B with an entering concentration of A equal to 2.0 kmol/$m^3$. Calculate the conversion that can be expected in this reactor (Figure E14-4.1).

TABLE E14-4.1 TRACER DATA

| $C_T$ (mg/dm$^3$) | 1000 | 1333 | 1500 | 1666 | 1750 | 1800 |
|---|---|---|---|---|---|---|
| $t$ (min) | 4 | 8 | 10 | 14 | 16 | 18 |

$C_{T0}$=2000 mg/dm$^3$

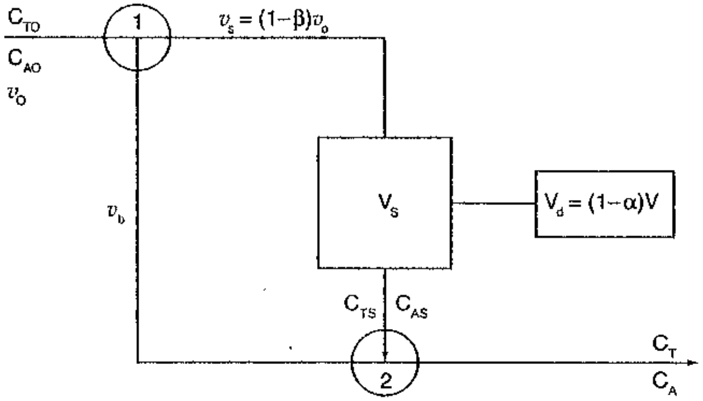
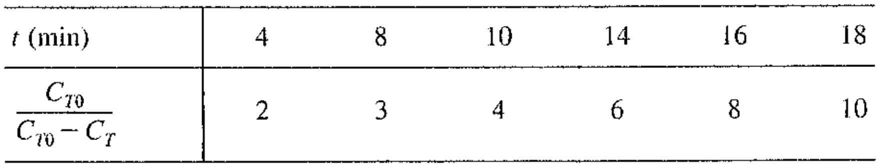


**Figure E14-4.1** Schematic of real reactor modeled with dead space ($V_d$) and bypass ($v_b$).

# Solution

$$\ln\left(\frac{C_{T0}}{C_{T0}-C_T}\right)=\ln\left(\frac{1}{1-\beta}\right)+\left(\frac{1-\beta}{\alpha}\right)\frac{t}{\tau}$$

TABLE E14-4.2. PROCESSED DATA



| $t$ (min) | 4 | 8 | 10 | 14 | 16 | 18 |
|---|---|---|---|---|---|---|
| $\frac{C_{T0}}{C_{T0}-C_T}$ | 2 | 3 | 4 | 6 | 8 | 10 |

$\longrightarrow$

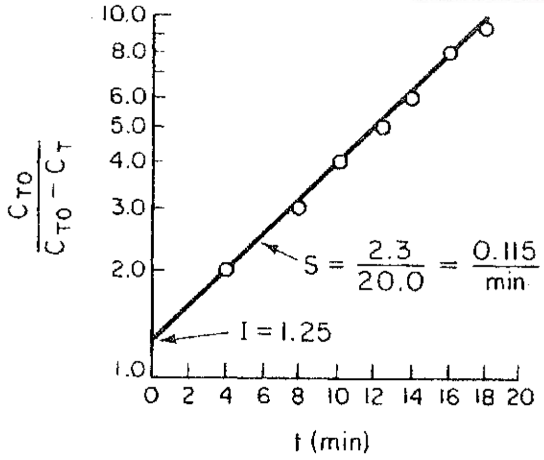


**Figure E14-4.2** Response to a step input.

$$\frac{1}{1-\beta}=I=1.25 \longrightarrow \beta=\frac{v_b}{v_0}=0.2$$

$$\frac{1-\beta}{\alpha\tau}=S=0.115\cdot\text{min}^{-1} \longrightarrow \alpha\tau=\frac{1-0.2}{0.115}=7\cdot\text{min}$$

$$\longrightarrow \alpha=\frac{7\cdot\text{min}}{10\cdot\text{min}}=0.7$$

$$\tau=\frac{V}{v_0}=\frac{1\cdot\text{m}^3}{0.1\cdot\text{m}^3/\text{min}}=10\cdot\text{min}$$

A mole balance on $V_s$ gives

$$v_s C_{A0} - v_s C_{As} + r_{As} V_s = 0 \xrightarrow[\text{equimolar feed}]{-r_{As} = kC_{As}C_{Bs} = kC_{As}^2} v_s C_{A0} - v_s C_{As} - kC_{As}^2 V_s = 0$$

$$\longrightarrow C_{As} = \frac{-1 + \sqrt{1 + 4\tau_s k C_{A0}}}{2\tau_s k}$$

$$V_s = \alpha V = 0.7 \times 1 \bullet m^3 = 0.7 \bullet m^3$$

$$v_s = (1-\beta)v_0 = (1-0.2) \times (0.1 \bullet m^3 / min) = 0.08 \bullet m^3 / min$$

$$\tau_s = \frac{V_s}{v_s} = \frac{0.7}{0.08} = 8.7 \bullet min$$

$$\longrightarrow C_{As} = \frac{-1 + \sqrt{1 + 4(8.7 \bullet min)(0.28 m^3 / kmol \cdot min)(2 kmol / m^3)} - 1}{2(8.7 \bullet min)(0.28 m^3 / kmol \cdot min)} = 0.724 \bullet kmol / m^3$$

A mole balance around junction point 2 gives

$$C_A = \beta C_{A0} + (1-\beta)C_{As} \longrightarrow$$

$$C_A = \beta C_{A0} + (1-\beta)C_{As}$$

$$\bullet\bullet\bullet = 0.2 \times 2 kmol / m^3 + 0.8 \times 0.724 kmol / m^3$$

$$\bullet\bullet\bullet\bullet = 0.979 kmol / m^3$$

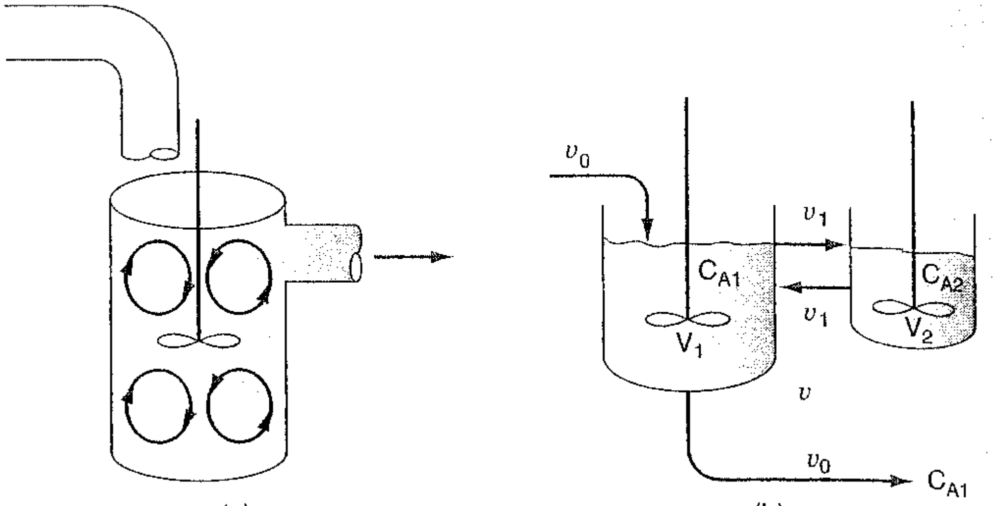
$$\longrightarrow X = 1 - \frac{0.979}{2} = 0.51$$

$$X = 0.66 \bullet\bullet (an \bullet ideal \bullet C \;\; STR)$$

# Real CSTR Modeled as Two CSTRs with Interchange

In this particular model there is a highly agitated region in the vicinity of the impeller; outside this region, there is a region with less agitation (Figure 14-17).

There is considerable material transfer between the two regions. Both inlet and outlet flow channels connect to the highly agitated region. We shall model the highly agitated region as one CSTR, the quieter region as another CSTR, with material transfer between the two.



(a) (b)

**Figure 14-17** (a) Real reaction system; (b) model reaction system.

## Solving the Model System for $C_A$ and X

$$v_1 = \beta v_0$$

$$V_1 = \alpha V$$

$$V_2 = (1-\alpha)V$$

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

→

$$C_{A1} = \frac{C_{A0}}{1+\beta+\alpha\tau k-\{\beta^2/[\beta+(1-\alpha)\tau k]\}}$$

$$X = 1-\frac{C_{A1}}{C_{A0}} = \frac{(\beta+\alpha\tau k)[\beta+(1-\alpha)\tau k]-\beta^2}{(1+\beta+\alpha\tau k)[\beta+(1-\alpha)\tau k]-\beta^2}$$

# Using a Tracer to Determine the Model Parameters in a CSTR with an Exchange Volume

A mole balance on a tracer pulse injected at t=0 for each of the tanks is

$$\text{Reactor 1}: V_1 \frac{dC_{T1}}{dt} = v_1 C_{T2} - (v_0 C_{T1} + v_1 C_{T2})$$

$$\text{Reactor 2}: V_2 \frac{dC_{T2}}{dt} = v_1 C_{T1} - v_1 C_{T2}$$

$C_{T1}$ and $C_{T2}$ are the tracer concentration in reactors 1 and 2, respectively, with initial conditions $C_{T10}=N_{T0}/V_1$ and $C_{T20}=0$.

$$v_1 = \beta v_0$$

$$V_1 = \alpha V$$

$$V_2 = (1-\alpha)V$$

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

$$\longrightarrow$$

$$\tau\alpha \frac{dC_{T1}}{dt} = \beta C_{T2} - (1+\beta)C_{T1}$$

$$\tau(1-\alpha)\frac{dC_{T2}}{dt} = \beta C_{T1} - \beta C_{T2}$$

$$\longrightarrow \left(\frac{C_{T1}}{C_{T10}}\right)_{\text{pulse}} = \frac{(\alpha m_1 + \beta + 1)e^{m_2 t/\tau} - (\alpha m_2 + \beta + 1)e^{m_1 t/\tau}}{\alpha(m_1 - m_2)} \longrightarrow$$

$$\alpha = ?$$

$$\beta = ?$$

where

$$m_1, m_2 = \left[\frac{1-\alpha+\beta}{2\alpha(1-\alpha)}\right]\left[-1 \pm \sqrt{1 - \frac{4\alpha\beta(1-\alpha)}{1-\alpha+\beta^2}}\right]$$

# Example 2-4

(a) Determine parameter $\alpha$ and $\beta$ that can be used to model two CSTRs with interchange using the tracer concentration data listed in Table E14-5.1.

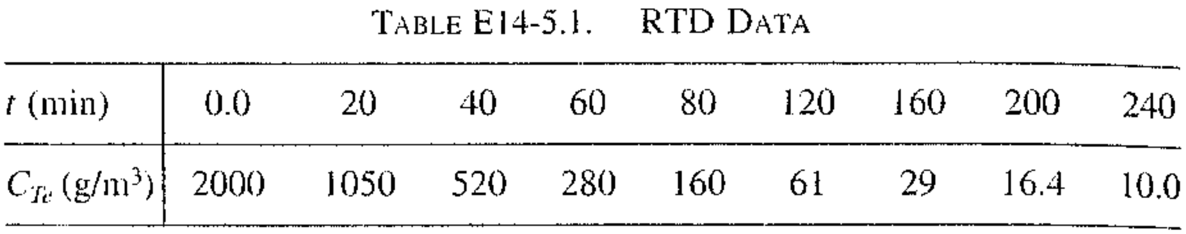


TABLE E14-5.1. RTD DATA

| $t$ (min) | 0.0 | 20 | 40 | 60 | 80 | 120 | 160 | 200 | 240 |
|---|---|---|---|---|---|---|---|---|---|
| $C_{Te}$ (g/m$^3$) | 2000 | 1050 | 520 | 280 | 160 | 61 | 29 | 16.4 | 10.0 |

(b) Determine the conversion of first-order reaction with k=0.03 min$^{-1}$ and $\tau$=40 min.

Solution

For $t \le 80$ min,

$$C_{Te} = 2000 - 59.6t + 0.642t^2 - 0.00146t^3 - 1.04\times10^{-5}t^4$$

For $t > 80$ min,

$$C_{Te} = 921 - 17.3t + 0.129t^2 - 0.000438t^3 - 5.6\times10^{-7}t^4$$

$C_{Te}$ is the exit concentration of tracer determined experimentally.

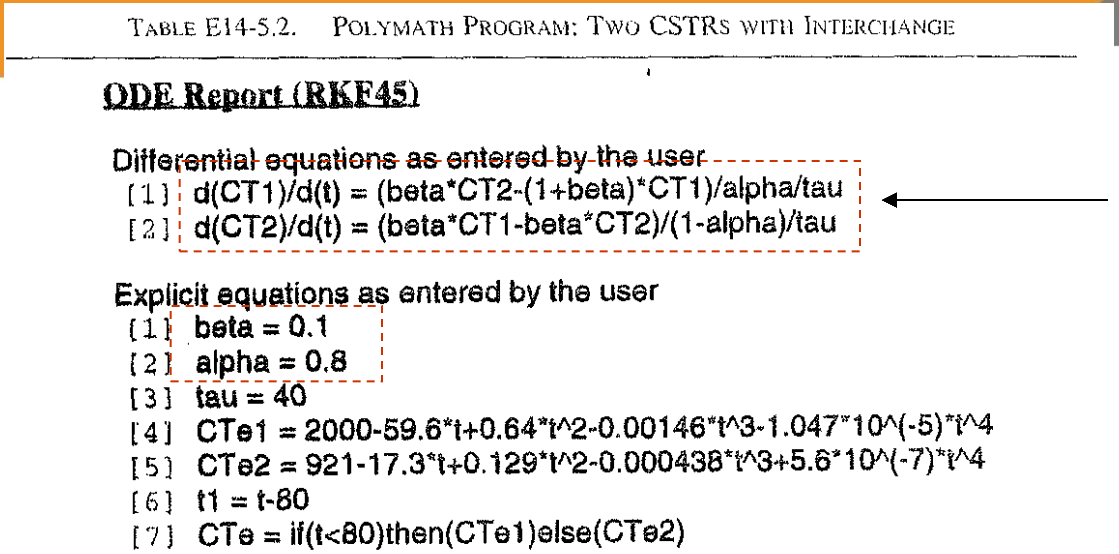


TABLE E14-5.2. POLYMATH PROGRAM: TWO CSTRS WITH INTERCHANGE

**ODE Report (RKF45)**

```
Differential equations as entered by the user
 [1]  d(CT1)/d(t) = (beta*CT2-(1+beta)*CT1)/alpha/tau
 [2]  d(CT2)/d(t) = (beta*CT1-beta*CT2)/(1-alpha)/tau

Explicit equations as entered by the user
 [1]  beta = 0.1
 [2]  alpha = 0.8
 [3]  tau = 40
 [4]  CTe1 = 2000-59.6*t+0.64*t^2-0.00146*t^3-1.047*10^(-5)*t^4
 [5]  CTe2 = 921-17.3*t+0.129*t^2-0.000438*t^3+5.6*10^(-7)*t^4
 [6]  t1 = t-80
 [7]  CTe = if(t<80)then(CTe1)else(CTe2)
```

$$\tau\alpha\frac{dC_{T1}}{dt} = \beta C_{T2} - (1+\beta)C_{T1}$$

$$\tau(1-\alpha)\frac{dC_{T2}}{dt} = \beta C_{T1} - \beta C_{T2}$$

$$\alpha = 0.8$$

$$\beta = 0.1$$

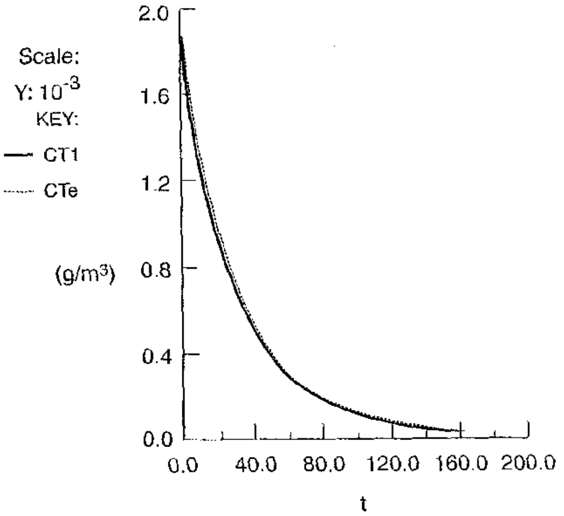


**Figure E14-5.1** Comparison of model and experimental exit tracer concentrations.

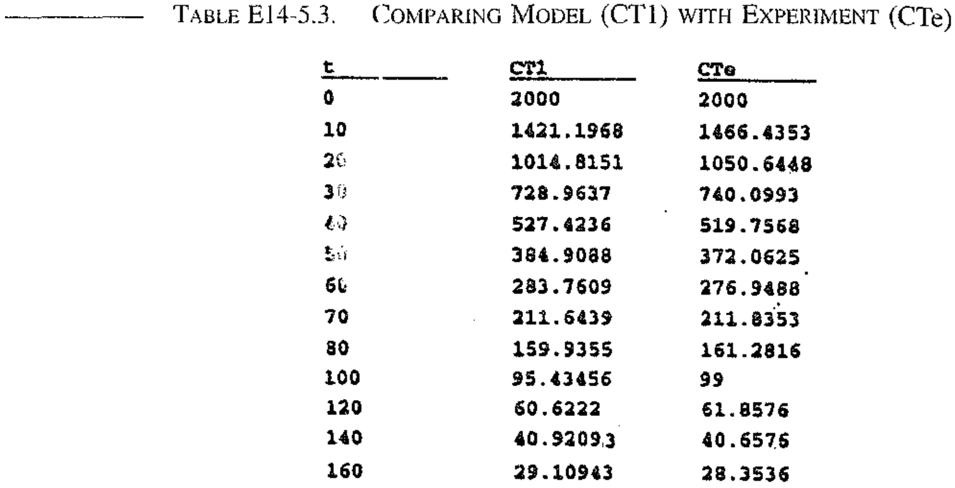


TABLE E14-5.3. COMPARING MODEL (CT1) WITH EXPERIMENT (CTe)

| t | CT1 | CTe |
|---|---|---|
| 0 | 2000 | 2000 |
| 10 | 1421.1968 | 1466.4353 |
| 20 | 1014.8151 | 1050.6448 |
| 30 | 728.9637 | 740.0993 |
| 40 | 527.4236 | 519.7568 |
| 50 | 384.9088 | 372.0625 |
| 60 | 283.7609 | 276.9488 |
| 70 | 211.6439 | 211.8353 |
| 80 | 159.9355 | 161.2816 |
| 100 | 95.43456 | 99 |
| 120 | 60.6222 | 61.8576 |
| 140 | 40.92093 | 40.6576 |
| 160 | 29.10943 | 28.3536 |

$$\tau k = (40\bullet\text{min})(0.03\bullet\text{min}^{-1}) = 1.2$$

$$X = \frac{[0.1+(0.8)(1.2)][0.1+(1-0.8)(1.2)]-(0.1)^2}{[1+0.1+(0.8)(1.2)][0.1+(1-0.8)(1.2)]-(0.1)^2} = 0.51$$

$$(X_{\text{model}} = 0.51) < (X_{\text{CSTR}} = 0.55) < (X_{\text{PFR}} = 0.7)$$

# Other Models of Nonideal Reactors Using CSTRs and PFRs

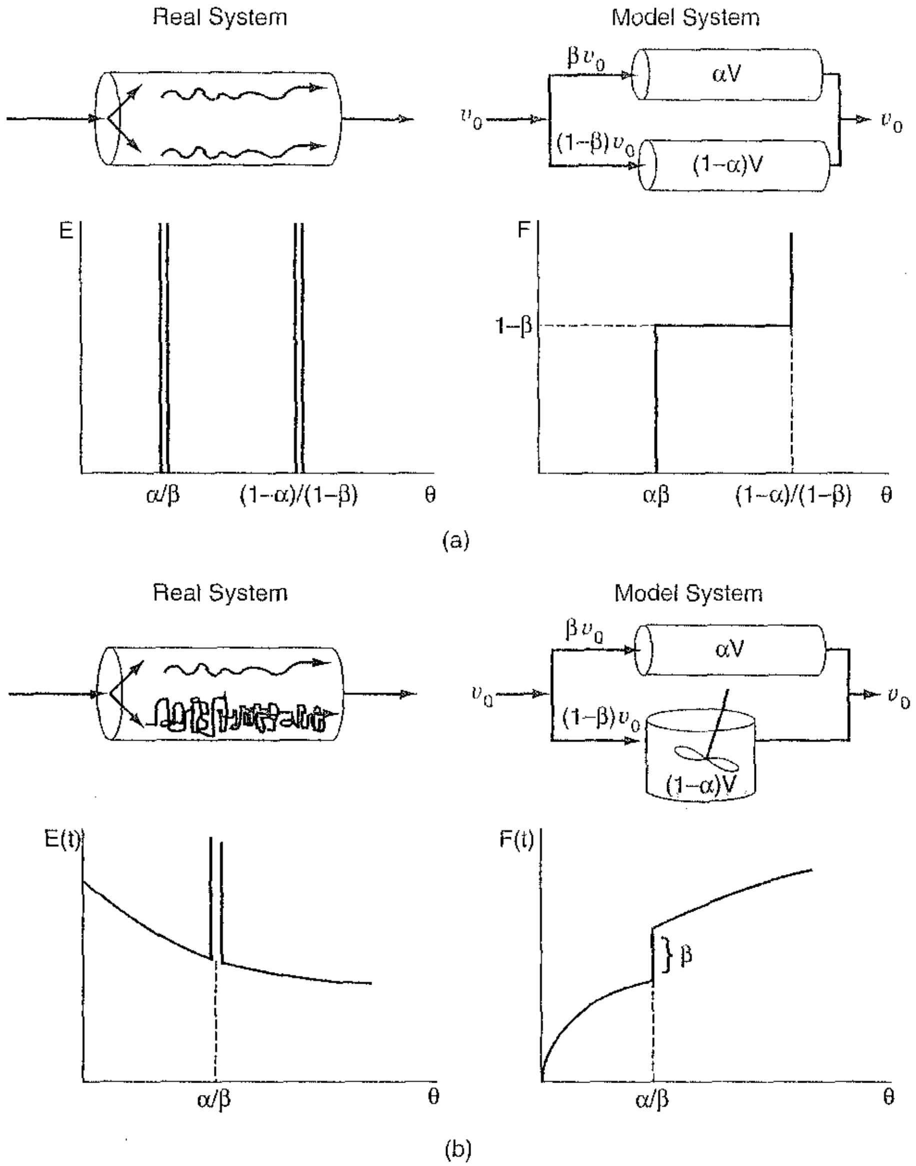


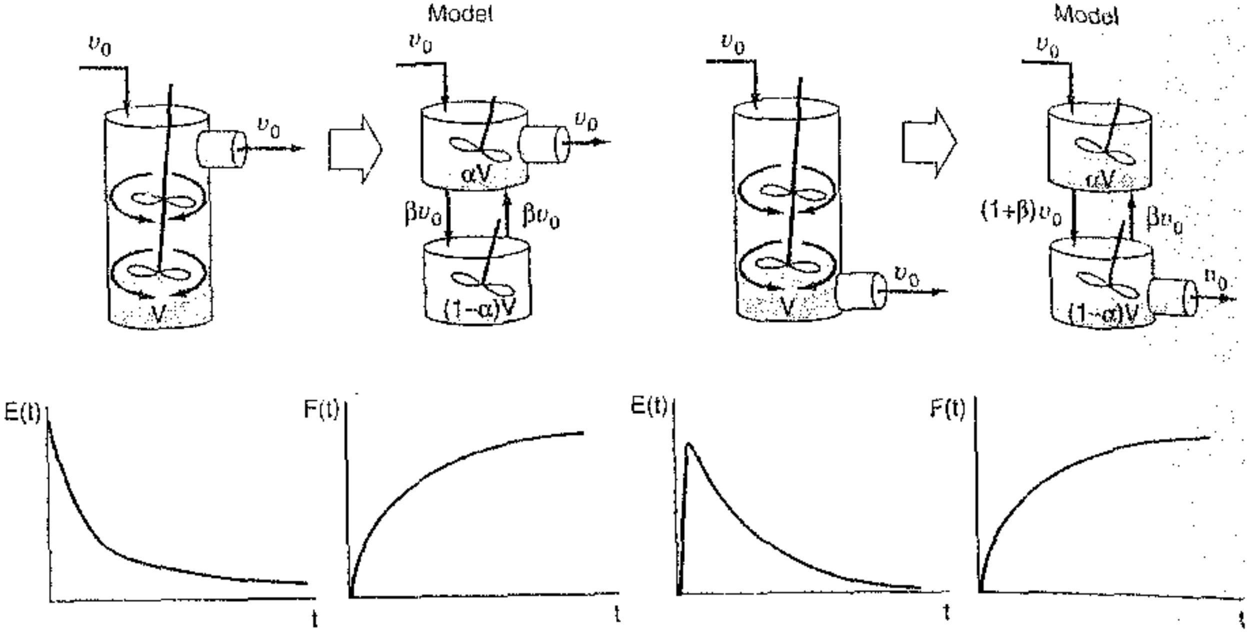
**Figure 14-18** Combinations of ideal reactors used to model real tubular reactor (a) two ideal PFRs in parallel (b) ideal PFR and ideal CSTR in parallel.

Figure 14-18(a) describes a real PFR or PBR with channeling that is modeled as two PFRs/PBRs in parallel. The two parameters are the fraction of flow to the reactors [i.e., β and (1-β)] and the fraction volume [i.e., α and (1-α)] of each reactor.

Figure 14-18(b) describes a real PFR/PBR has a backmix region and is modeled as a PFR/PBR in parallel with a CSTR.

Figure 14-19 (a) and (b) show a real CSTR modeled as two CSTRs with interchange. In one case, the fluid exits from the top CSTR (a) and in other case the fluid exits from the bottom CSTR (b).

The parameter β represents the interchange volumetric flow rate and α the fractional volume of the top reactor, where the fluid exits the reaction system.



(a)

(b)

**Figure 14-19** Combinations of ideal reactors to model a real CSTR. Two ideal CSTRs with interchange (a) exit from the top of the CSTR (b) exit from the bottom of the CSTR.

# Closure

~In this section, models were developed for existing reactors to obtain a more precise estimate of the exit conversion and concentration than estimates of the examples given by the zero-order parameter models of segregation and maximum mixedness.

~After completing this section, the student will use the RTD data and kinetic rate law and reactor model to make predictions of the conversion and exit concentrations using the tank-in-series and dispersion one-parameter models.

~In addition, the student should be able to create combinations of ideal reactors that mimic the RTD data and to solve for the exit conversions and concentrations.

~Models of real reactors usually consist of combinations of PFRs, perfectly mixed CSTRs, and dead spaces in a configuration that matches the flow patterns in the reactor.

~For tubular reactors, the simple dispersion model has proven most popular.

~The parameters in the model, which with rare exception should not exceed two in number, are obtained from the RTD data. Once the parameters are evaluated, the conversion in the model, and thus in the real reactor can be calculated.

~For typical tank-reactor models, this is the conversion in a series-parallel reactor system. For the dispersion model, the second-order differential equation must be solved, usually numerically.

~Analytical solution exist for first-order reactions, but as pointed out previously, no model has to be assumed for the first-order system if the RTD is available.

~Correlations exist for the amount of dispersion that might be expected in common packed-bed reactors, so these systems can be designed using the dispersion model without obtaining or estimating the RTD. This situation is perhaps the only one where an RTD is not necessary for designing a nonideal reactor.

# Introduction

- This presentation covers models for nonideal reactors with a focus on residence time distribution (RTD) and reactor flow behavior.

# Topics to be Addressed

- - Residence Time Distribution (RTD)
- - Nonideal Flow Patterns
- - Models for Mixing
- - Calculation of Exit Conversion
- - Reactor Performance Assessment

# Objectives

- \- Understand the principles of nonideal flow in reactors
- \- Learn how to use RTD for analyzing reactor performance
- \- Apply mathematical models for mixing and conversion calculation
- \- Compare different reactor modeling approaches