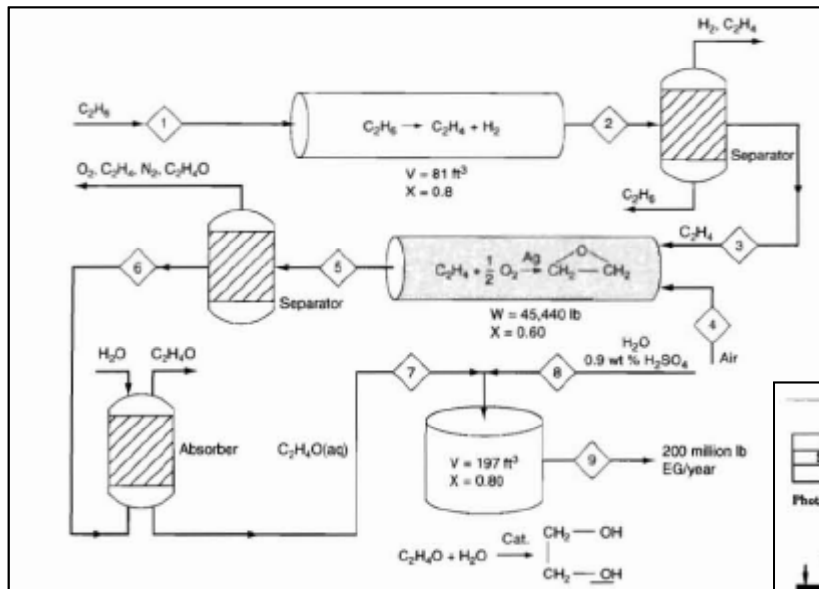# Chemical Reaction Engineering

Lecture 5

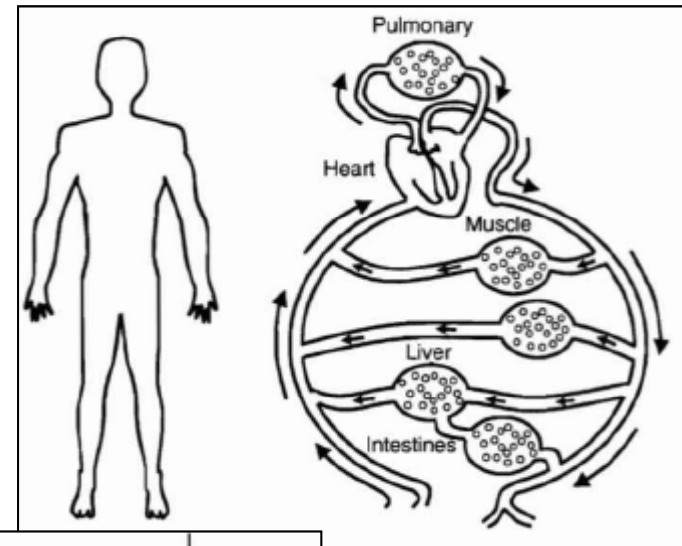# The Scope

- ## The Aim of the Course:
  - To learn how to describe a system where a (bio)chemical reaction takes place (further called reactor)
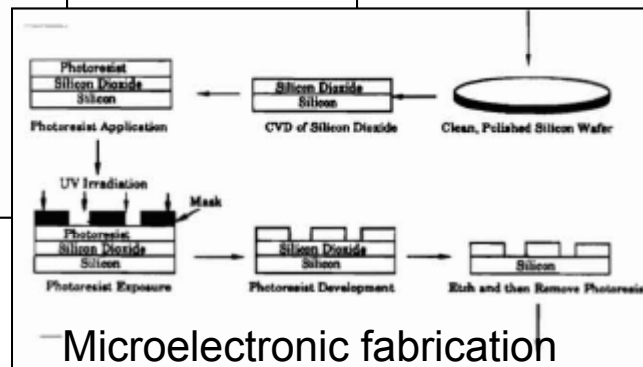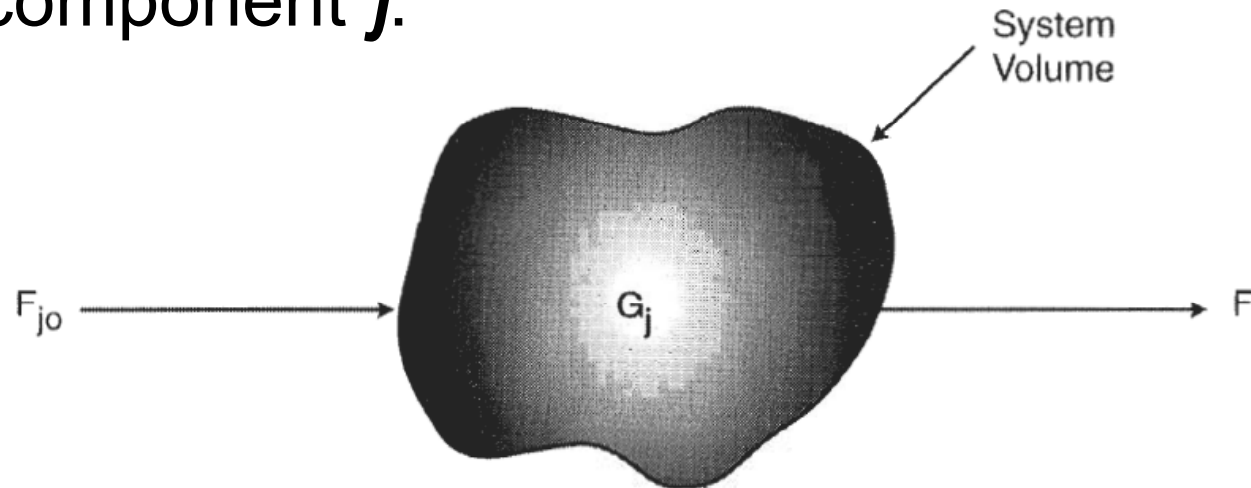
- ## Reactors

Chemical plant for ethylene glycol

Microelectronic fabrication

Pharmacokinetics

The general mole balance equation

- For any component **_j_**:

- ## Mass balance:
  Rate of flow IN – Rate of flow OUT + Generation=Accumulation

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

  $$G_i = r_i \cdot V$$

moles/time	moles/(time·volume)	volume

Chemical Reaction Engineering

- Lecture plan (Lectures 5-10)
  - Lecture 5: Mole balance and design equations for batch and continuous mode reactors.
  - Lecture 6: Rate laws in the reactor design
  - Lecture 7: Isothermal reactor design
  - Lecture 8: Bioreactors. Comsol modelling of reactions and reactors. H-cell with chemical reaction.
  - Lecture 9. Non-isothermal reactors. Comsol modelling: flow through porous bed and stirred batch reactor.
  - Lectures 10-11. Diffusion and Reactions. Comsol modelling of biochips: reaction on the surface.

Rates of chemical reactions

$$A + 2B \longrightarrow 3C + D$$

Instantaneous rate of **consumption** of a reactant:

$$-d[R]/dt$$

Instantaneous rate of **formation** of a product:

$$d[P]/dt$$
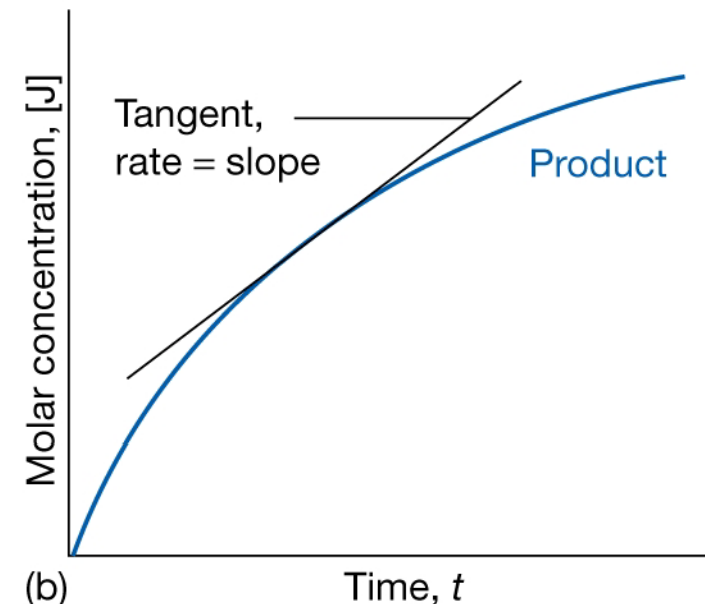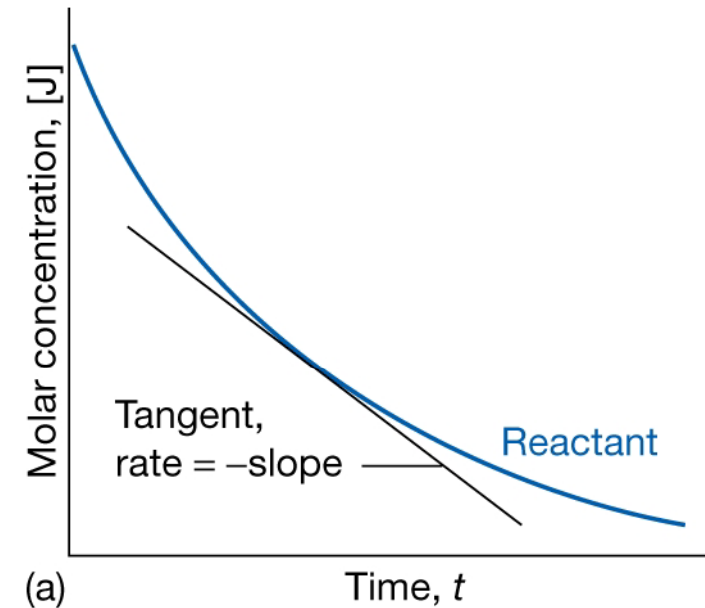
From stoichiometry

$$\frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

Rate of the reaction: $\quad v = \dfrac{1}{v_i}\dfrac{dn_i}{dt} = \dfrac{d\xi}{dt}$

! In the case of heterogeneous reaction the rate will be defined per unit area of catalyst as mol/m²s
! In the case of continuous flow reactor change of concentration is not equal to the reaction rate


(a) Molar concentration, [J] vs Time, t — Reactant; Tangent, rate = −slope

(b) Molar concentration, [J] vs Time, t — Product; Tangent, rate = slope

Rates of chemical reactions

$$A + 2B \longrightarrow 3C + D$$

- Usually we interested in the concentration of one particular reagent, say A.
  The reaction rate in terms of reagent A is the number of moles of A reacting per unit time, per unit volume (mol·m^{-3}·s^{-1})

$$-r_A = d[A]/dt$$

However this definition is inconvenient in the case of a reactor and can be misleading as the concentration of A is varying with time and position inside the reactor:

(a)
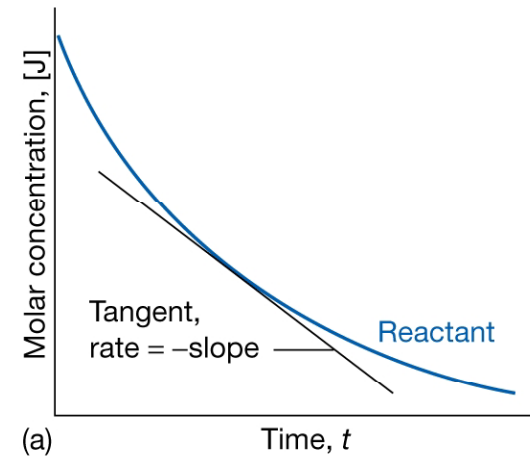
Rates of chemical reactions

- So, we should rather say that:

- Rate of chemical reaction is an **algebraic function** involving concentration, temperature, pressure and type of catalyst **at a point in the system**

$$A \rightarrow product$$
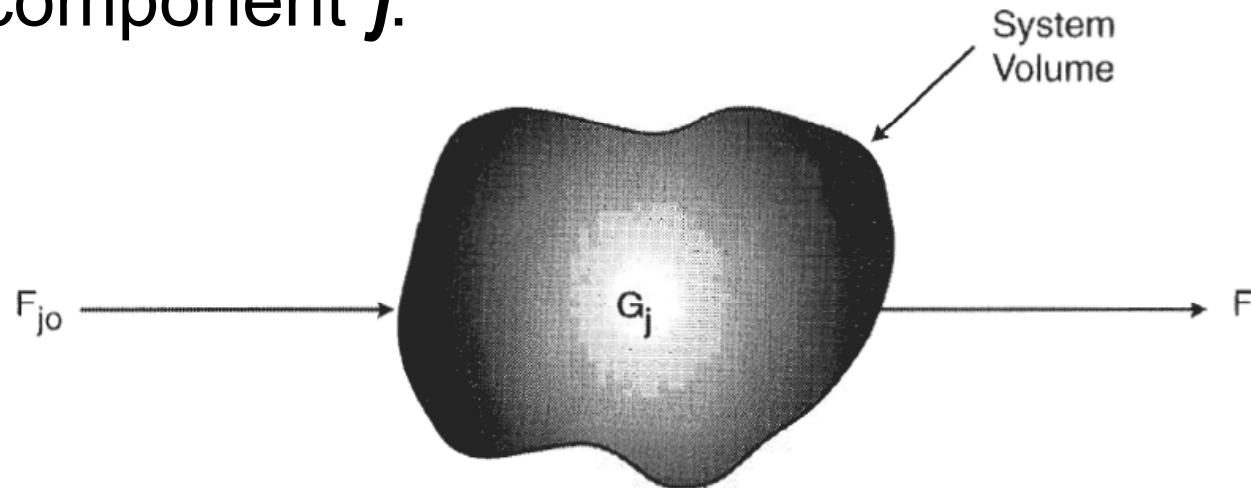
- e.g. 1st order reaction

$$-r_A = kC_A$$

- 2nd order reaction

$$-r_A = kC_A{}^2$$

The general mole balance equation

- For any component **_j_**:

- ## Mass balance:

Rate of flow IN – Rate of flow OUT + Generation=Accumulation

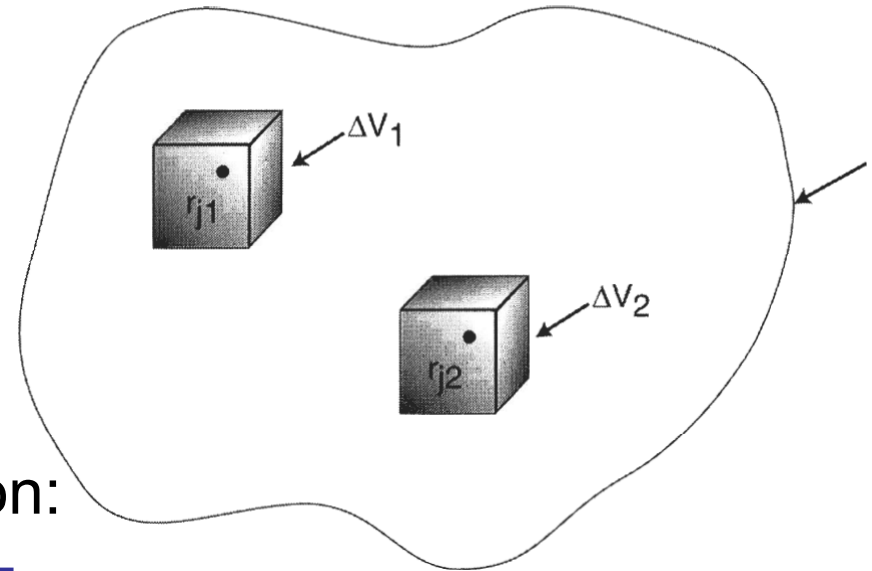$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

$$G_i = r_i \cdot V$$

| moles/time | moles/(time·volume) | volume |

The general mole balance equation

- Generally, the rate of reaction varies from point to point in the reactor:
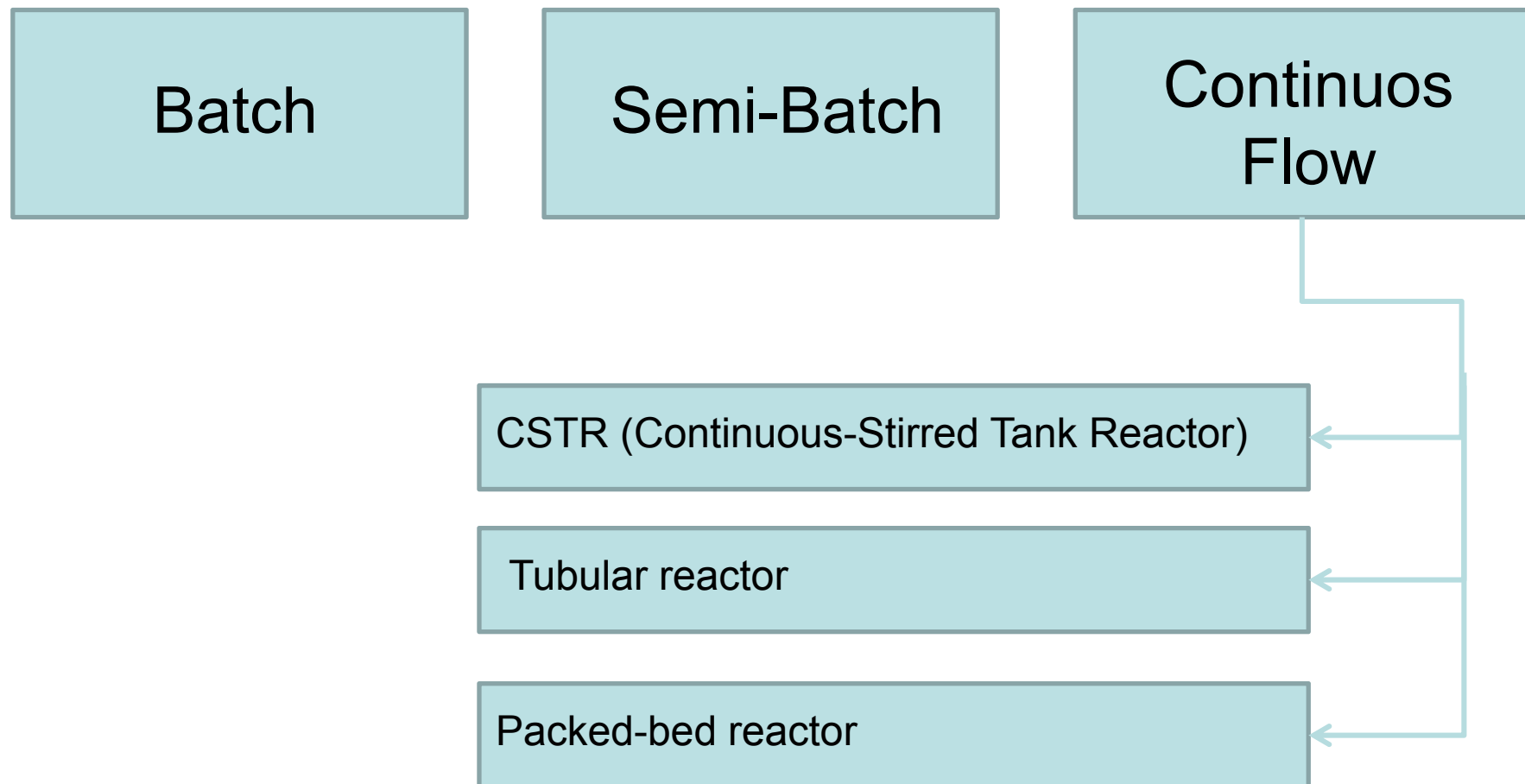
$$G_i = \int\limits^{V} r_i dV$$

- The general mole balance equation:

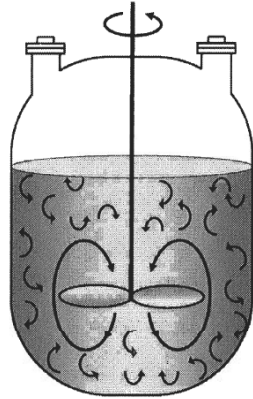$$F_{j0} - F_j + \int\limits^{V} r_i dV = \frac{dN_j}{dt}$$

- From here, design equation for different types of the reactors can be developed

Types of Chemical Reactors

- Depending on loading/unloading of the reactor

Batch	Semi-Batch	Continuos Flow

CSTR (Continuous-Stirred Tank Reactor)

Tubular reactor

Packed-bed reactor

Batch reactors

Hand holes for charging reactor

Connection for heating or cooling jacket

Agitator

- for small-scale operation;
- testing new processes
- manufacturing expensive products
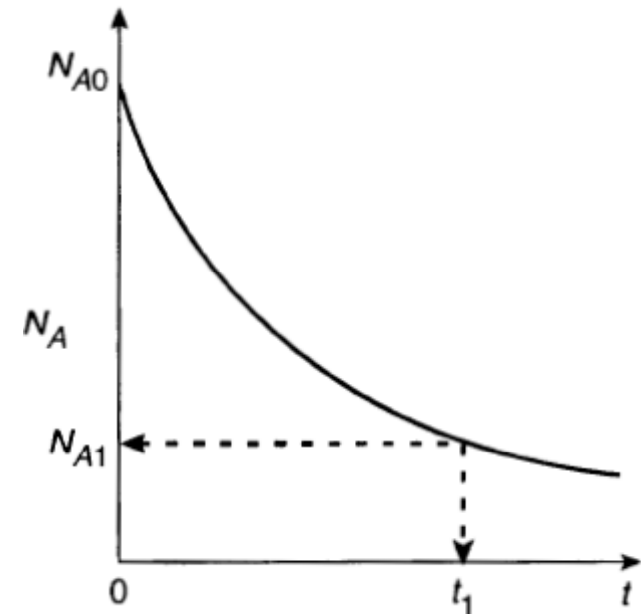- processes difficult to convert to continuous operation
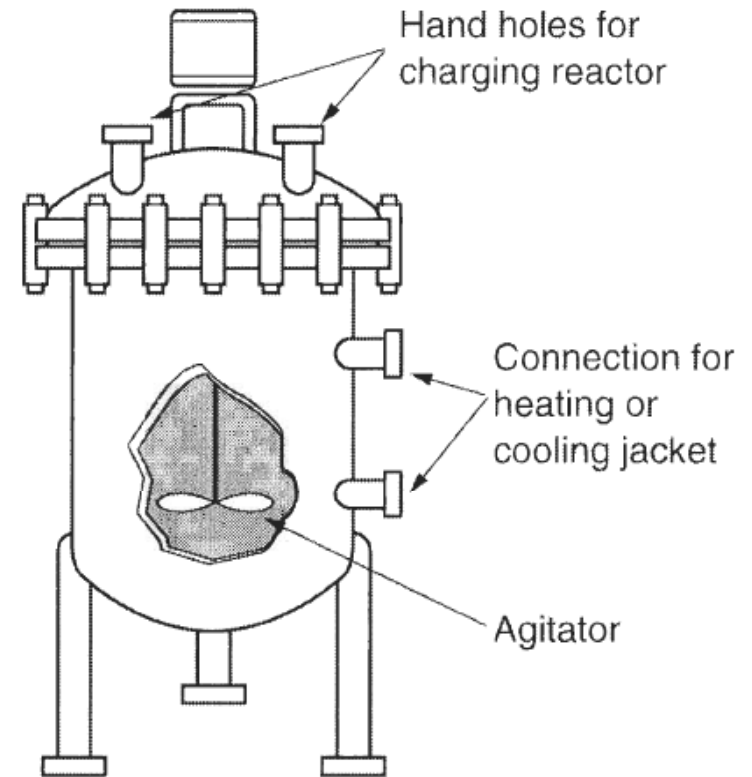
Batch reactors

$$F_{j0} - F_j + \int^V r_i dV = \frac{dN_j}{dt} \implies \int^V r_i dV = \frac{dN_j}{dt}$$

0

- assuming perfect mixing, reaction rate the same through the volume

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

- integrating the equation we can get N_j vs t – "mole-time trajectory"
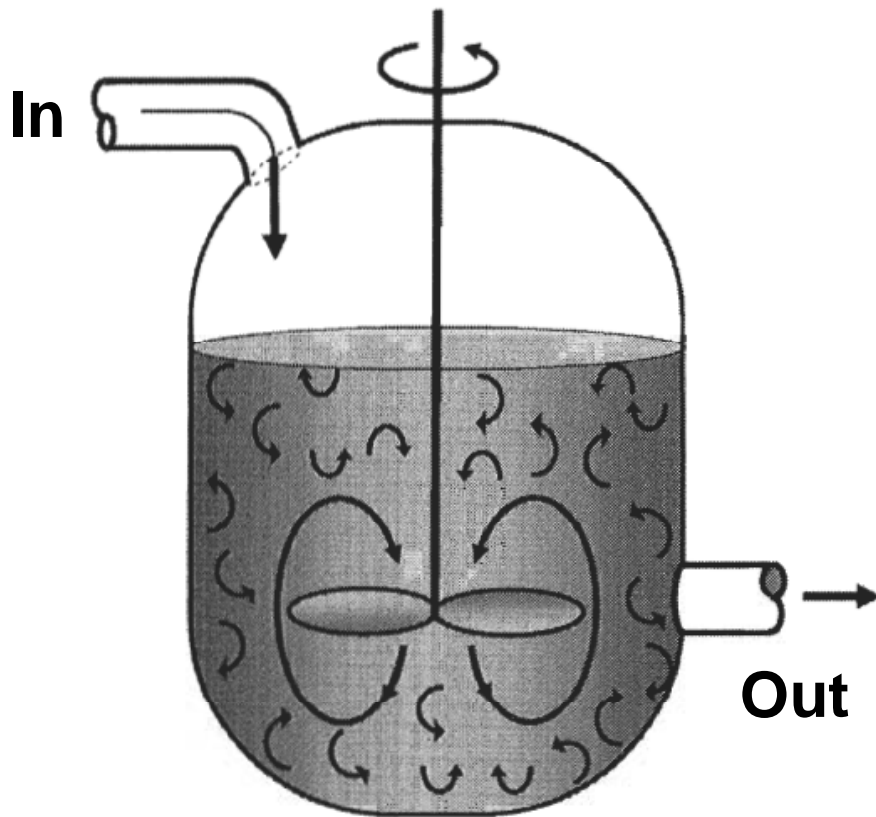
Batch reactors

Pfaudler's Batch reactor

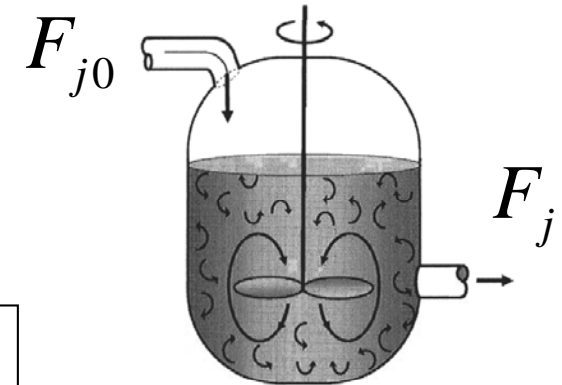# Continuous Flow Reactors

- CSTR (Continuous-Stirred Tank Reactor)

In

Out

Pfaudler's CSTR reactor

Continuous Flow Reactors

- ## CSTR (Continuous-Stirred Tank Reactor)

$$F_{j0} - F_j + \int^V r_i dV = \frac{dN_j}{dt}$$
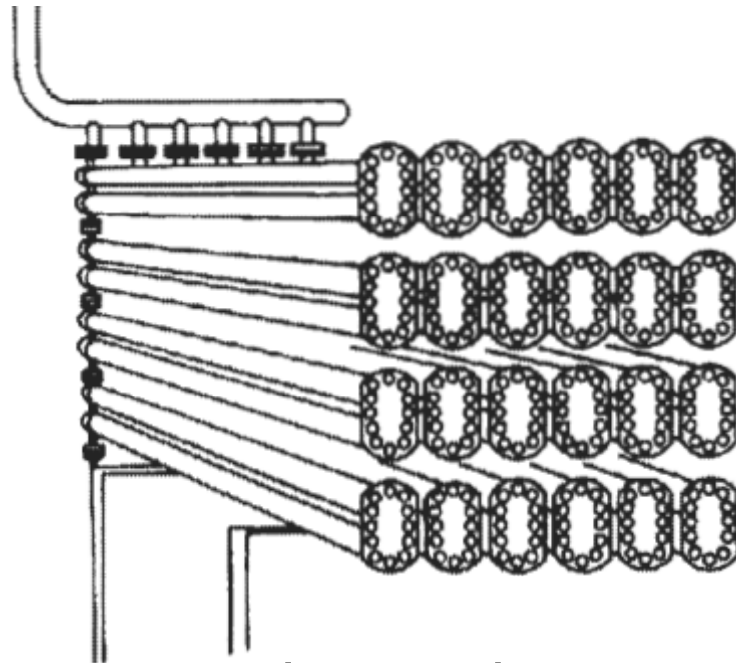
=0, operation in a **steady mode**

- assuming **perfect mixing**, so
  - Reaction rate is the same through the volume
  - Conditions of exit stream are the same as in the reactor

$$F_{j0} - F_j = -r_j V \implies V = \frac{F_{j0} - F_j}{-r_j} \quad \text{or} \quad V = \frac{v_0 C_{A0} - v C_A}{-r_A}$$

Design equation of CSTR

Continuous Flow Reactors

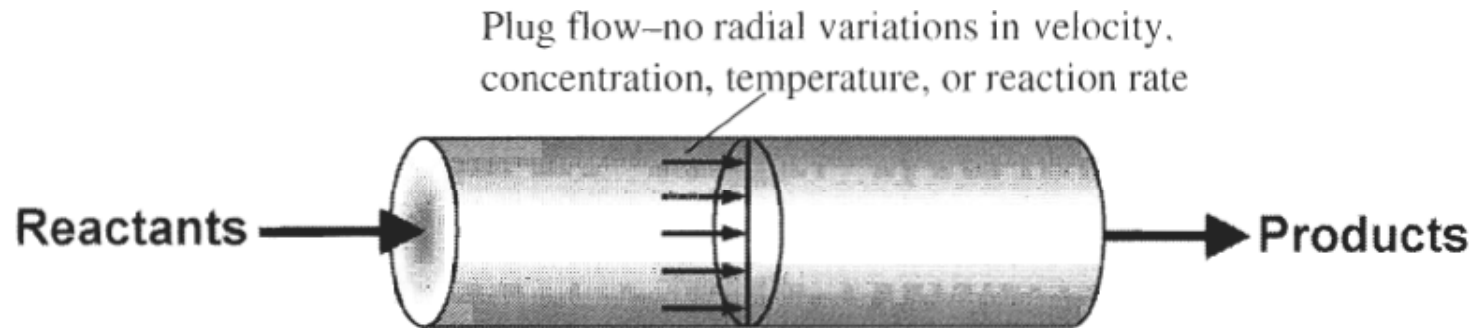- ## Tubular reactor

- usually operates in steady state

- primarly used for gas reactions

- easy to maintain, no moving parts

- produce highest yield

- temperature could be difficult to control, hot spots might occur

Continuous Flow Reactors

Plug flow–no radial variations in velocity, concentration, temperature, or reaction rate

Reactants ⟶ Products

- Tubular reactor
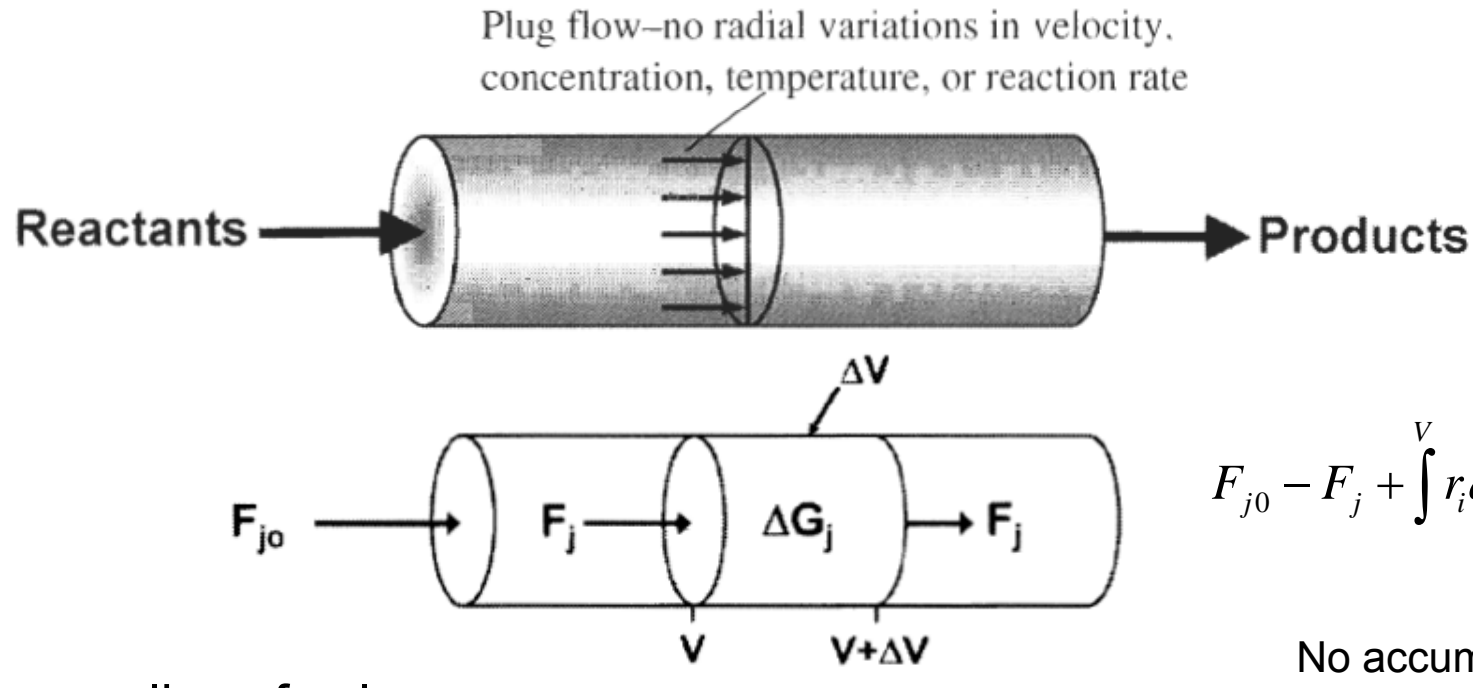 - Reaction continuously progresses along the length of the reactor, so the **concentration** and consequently the **reaction rate varies in axial direaction**
  - in the model of Plug Flow Reactor (PFR) the velocity is considered uniform and there are no **variation of concentration (and reaction rate) in the radial direction**
  - If it cannot be neglected we have a model of Laminar Flow Reactor.

Continuous Flow Reactors

- PFR (plug flow reactor) – useful approximation of a tubular reactor

Plug flow—no radial variations in velocity, concentration, temperature, or reaction rate

Reactants ⟶ Products

$$F_{j0} - F_j + \int\limits_{}^{V} r_i dV = \frac{dN_j}{dt}$$

No accumulation $\boxed{0}$

- For every slice of volume:

$$F_{j0} - F_j + r_i \Delta V = 0 \quad \Rightarrow \quad r_i = \frac{F_{j|V} - F_{j|V+\Delta V}}{\Delta V} \quad \Rightarrow \quad r_i = \frac{dF_j}{dV}$$
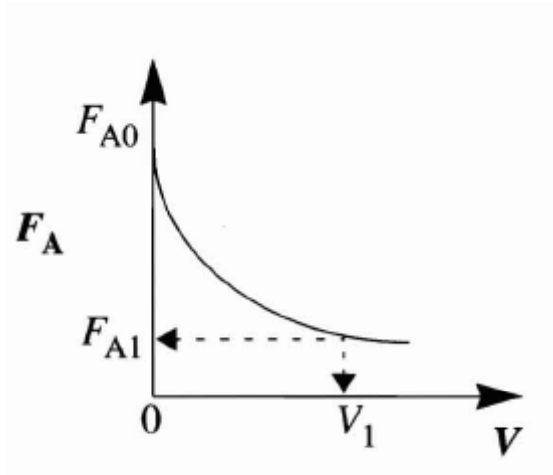
- From here, a volume required to produce given molar flow rate of product can be determined

Continuos Flow Reactors

- ## Design equation for PFR

$$r_j = \frac{dF_j}{dV} \implies dV = \frac{dF_j}{r_j} \qquad V = \int_{F_{j0}}^{F_j} \frac{dF_j}{r_j} = \int_{F_j}^{F_{j0}} \frac{dF_j}{-r_j}$$
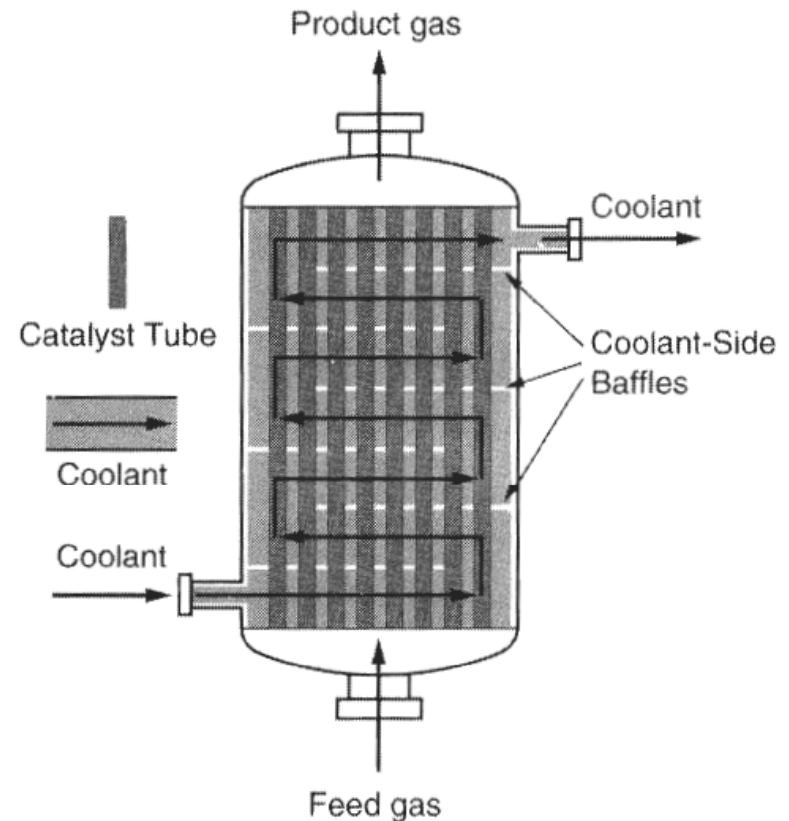
- If we know a profile of molar flow rate vs. Volume we can calculate the required volume to produce given molar flow rate at the outlet.
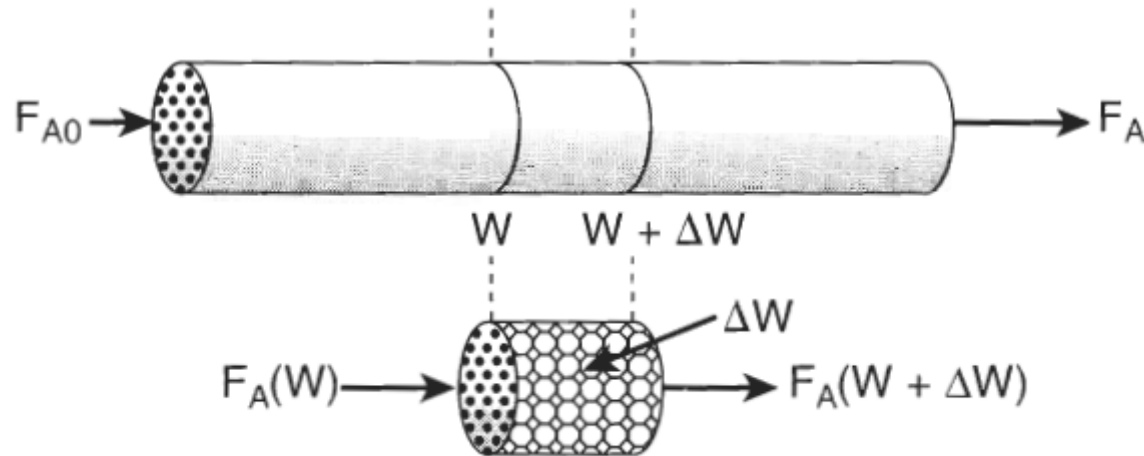
Continuous Flow Reactors

- Packed-Bed reactor – here the reaction takes place on the surface of catalyst

- reaction rate defined per unit area (or mass) of catalyst

$$-r_A = \text{mol A reacted/s} \cdot \text{g catalyst}$$

Product gas

Coolant

Catalyst Tube

Coolant-Side Baffles
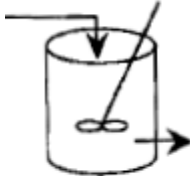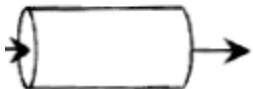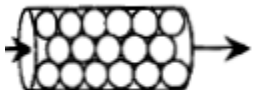
Coolant

Coolant

Feed gas

Continuous Flow Reactors

W – catalyst weight coordinate

- as in the PFR case, we can calculate design equation now in terms of catalyst weight coordinate

$$F_{A|W} - F_{A|W+\Delta W} + r_i \Delta W = 0 \implies r_i = \frac{F_{A|W} - F_{A|W+\Delta W}}{\Delta W} \implies r_A' = \frac{dF_A}{dW}$$

Reactors Mole Balance: Summary

| Reactor	Comment	Mole Balance Differential Form	Algebraic Form	Integral Form
Batch	No spatial variations	$\dfrac{dN_A}{dt} = r_A V$		$t_1 = \displaystyle\int_{N_{A1}}^{N_{A0}} \dfrac{dN_A}{-r_A V}$
CSTR	No spatial variations, steady state	—	$V = \dfrac{F_{A0} - F_A}{-r_A}$	—
PFR	Steady state	$\dfrac{dF_A}{dV} = r_A$		$V_1 = \displaystyle\int_{F_{A1}}^{F_{A0}} \dfrac{dF_A}{-r_A}$
PBR	Steady state	$\dfrac{dF_A}{dW} = r'_A$		$W_1 = \displaystyle\int_{F_{A1}}^{F_{A0}} \dfrac{dF_A}{-r'_A}$

Sizing of reactors

Here we'll find how to find the size of a reactor is relation between the reaction rate and conversion factor is known

Conversion in the reactors

$$aA + bB \longrightarrow cC + dD$$

- if we are interested in species A we can define the reactant A as the **basis of calculation**

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D$$
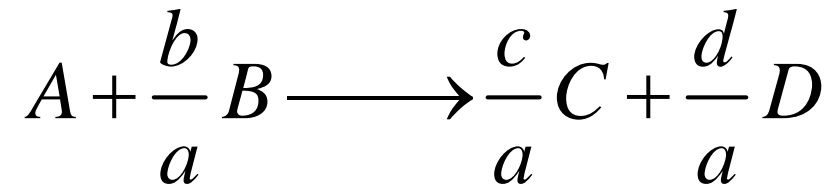
- **conversion**: $X_A = \dfrac{\text{Moles of A reacted}}{\text{Moles of A fed}}$

- maximum conversion for reversible reactions is the equilibrium conversion X_e.

Batch reactor design equations

$$[\text{Moles of A reacted}] = [N_{A0}] \cdot X_A$$

$$[\text{Moles of A in reactor, } N_A] = [N_{A0}] - [N_{A0}] \cdot X_A$$

differentiating

$$-\frac{dN_A}{dt} = (-r_A)V$$

$$\frac{dN_A}{dt} = -N_{A0}\frac{dX}{dt}$$

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

Design equation for Batch Reactor

- the equation can be integrated to find the time necessary to achieve required conversion
- the longer reactants spend in the chamber the higher is the degree of conversion

Design equations for flow reactors

$$[F_{A0}][X] = \frac{[\text{Moles of A fed}]}{[\text{time}]} \frac{[\text{Moles of A reacted}]}{[\text{Moles of A fed}]}$$

$$[F_{A0}][X] = \frac{[\text{Moles of A fed}]}{[\text{time}]}$$

Molar flow rate
fed to the system

Molar flow rate of the consumption
of A in the system

Molar flow rate of
A leaving the system

$$[F_{A0}] - [F_{A0}] \cdot X = [F_A]$$

- molar flow rate is concentration * volume rate

$$[F_A] = [F_{A0}](1-X) = C_{A0}v_0$$

Design equations for flow reactors

- CSTR:

$$[F_A] = [F_{A0}](1 - X)$$

$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{F_{A0} \cdot X}{-r_A}$$

- Because the reactor is perfectly mixed, the exit composition is identical to the composition inside the reactor

Design equations for flow reactors

- Tubular Flow Reactor (PFR):

$$-r_A = \frac{-dF_A}{dV}$$

$$[F_A] = [F_{A0}](1-X) \quad\Longrightarrow\quad -r_A = \frac{F_{A0}\,dX}{dV}$$

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

- to integrate we need to know r_A depends on the concentration (and therefore on conversion)

Design equations for flow reactors

- Packed-Bed Reactor: similar derivation, but W instead of V

$$-r_A' = \frac{-dF_A}{dW}$$

$$[F_A] = [F_{A0}](1-X)$$

$$\Longrightarrow \quad -r_A' = \frac{F_{A0}dX}{dW}$$

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

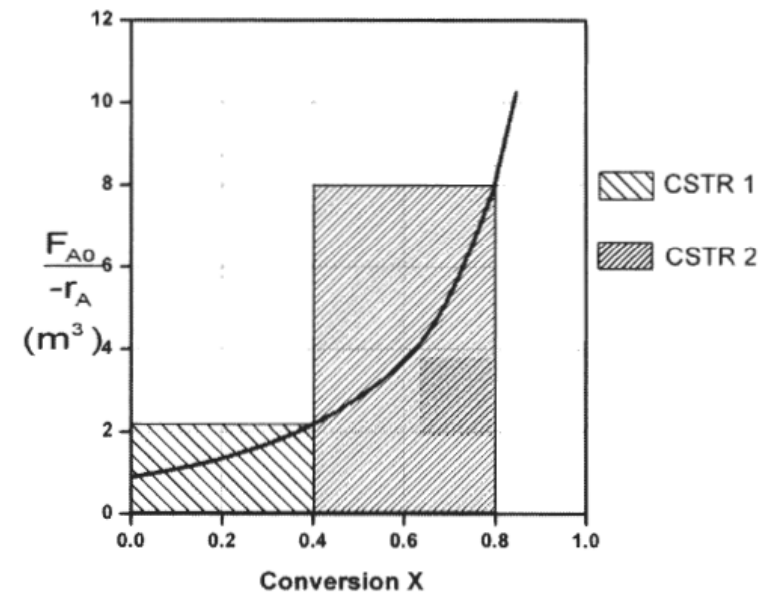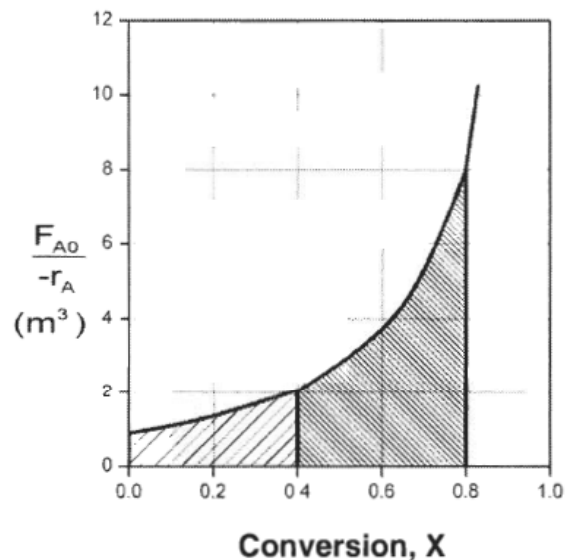- from this equation we can find weight of catalyst W required to achieve the conversion X

Levenspiel plot

- reactor volume required is always reciprocal in r_A and proportional to X.

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

CSTR: $$V = \frac{F_{A0} \cdot X}{-r_A}$$

- Levenspiel plot:

Example (2.2, p.48)

- Reaction A→B described by the data below and the species A enter the reactor at a molar flow rate of 0.4 mol/s:

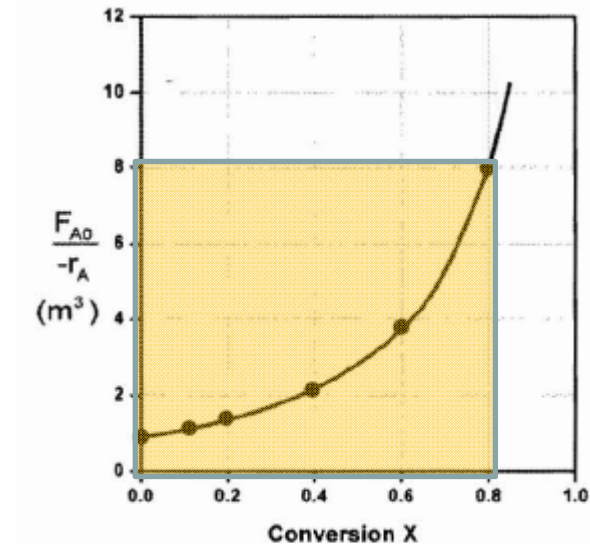| X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$-r_A \left(\dfrac{mol}{m^3 \cdot s} \right)$	0.45	0.37	0.30	0.195	0.113	0.079	0.05
$(1/-r_A) \left(\dfrac{m^3 \cdot s}{mol} \right)$	2.22	2.70	3.33	5.13	8.85	12.7	20
$[F_{A0}/-r_A](m^3)$	0.89	1.08	1.33	2.05	3.54	5.06	8.0

- Calculate the volume necessary for 80% conversion

Example (2.2, p.48)

- **Solution:**
  - **Based on the table the Levenspiel plot can be constructed**

X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$-r_A\left(\dfrac{mol}{m^3 \cdot s}\right)$	0.45	0.37	0.30	0.195	0.113	0.079	0.05
$(1/-r_A)\left(\dfrac{m^3 \cdot s}{mol}\right)$	2.22	2.70	3.33	5.13	8.85	12.7	20
$[F_{A0}/-r_A](m^3)$	0.89	1.08	1.33	2.05	3.54	5.06	8.0

  - **The design equation for the CSTR:**

$$V = \frac{F_{A0}}{\left(-r_{A1}\right)_{exit}} X \qquad\qquad V = 0.4\frac{mol}{s} 20\frac{m^3 \cdot s}{mol} 0.8 = 6.4m^3$$
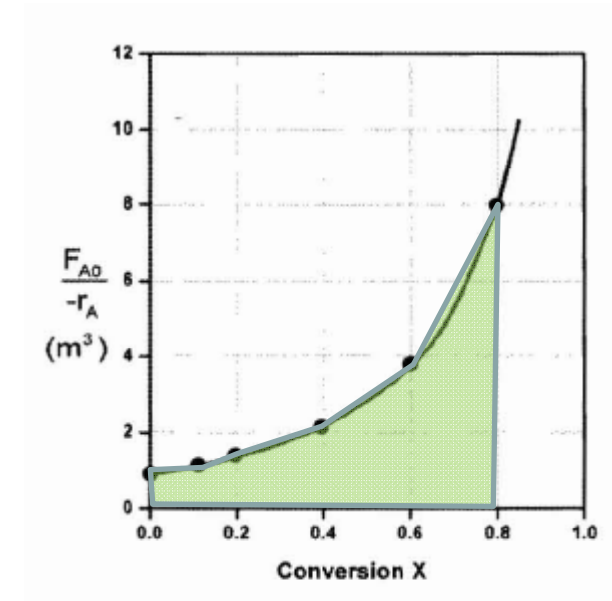
Example (2.3, p.50)

- **Calculate based on the same data the volume of PFR:**
  – **Again, we construct the Levenspiel plot**

X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$-r_A\left(\dfrac{\text{mol}}{\text{m}^3\cdot\text{s}}\right)$	0.45	0.37	0.30	0.195	0.113	0.079	0.05
$(1/-r_A)\left(\dfrac{\text{m}^3\cdot\text{s}}{\text{mol}}\right)$	2.22	2.70	3.33	5.13	8.85	12.7	20
$[F_{A0}/-r_A](\text{m}^3)$	0.89	1.08	1.33	2.05	3.54	5.06	8.0

  – **The design equation for the PFR:**

$$V = \int_0^{0.8} \frac{F_{A0}}{-r_{A1}}\, dX = 2.165 m^3$$
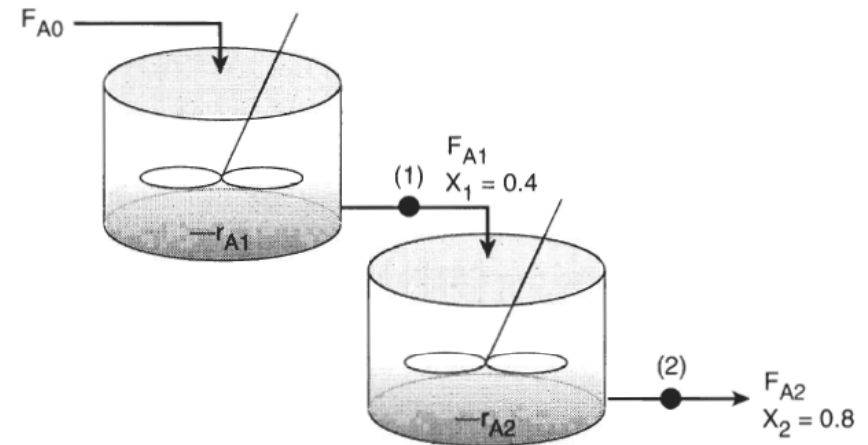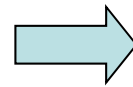
Reactors in series

- ## CSTR in series

Figure 2-4   Two CSTRs in series.

- – 1st reactor

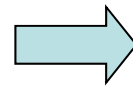$$F_{A0} - F_{A1} + r_{A1}V_1 = 0$$

$$F_{A1} = F_{A0} - F_{A0}X_1$$

$$\Longrightarrow \quad V_1 = F_{A0}\frac{1}{-r_{A1}}X_1$$

- – 2nd reactor

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

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

$$\Longrightarrow \quad V_2 = F_{A0}\frac{1}{-r_{A2}}\left(X_1 - X_2\right)$$

Mean residence time (Space Time)

- mean residence time defined as:

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

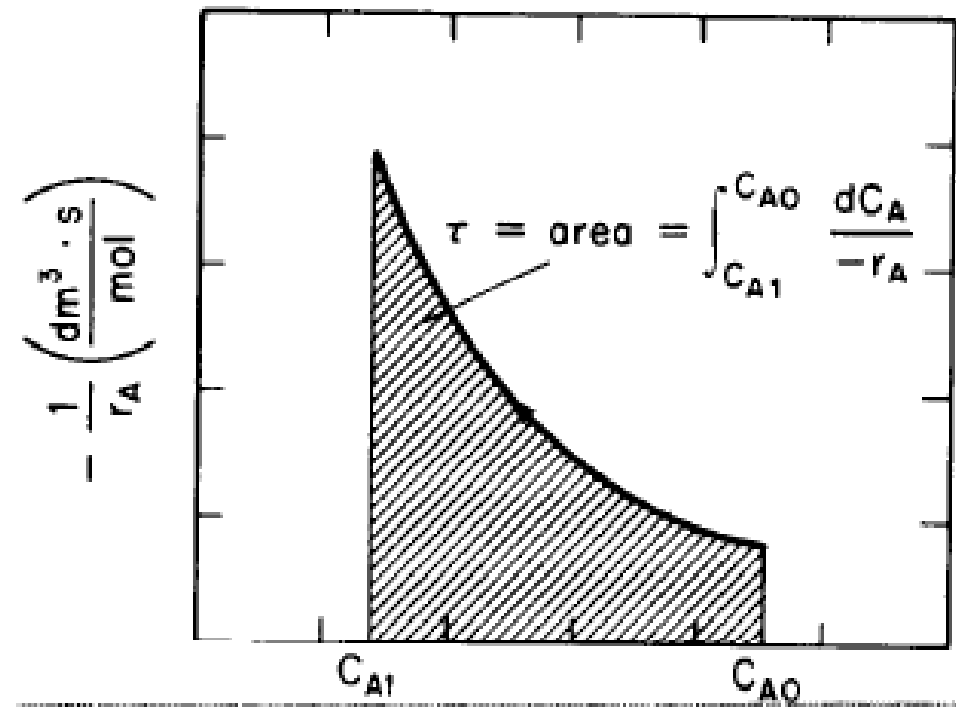$$X = \frac{F_{A0} - F_A}{F_{A0}} = \frac{C_{A0}v_0 - C_A v}{C_{A0}v_0} = \frac{C_{A0} - C_A}{C_{A0}}$$

when $X = 0$, $C_A = C_{A0}$
when $X = X$, $C_A = C_A$

$$dX = \frac{-dC_A}{C_{A0}}$$

$$V = v_0 \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A}$$

$$\boxed{\tau = \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A}}$$

$$\tau = \text{area} = \int_{C_{A1}}^{C_{A0}} \frac{dC_A}{-r_A}$$

Reactor design equations: Summary

	Differential Form	Algebraic Form	Integral Form
Batch	$N_{A0}\dfrac{dX}{dt} = -r_A V$		$t = N_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A V}$
CSTR		$V = \dfrac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}}$	
PFR	$F_{A0}\dfrac{dX}{dV} = -r_A$		$V = F_{A0}\displaystyle\int_{X_{in}}^{X_{out}} \dfrac{dX}{-r_A}$
PBR	$F_{A0}\dfrac{dX}{dW} = -r'_A$		$W = F_{A0}\displaystyle\int_{X_{in}}^{X_{out}} \dfrac{dX}{-r'_A}$

Problems

- Class problem: P2-7b (p.74)

- Home problems:
  - P2-5b
  - P2-6a "Hippopotamus stomack"
    http://www.engin.umich.edu/~cre/web_mod/hippo/index.htm