Chemical Reaction Engineering

Lecture 1

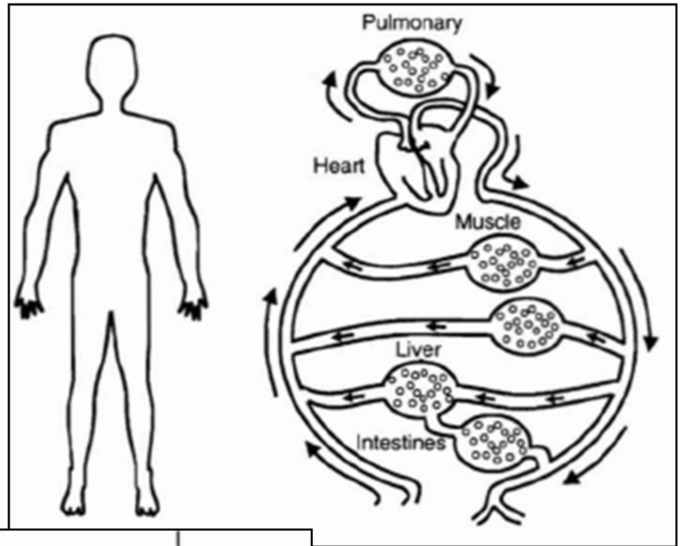
Chemical Reaction Engineering

- Course plan (Total 15 Lectures)
  - Mole balance and design equations for batch and continuous mode reactors.
  - Rate laws in the reactor design
  - Isothermal reactor design
  - Bioreactors (Eva)
  - Comsol modelling of reactions and reactors. H-cell with chemical reaction.
  - Non-isothermal reactors. Comsol modelling: flow through porous bed and stirred batch reactor.
  - Diffusion and Reactions. Comsol modelling of biochips: reaction on the surface
  - Molecular Electronics block (5 Lectures).

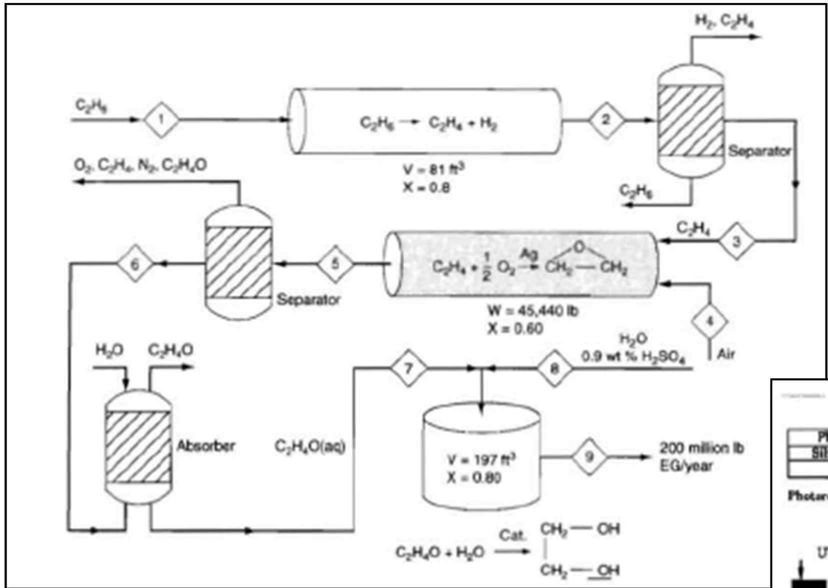
The Scope

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

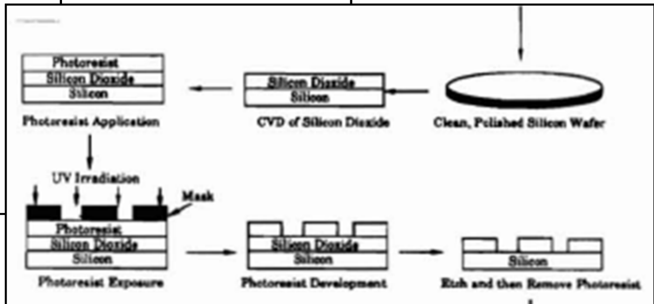
- Reactors



Pharmacokinetics



Chemical plant for ethylene glycol



Microelectronic fabrication

General algorithm of Chemical Reaction Engineering

- Mole balance
- Rate laws
- Stoichiometry
- Energy balance

- Combine and Solve

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:

$$d[P]/dt$$

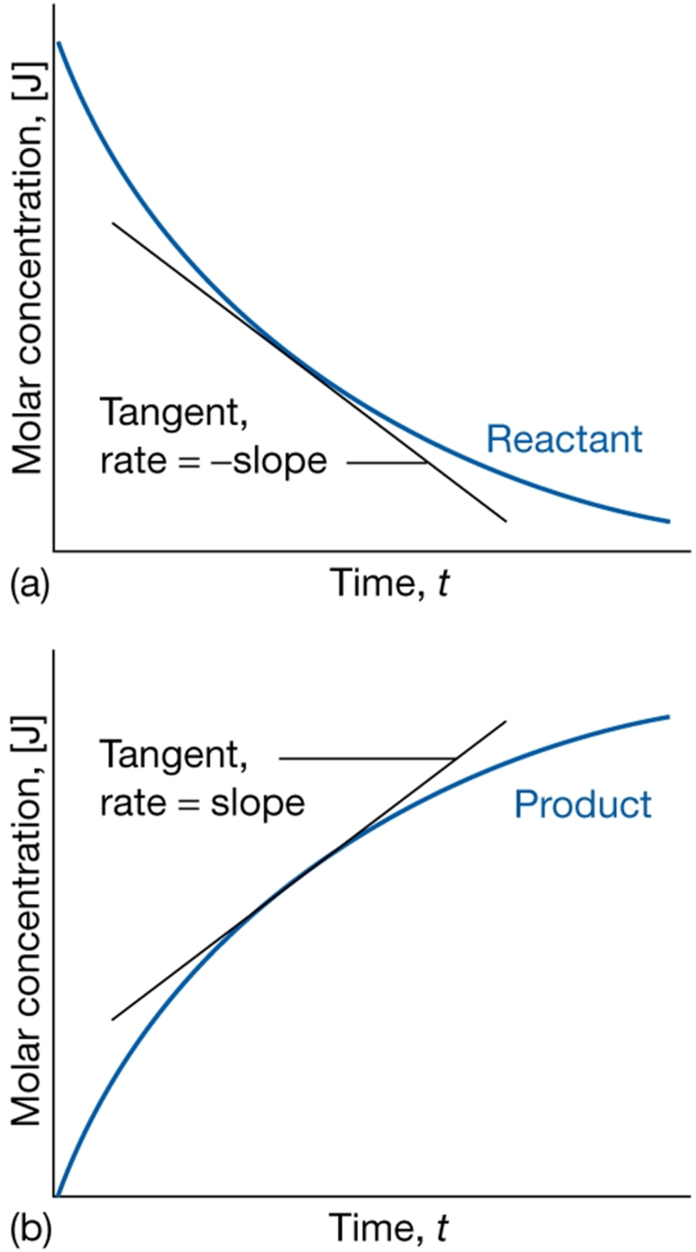
From stoichiometry

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

Rate of the reaction: $$v = \frac{1}{\nu_i}\frac{dn_i}{dt} = \frac{d\xi}{dt}$$

! In the case of heterogeneous reaction the rate will be defined per unit area of catalyst as mol/m^{2}s

! In the case of continuous flow reactor change of concentration is not equal to the reaction rate



Rates of chemical reactions

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

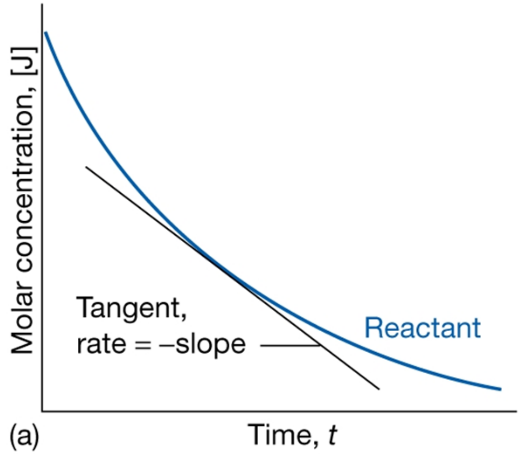
- Usually we interested in the concentration of one particular reagent, say A.
- **The *reaction rate* in terms of reagent A is the number of moles of A reacting per unit time, per unit volume (mol·m^{-3}·s^{-1})**
  In the case of heterogeneous reaction the rate will be defined per unit area of catalyst as mol/m^2·s or per unit mass of catalyst mol/kg·s

$$\cancel{-r_A = d[A]/dt}$$

Ok for closed well stirred system but,

this definition is inconvenient and can be misleading because

- the concentration of A is varying with time and position inside the reactor,
- for a continuous reactor in steady state, the concentration at a given point is constant in time



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

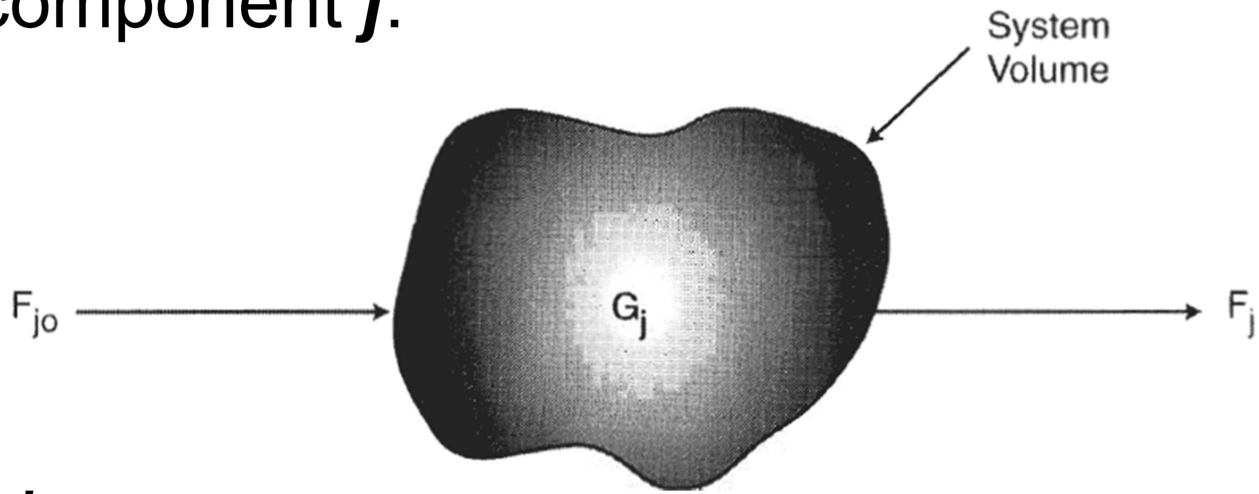
$$-r_A = kC_A$$

- 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 + Rate of Generation =Rate of Accumulation

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

moles/time

$$G_i = r_i \cdot V$$

moles/time

moles/(time·volume)

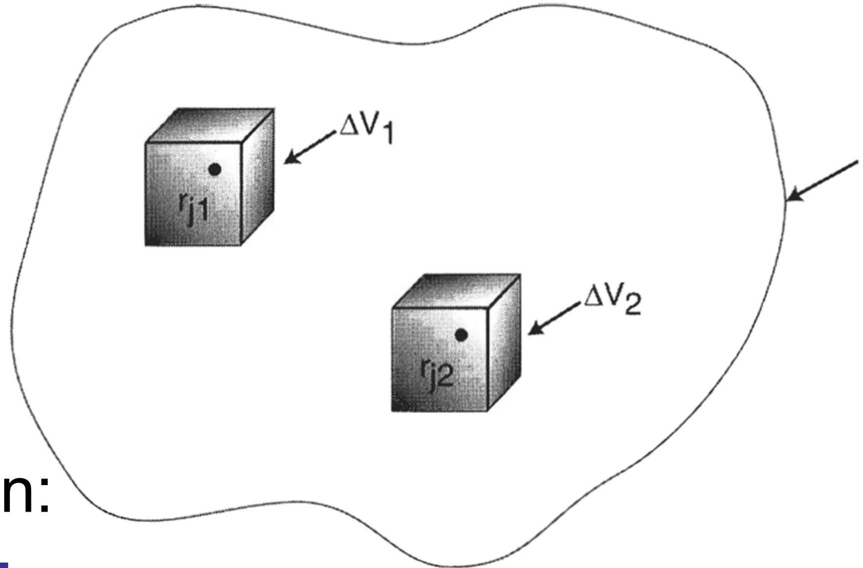
volume

rate of reaction

The general mole balance equation

- Generally, the rate of reaction varies from point to point in the reactor:

$$G_i = \int^{V} r_i dV$$



- The general mole balance equation:

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

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

Types of Chemical Reactors

- Depending on loading/unloading of the reactor

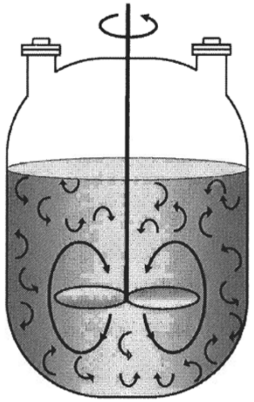
Batch

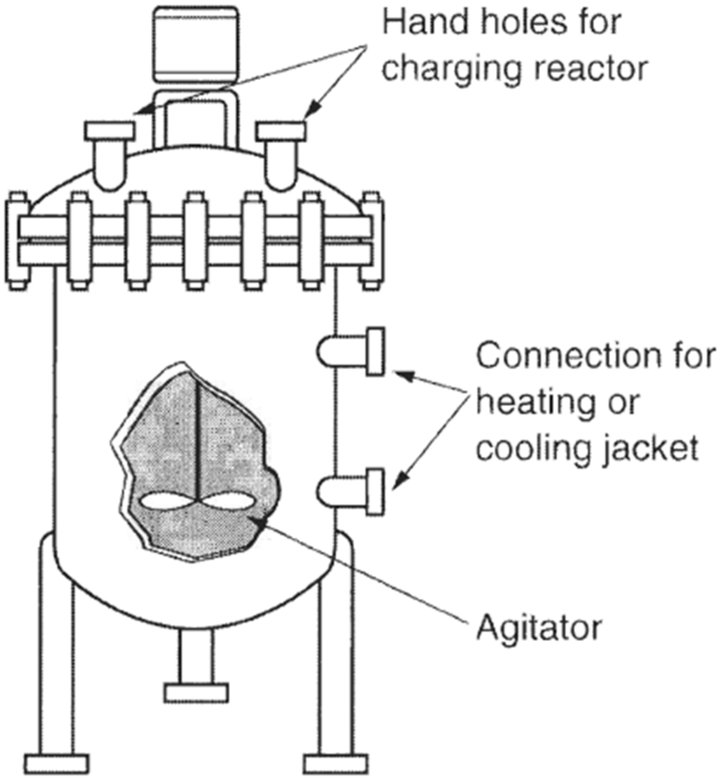
Semi-Batch

Continuos Flow

- CSTR (Continuous-Stirred Tank Reactor)
- Tubular reactor
- Packed-bed reactor

Batch reactors





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

Batch reactors

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

$\boxed{0}$

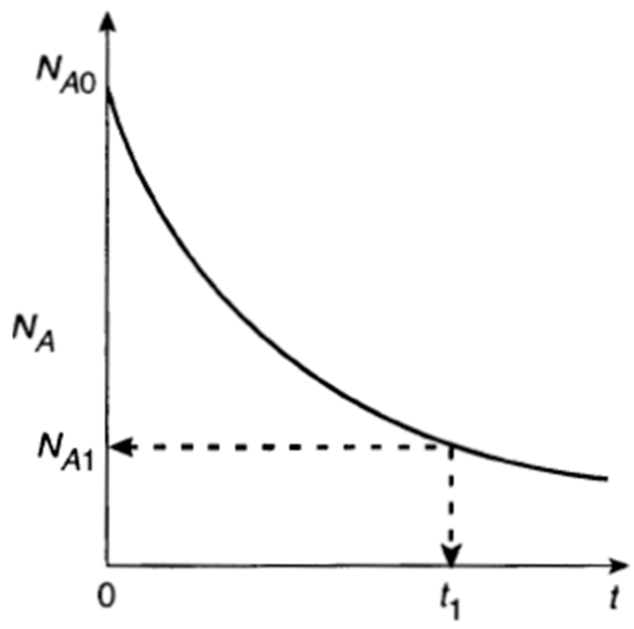
- assuming perfect mixing, reaction rate the same through the volume

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

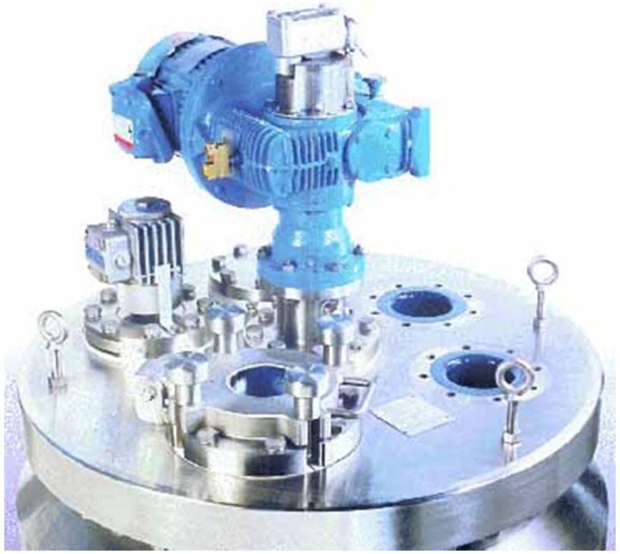
- integrating the equation we can get N_j vs t – "***mole-time trajectory***"

$$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$$

time to reach concentration N_{A1} in the reactor can be found



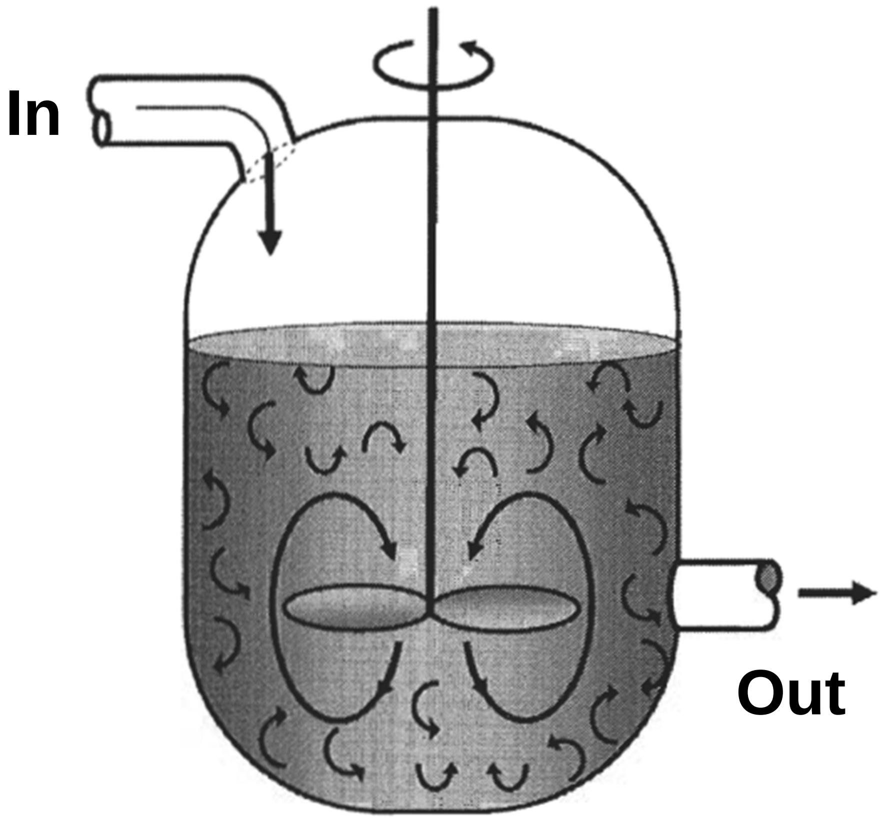
Batch reactors



Pfaudler's Batch reactor

Continuous Flow Reactors

- CSTR (Continuous-Stirred Tank Reactor)

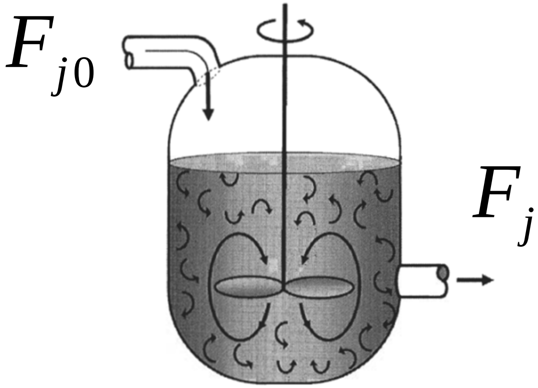


Pfaudler's CSTR reactor

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**

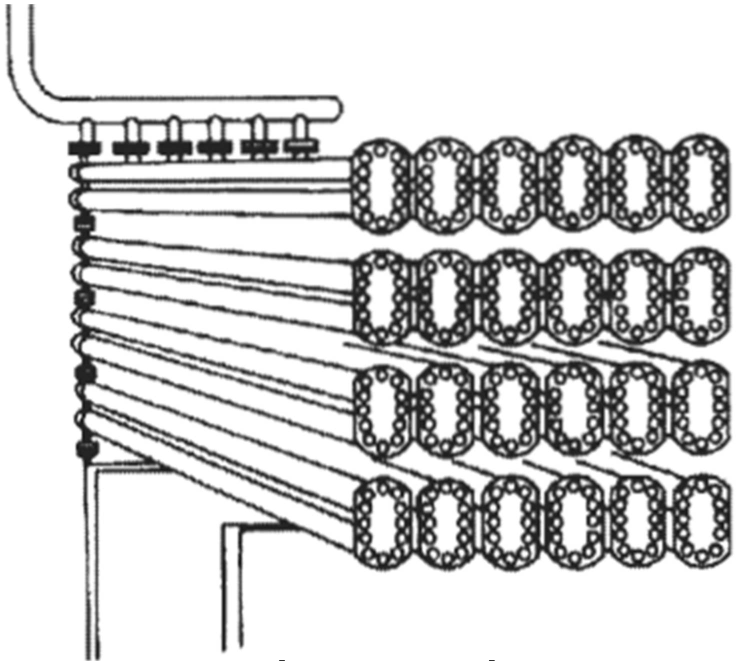
- assuming **perfect mixing**, so
  - Reaction rate is the same through the volume
  - Conditions of exit stream are the same as in the reactor

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

Design equation of CSTR

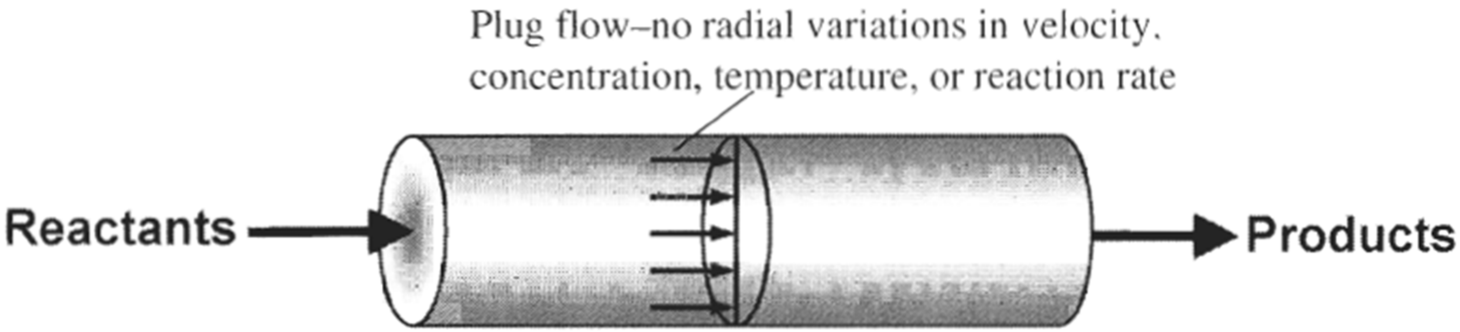
Continuous Flow Reactors

- 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

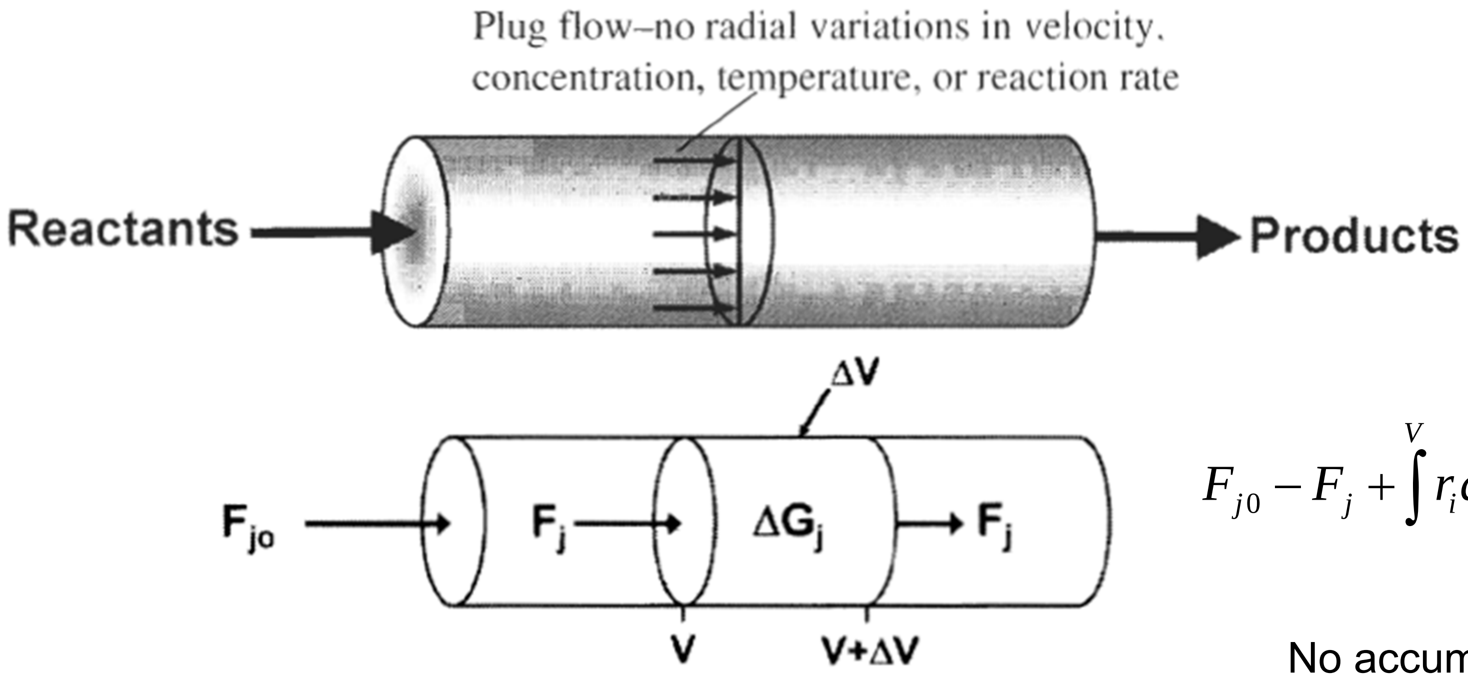
Continuous Flow Reactors



- 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



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

No accumulation $\boxed{0}$

- For every slice of volume:

$$F_{j0} - F_j + r_i \Delta V = 0 \quad \Rightarrow \quad r_i = \frac{F_{j|V+\Delta V} - F_{j|V}}{\Delta V} \quad \Rightarrow \quad r_i = \frac{dF_j}{dV}$$

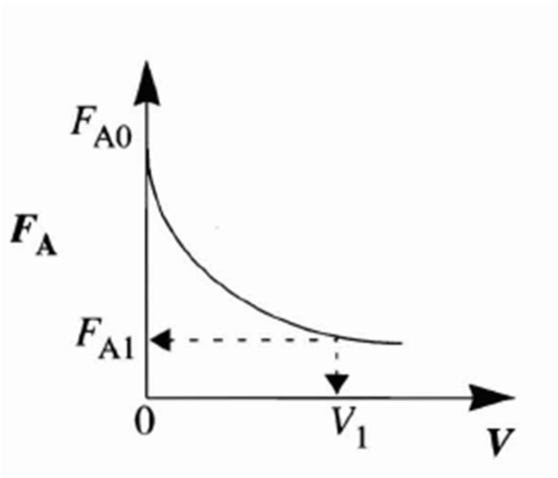
- From here, a volume required to produce given molar flow rate of product can be determined

Continuos Flow Reactors

- Design equation for PFR

$$r_j = \frac{dF_j}{dV} \Rightarrow dV = \frac{dF_j}{r_j} \qquad V = \int_{F_{j0}}^{F_j} \frac{dF_j}{r_j} = \int_{F_j}^{F_{j0}} \frac{dF_j}{-r_j}$$

- 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.

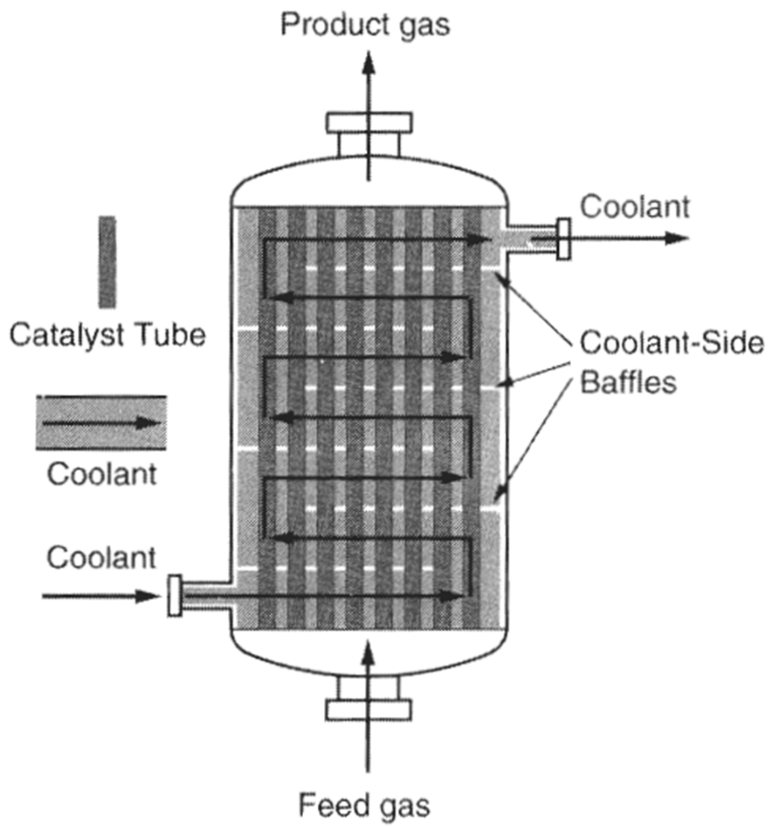


Continuous Flow Reactors

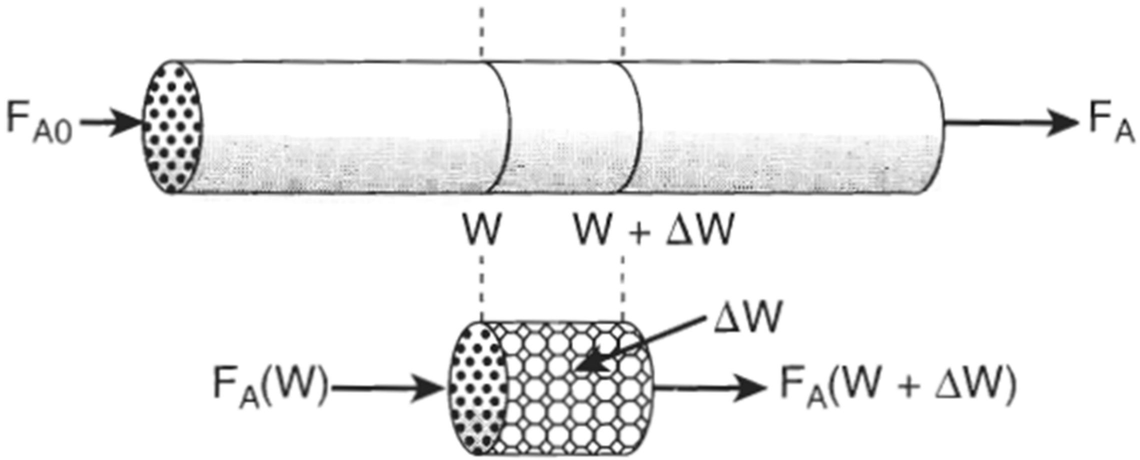
- Packed-Bed reactor – here the reaction takes place on the surface of catalyst

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

$$-r_A' = \left(\text{mol A reacted}\right)/\text{s}\cdot\left(\text{g catalyst}\right)$$



Continuous Flow Reactors

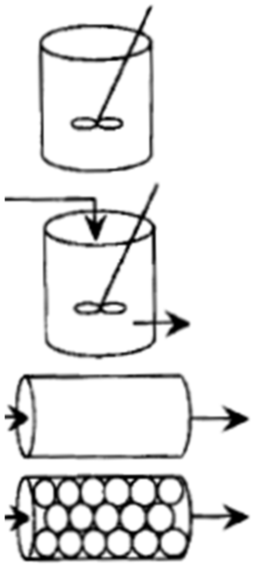


W – catalyst weight coordinate

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

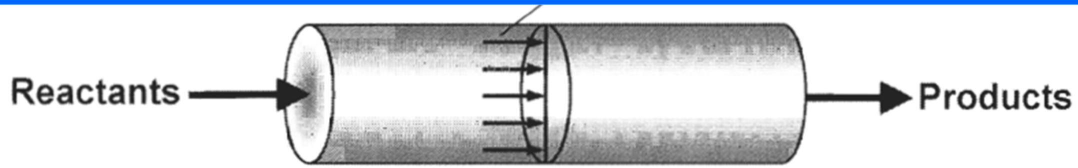
$$F_{A|W} - F_{A|W+\Delta W} + r'_A \Delta W = 0 \Rightarrow r'_A = \frac{F_{A|W+\Delta W} - F_{A|W}}{\Delta W} \Rightarrow r'_A = \frac{dF_A}{dW}$$

Reactors Mole Balance: Summary



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

How we can use design equations: Example 1-1



- **Problem**

  An isomerization reaction A->B (first order reaction, k=0.23 min^{-1}) is run in a tubular reactor with a constant volumetric flow rate v_0= 10 l/min.
  Derive design equation, sketch concentration profile and determine the reactor volume required to achive 10% of A at the exit.

- **Solution**

  From the mole balance for PFR: $$\frac{dF_A}{dV} = r_A$$

  Reaction rate law: $$-r_A = kC_A$$

  As the volumetric flow is kept constant: $$\frac{dF_A}{dV} = v_0 \frac{dC_A}{dV}$$

  Combining with the rate law: $$v_0 \frac{dC_A}{dV} = -kC_A \Rightarrow V = -\frac{v_0}{k} \int_{C_{A0}}^{C_{A1}} \frac{dC_A}{C_A} = 100dm^3$$

Sizing of reactors

Here we'll find how to find the size of a reactor if the 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

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

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

differentiating

$$\begin{cases} -\dfrac{dN_A}{dt} = (-r_A)V \\ \dfrac{dN_A}{dt} = -N_{A0}\dfrac{dX}{dt} \end{cases} \Rightarrow \boxed{N_{A0}\dfrac{dX}{dt} = (-r_A)V}$$

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

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

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

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

$$\left[F_{A0}\right]-\left[F_{A0}\right]\cdot X=\left[F_{A}\right]$$

- molar flow rate can be expressed as
  concentration * volume rate

$$\left[F_{A}\right]=\left[F_{A0}\right](1-X)=C_{A0}v_{0}(1-X)$$

Design equations for flow reactors

- CSTR:

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

$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{F_{A0} \cdot X}{(-r_A)_{exit}}$$

- 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):

$$\left.\begin{aligned} -r_A &= \frac{-dF_A}{dV} \\ [F_A] &= [F_{A0}](1-X) \end{aligned}\right\} \Rightarrow -r_A = \frac{F_{A0}dX}{dV}$$

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

- 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

$$\left.\begin{aligned} -r_A' &= \frac{-dF_A}{dW} \\ [F_A] &= [F_{A0}](1-X) \end{aligned}\right\} \Rightarrow \quad -r_A' = \frac{F_{A0}\,dX}{dW}$$

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

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

Accounting for the reaction rate law

- As we see, to find the volume of the reactor we need to know the ***$1/r_A$*** dependence on ***X***

- Let's consider a first-order reaction:

$$-r_A = kC_A = kC_{A0}(1 - X)$$

$$\frac{1}{-r_A} = \frac{1}{kC_{A0}} \frac{1}{(1 - X)}$$

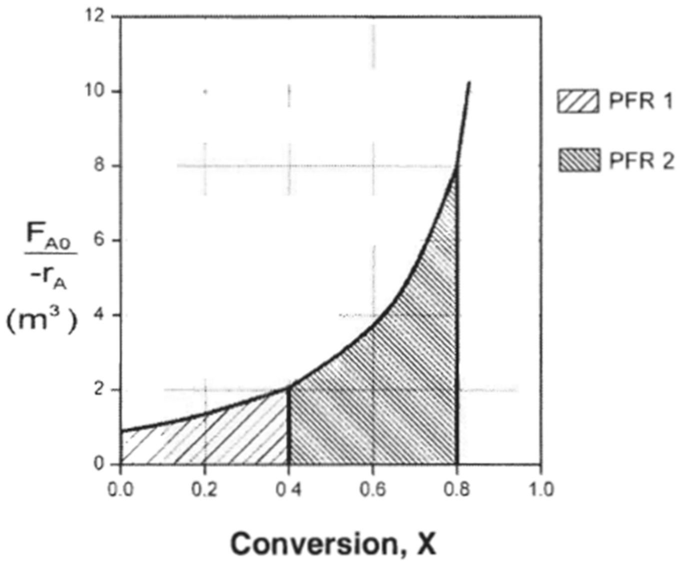
Levenspiel plot

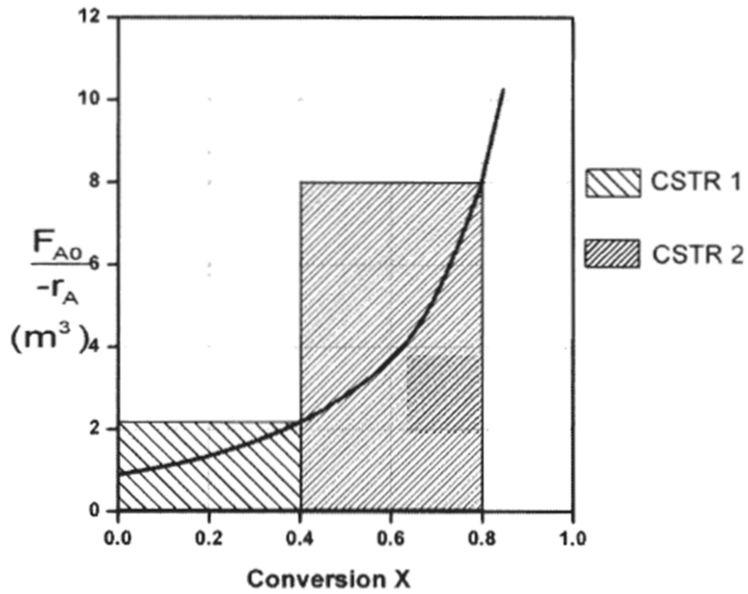
- reactor volume required is always reciprocal in r_A and proportional to X.

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:

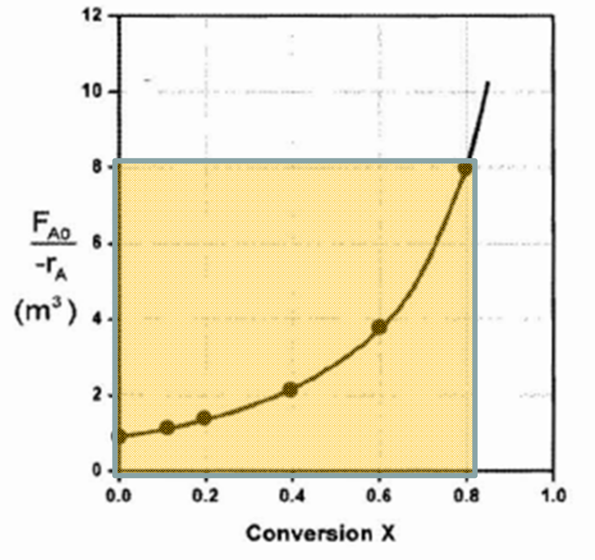
X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$-r_A\left(\frac{\text{mol}}{\text{m}^3 \cdot \text{s}}\right)$	0.45	0.37	0.30	0.195	0.113	0.079	0.05
$(1/-r_A)\left(\frac{\text{m}^3 \cdot \text{s}}{\text{mol}}\right)$	2.22	2.70	3.33	5.13	8.85	12.7	20
$[F_{A0}/-r_A](\text{m}^3)$	0.89	1.08	1.33	2.05	3.54	5.06	8.0

- 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
$-r_A\left(\frac{mol}{m^3 \cdot s}\right)$	0.45	0.37	0.30	0.195	0.113	0.079	0.05
$(1/-r_A)\left(\frac{m^3 \cdot s}{mol}\right)$	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:**

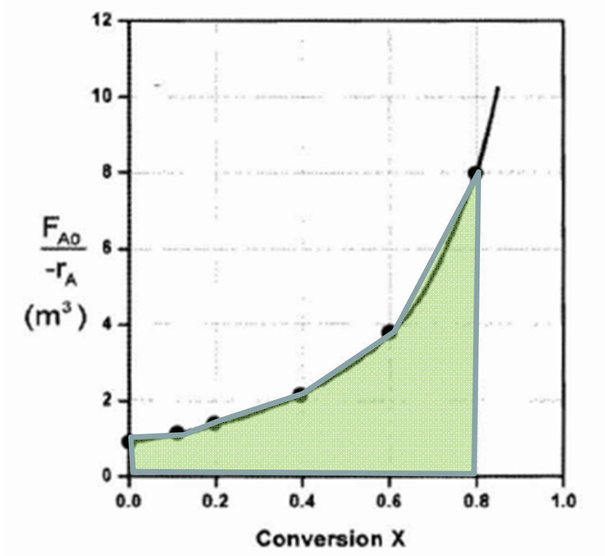
$$V = \frac{F_{A0}}{(-r_{A1})_{exit}} X$$

$$V = 0.4\frac{mol}{s} 20 \frac{m^3 \cdot s}{mol} 0.8 = 6.4 m^3$$

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
$-r_A\left(\frac{\text{mol}}{\text{m}^3\cdot\text{s}}\right)$	0.45	0.37	0.30	0.195	0.113	0.079	0.05
$(1/-r_A)\left(\frac{\text{m}^3\cdot\text{s}}{\text{mol}}\right)$	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

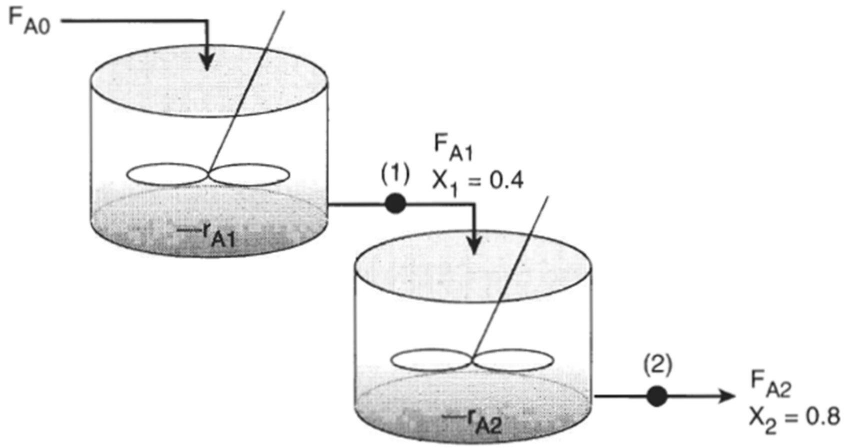


Figure 2-4 Two CSTRs in series.

  - 1st reactor

$$F_{A0} - F_{A1} + r_{A1}V_1 = 0$$
$$F_{A1} = F_{A0} - F_{A0}X_1$$

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

  - 2nd reactor

$$F_{A1} - F_{A2} + r_{A2}V_2 = 0$$
$$F_{A2} = F_{A0} - F_{A0}X_2$$

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

Mean residence time (Space Time)

- ***space time*** is defined as:

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

equal to the mean rresidence time in the absence of dispersion

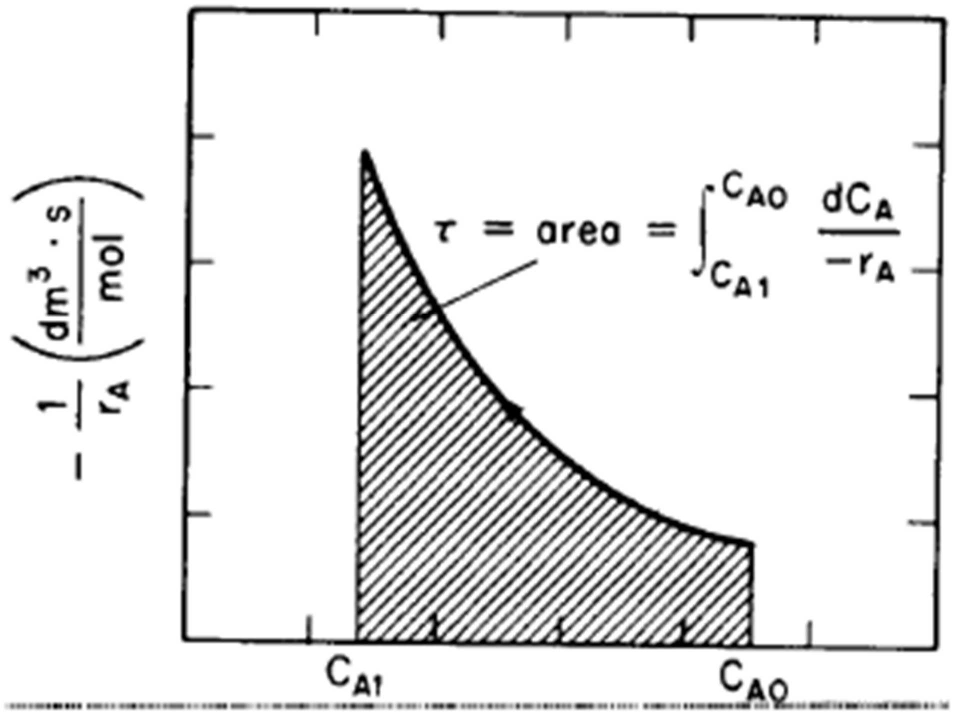
$$X = \frac{F_{A0} - F_A}{F_{A0}} = \frac{C_{A0} v_0 - C_A v}{C_{A0} v_0} = \frac{C_{A0} - C_A}{C_{A0}}$$

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

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

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

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



Reactor design equations: Summary

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

Problems

- Class problem:
  - P1-6b (p.30): Calculate the volume of CSTR for the conditions of example 1-1.
  - P2-7b (p.74)
- Home problems:
  - P2-5b
  - P2-6a ”Hippopotamus stomack”
    http://www.engin.umich.edu/~cre/web_mod/hippo/index.htm