CHEE 321: Chemical Reaction Engineering

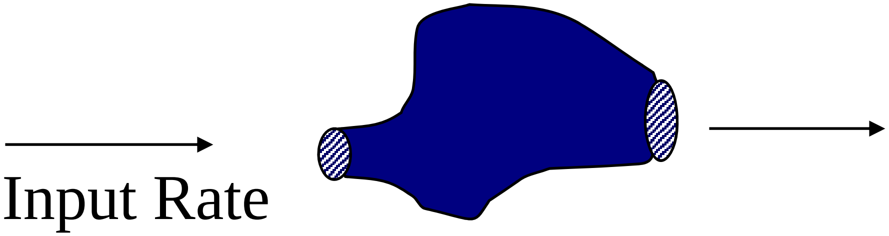
1. Introductory Material

1b. The General Mole Balance Equation (GMBE) and Ideal Reactors

(Fogler Chapter 1)

Recap: Module 1a

System with Rxn: use mole balances



Rate of INPUT – Rate of OUTPUT + Rate of GENERATION – Rate of CONSUMPTION

= *Rate of ACCUMULATION*

Note: Rates refer to molar rates (moles per unit time).

Before we get into the details of the mole balance equation, we must introduce a definition for reaction rate as well as associated notation.

Reaction Rate and Rate Law (recap) $A + 2B \rightarrow C$

Reaction Rate

- Rate of reaction of a chemical species will depend on the local conditions (concentration, temperature) in a chemical reactor
  (Units: mols per unit volume per unit time)

Rate Law

- Rate law is an algebraic equation (constitutive relationship) that relates reaction rate to species concentrations.
- Rate law is independent of reactor type

$(-r_A) = k \cdot$[concentration terms] e.g. $(-r_A) = k\,C_A$ or $(-r_A) = k\,C_A^2$

where, k is the rate coefficient that varies exponentially with temperature according to the Arrhenius relationship [$k = A\exp(-E_a/RT)$]

Stoichiometry

- Reaction stoichiometry links together the generation/consumption rates of products and reactants.

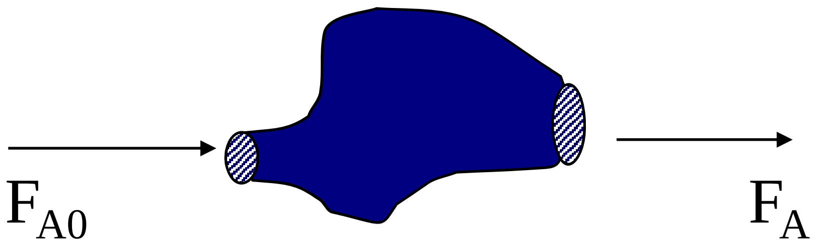
General Mole Balance Equation (GMBE)

General mole balance equation is the foundation of reactor design.

Rate of INPUT – Rate of OUTPUT + Rate of GENERATION/CONSUMPTION = Rate of ACCUMULATION

$$F_{A0} - F_A + G_A = \frac{dN_A}{dt}$$

All terms with units of mol/s



System volume V

G_A = (rate of generation of A) · V

$$= \int^{V} r_A dV'$$

If A is consumed, add a –ve sign

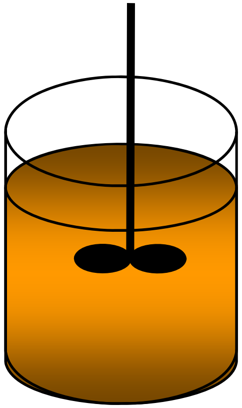
Need to integrate over reactor volume, as reaction conditions (T, C_A) may vary with position

Common Reactor Types

- Chemical Reactors are commonly classified by:
  - Mode of operation (batch, continuous, semibatch)
  - Geometric configuration (tubular, agitated tank)
  - For heterogeneous systems, contacting patterns between phases (packed bed, fluidized bed, bubble column, membrane reactor, …)

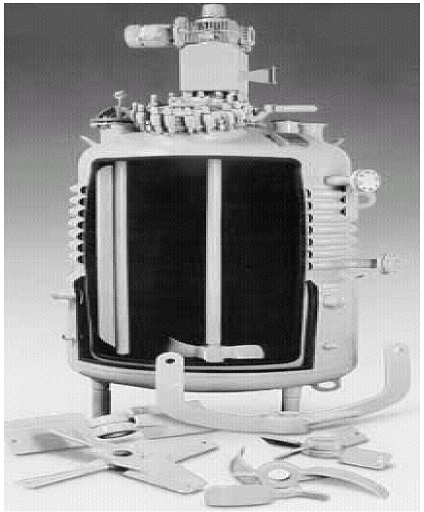
- Ideal reactors we will first consider
  - *Batch reactor (well-mixed)*
  - *Continuous-Stirred Tank Reactor (CSTR)*
  - *Plug Flow Reactor (PFR)*
  - *Packed Bed Reactor (PBR)*

Batch Reactor



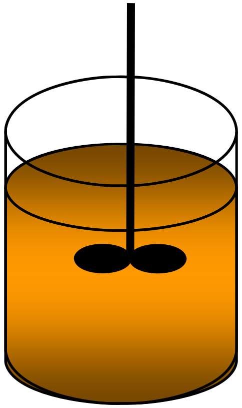
<u>*Key Characteristics*</u>

- No inflow or outflow of material
- Unsteady-state operation (by definition)
- Mainly used to produce low-volume high-value products (e.g., pharmaceuticals)
- Often used for product development
- Mainly (*not exclusively*) used for liquid-phase reactions
- Charging (filling/heating the reactor) and clean-out (emptying and cleaning) times can be large



For an ideal batch reactor, we assume no spatial variation of concentration or temperature. i.e.; *lumped parameter system* (well-mixed)

General Mole Balance for an Batch Reactor



Input = Output = 0

$$\frac{dN_A}{dt} = \int^{V} r_A dV'$$

If well-mixed (no temperature or concentration gradients in reactor):

differential form

$$\frac{dN_A}{dt} = r_A V \quad ; \qquad N_A = N_{A0} \text{ at } t = 0$$

integral form

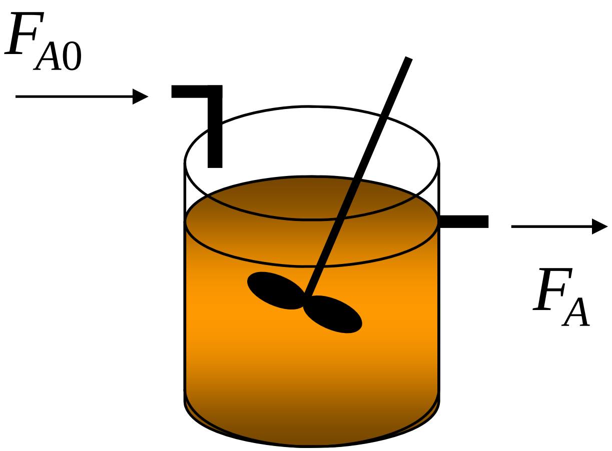
$$t = \int_{N_{A0}}^{N_A} \frac{dN'_A}{r_A V}$$

Exercise:

Derive concentration vs. t profiles for A and B for A→B with r_B=-r_A=kC_A for a well-mixed constant-volume isothermal batch reactor.

At t=0, C_A=C_{A0} and C_B=0

Continuous Stirred Tank Reactor (CSTR)



- Can be used in series
- Mainly used for liquid phase reaction, high-volume products
- Suitable for viscous liquids

$$\frac{dN_A}{dt} = F_{A0} - F_A + \int^V r_A dV'$$

For an ideal CSTR, we assume no spatial variation of concentration or temperature. i.e.; *lumped parameter system* (well-mixed)

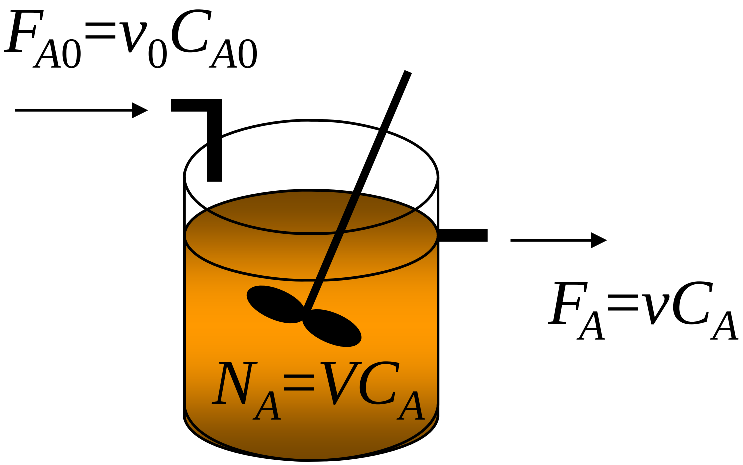
$$\frac{dN_A}{dt} = F_{A0} - F_A + r_A V$$

For an ideal CSTR operating at steady-state (no time variation of flows, concentrations, temperature, volume)

$$F_{A0} - F_A + r_A V = 0$$

Picture Source: http://www-micrbiol.sci.kun.nl/galleries/two.html

General Mole Balance for Ideal CSTR at Steady-State



CSTRs are also known as "back-mix" reactors, as concentrations in the outlet stream are the same as concentrations in the reactor (a consequence of being well-mixed)

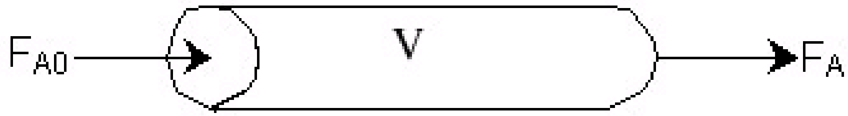
v_0, v= volumetric flowrates (L/min, m^3/s) of inlet and exit;
if at steady-state *and* constant density, $v_0 = v$

Average *residence* or *space time* of fluid in vessel based on inlet conditions $\tau = V/v_0$

Exercise:

Derive expressions for concentration of A and B for A→B with r_B=-r_A=kC_A for a well-mixed steady-state CSTR with inlet concentrations C_A=C_{A0} and C_B=0, assuming no density change.

Plug Flow Reactor (PFR)



$$\frac{dN_A}{dt} = F_{A0} - F_A + \int^{V} r_A dV'$$

<u>*Key Characteristics*</u>

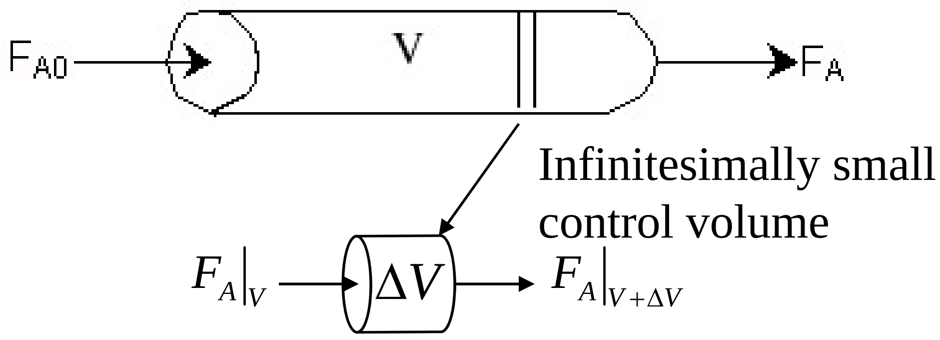
- Generally a long cylindrical pipe with no moving parts (*tubular reactor*)
- Suitable for fast reactions (good heat removal), mainly used for gas phase systems
- Concentrations vary along the length of the tube (axial direction)

For an ideal PFR, we assume:

- constant inlet flowrate
- no variation of fluid velocity or species concentration in radial direction

We also generally assume reactor is operating at steady-state: i.e.; no variation in properties with time at any position along reactor length

General Mole Balance for Ideal PFR at Steady-State



integral form

$$V = \int_{F_{A0}}^{F_A} \frac{dF'_A}{r_A}$$

At steady state: $F_A|_V - F_A|_{V+\Delta V} + r_A \Delta V = 0$ ⟶ *differential form*

$$\frac{dF_A}{dV} = r_A \quad ;$$

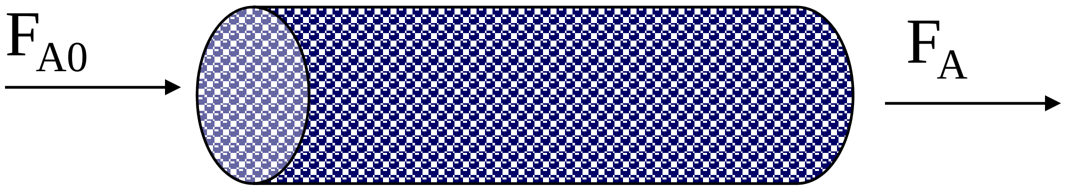
$$F_A = F_{A0} \text{ at } V = 0$$

Exercise:

Derive concentration profiles for A and B for A→B with r_B=-r_A=kC_A for a isothermal PFR at steady-state, assuming constant volumetric flowrate.

At the reactor inlet, C_A=C_{A0} and C_B=0

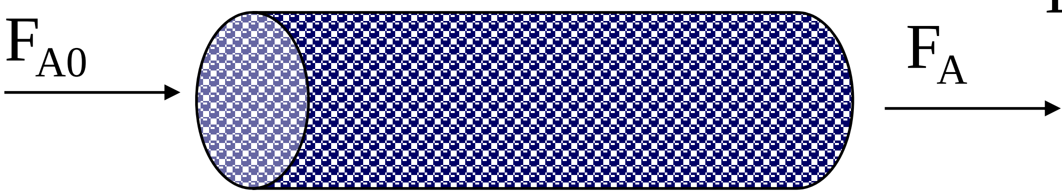
Packed Bed Reactor (PBR)



Key Characteristics

- Can be thought of as PFR packed with solid particles, usually some sort of catalyst material.
- Mainly used for gas phase catalytic reaction although examples for liquid-phase reaction are also known.
- Pressure drop across the packed bed is an important consideration.

Mole Balance for PBR



Let W = Weight of the packing

Making the same assumptions as for a PFR:

- no variation of fluid velocity or species concentration in radial direction
- operating at steady-state

differential form

$$\frac{dF_A}{dW} = r'_A \quad ;$$

$$F_A = F_{A0} \text{ at } W = 0$$

integral form

$$W = \int_{F_{A0}}^{F_A} \frac{dF'_A}{r'_A}$$

Same as PFR, but with rate (r) specified per mass of catalyst (instead of per unit volume) and using catalyst wt (W) instead of V as the coordinate

Summary - Design Equations of Ideal Reactors

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

Conversion (X) [Single Reaction System]

- *Quantification of how far a reaction has progressed*

Continuous (or Flow) Reactors

$$X_j = \frac{\text{mols of species-}j\text{ reacted}}{\text{mols of species-}j\text{ fed}} = \frac{F_{j0} - F_j}{F_{j0}}$$

Batch Reactors

$$X_j = \frac{\text{mols of species-}j\text{ reacted}}{\text{mols of initial species-}j} = \frac{N_{j0} - N_j}{N_{j0}}$$

- *Usually defined in terms of limiting reactant*

Reactants → Products

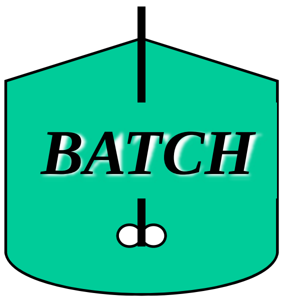
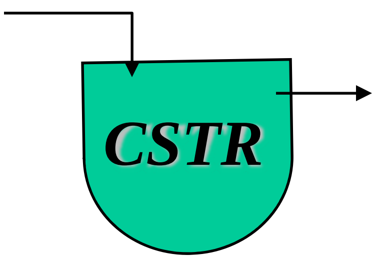
$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$

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

Assume "A" is our limiting reactant
(Know how to identify this!)

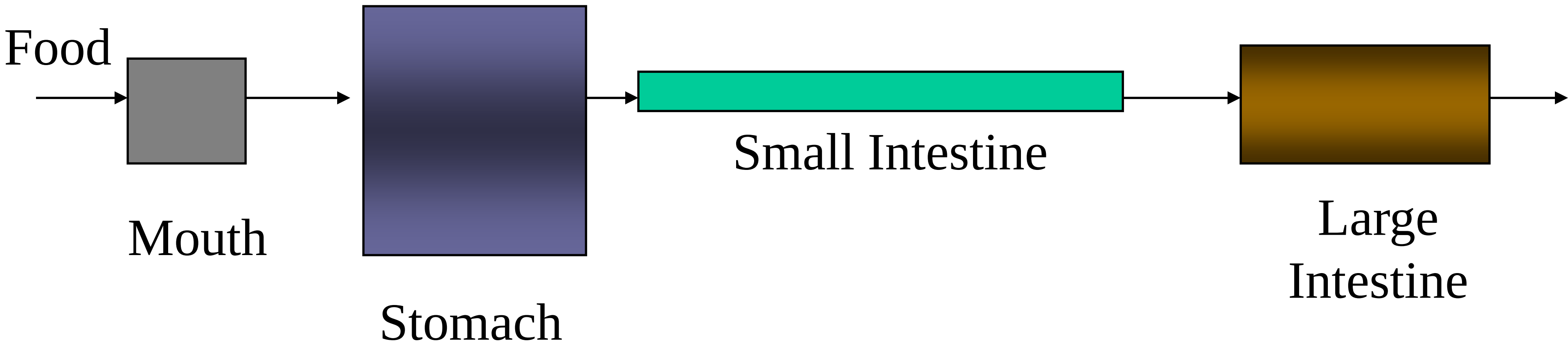
Fogler 2.1

Design Equation in Terms of Conversion (limiting reactant A)

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

Fogler 2.2-2.3

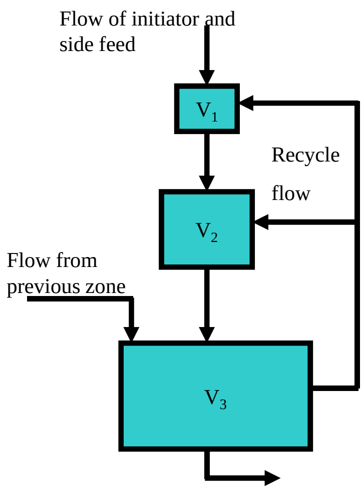
Human Body as a System of Reactors



What reactor type can we represent the various body parts with?

- We can often approximate behaviour of complex reactor systems by considering combinations of these basic reactor types (batch, PFR, CSTR)
- Next step (Fogler Ch 2):
  - ➢Formulate design equations in terms of conversion
  - ➢Apply to reactor sizing

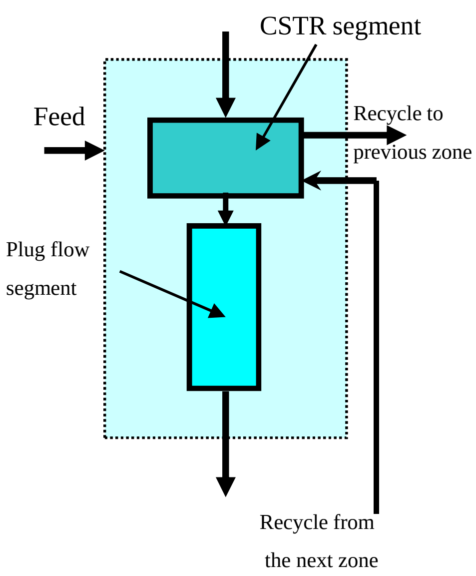
Approaches in modeling imperfect mixing in LDPE Autoclave Reactors



Compartments model

Each reaction zone is considered as a set of interconnected three CSTR's. Recycle flow models the effect of imperfect mixing in initiator injection point and backmixing in the reaction space. The model parameters are based on geometrical and flow dynamic of the industrial system.

Marini, L., Georgakis, C., *AIChE J.* **30**, 401 (1984).



Segments model

Each reaction zone is considered as a CSTR section followed by a plug flow section. The plug flow is considered as a series of CSTR's in series due to complex mathematical difficulties. Recycle streams show the effects of imperfect mixing.

Chan ,W., Gloor, P. E., & Hamielec, A. E., *AIChE J.* ***39***, 111 (1993).