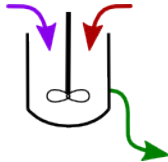


# Introduction to Reactor Design

## ChE 3K4



Kevin Dunn, 2013

(with credit to Dr. P. Mhaskar for many of the slides)

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<http://learnche.mcmaster.ca/3K4>

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# Slide credits and notes

- ▶ These slides were created by Dr. Mhaskar.
  - ▶ Minor modifications/additions by Kevin Dunn.
  - ▶ Words in purple are definitions
  - ▶ Words in this colour are hyperlinks
  - ▶ Other colours are to emphasize points
- 
- ▶ Version numbering: first page shows an integer version number, and refers to each revision; also includes the month and year for reference.
  - ▶ File names: 2013-3K4-class-01B.pdf implies today, which is week 1 of the term, second class (1A, 1B, 1C, 2A, 2B *etc*)
  - ▶ Also used on course website

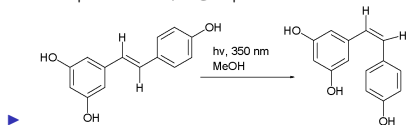
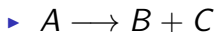
# What we are going to learn here

Review of chemistry and chemical engineering topics

- ▶ Rate of reaction
- ▶ Mole balances
- ▶ Batch reactors
- ▶ Continuous Tank Reactors (CSTRs)
- ▶ Tubular reactors
- ▶ Packed-bed reactors

# Rate of reaction

- ▶ Chemical reactions are said to occur when species lose their identity, e.g. by decomposition, combination or isomerization.



[<http://en.wikipedia.org/wiki/Isomerization>]

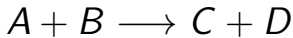
- ▶ **Rate of reaction** is expressed as the rate of formation of products.

# Rate of reaction

By definition:

$r_j$  is defined as the rate of formation of species  $j$  per unit volume

- ▶ formation  $\equiv$  generation disappeared  $\equiv$  consumed
- ▶ Consider the reaction



- ▶  $r_A$  is the number of moles of species  $A$  **formed** per unit time per unit volume  $\left[ \frac{\text{mol}}{\text{s.L}} \right]$  or  $\left[ \frac{\text{mol}}{\text{s.m}^3} \right]$   $-r_A$  (now a positive quantity) is the number of moles of species  $A$  **disappearing** per unit time per unit

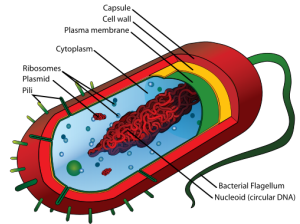
# What affects $-r_A$ ?

- ▶ Reaction rate is an *intensive property* — function of concentration and temperature, but not size or configuration of reactor.
- ▶ Thermo recall: an *intensive property* does **not** depend on the size or scale of the system.  
These are great properties to deal with: they apply whether we are dealing with



25m  $\times$  5m

or



$\sim 1$  to  $5\mu\text{m}$

# What affects $-r_A$ ?

- ▶ Generally:
  1. temperature,  $T$
  2. concentration,  $C_j$
  3. pressure (for gas systems we generally use pressure instead of concentration),  $P_j$
  4. catalysts (we won't consider this for now)
- ▶ Rate law is an algebraic expression of the form

$$-r_A = \left( k_A(T) \right) \left( f(C_A, C_B, \dots) \right)$$

# Analyzing $-r_A$ dependence

- ▶ A bank lends money at the rate of 5%. Does the interest depend on the amount borrowed?
- ▶ No, the interest rate is independent of the amount borrowed

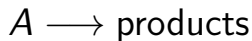


# Analyzing $-r_A$ dependence

- ▶ Does the “amount” of reaction depend on the volume, i.e. the size of the system, *etc*?
- ▶ No, the reaction rate is independent of the volume.
- ▶ The **number of moles** per unit volume determines concentration, which in turn determines the rate.
- ▶ So there is a dependence on the concentration, but not on the volume.

# Examples of reaction rate expressions

For



we might have

$$-r_A = kC_A$$

or

$$-r_A = kC_A^2$$

or

$$-r_A = k \frac{k_1 C_A}{1 + k_2 C_A}$$

*and many others are possible.*

The last equation is common in bioreactor systems.

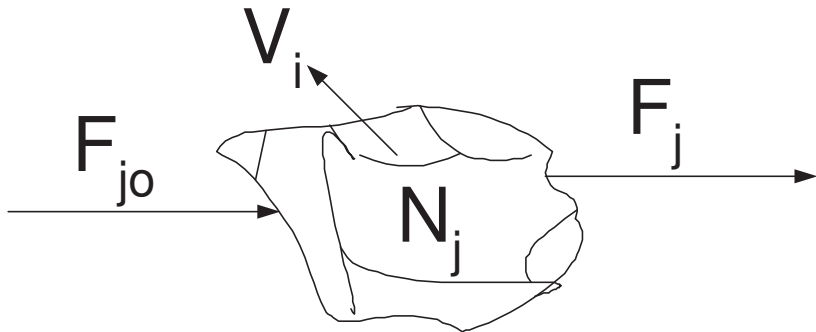
# How do we obtain these rate expressions?

- ▶ Structure of the rate expression is guided by theory; trial and error testing
- ▶ We obtain the parameters from experiments (covered later)
  - ▶ e.g.  $-r_A = kC_A^n$
  - ▶ determine  $k$  and  $n$  from experimental data

# The general mole balance equation

We will use this over and over in the course. **Let's understand this.**

A mole balance on species  $j$  at any instant of time  $t$ , in an arbitrary system volume ( $V_i$ ):



# The general mole balance equation

A **mole balance** (not a mass balance) on species  $j$  at any instant of time  $t$ :

In + Generated – Out = Accumulated

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

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

- ▶  $G_j = \frac{\text{moles}}{\text{time}} = r_j \cdot V = \frac{\text{moles}}{(\text{time})(\text{volume})} \cdot \text{volume}$
- ▶ Why don't we have a term for "consumed"?

# The general mole balance equation

- ▶ We can subdivide the region into many subvolumes ( $M$  of them), and for each subvolume  $i = 1, 2, \dots M$ :

$$\Delta G_{ji} = r_{ji} \Delta V_i$$

$\Delta G_{ji}$  is the rate of generation of  $j$  within subvolume  $i$  (chosen to be small enough so that all variables are constant, and therefore the reaction rate is the same in the subvolume)

# The general mole balance equation

- Then

$$G_j = \sum_1^M \Delta G_{ji} = \sum_1^M r_{ji} \Delta V_i$$

an in the limit as  $\Delta V_i \rightarrow 0$  and  $M \rightarrow \infty$

$$G_j = \int_V r_j dV$$

giving

$$F_{j0} - F_j + \int_V r_j dV = \frac{dN_j}{dt} \quad (1-4)$$

# The general mole balance equation

- ▶ **Note:**  $\int_V r_j dV$   $\leftarrow$  the  $r_j$  term is a function of  $V$  and cannot be taken out of the integral.
- ▶ Wait a minute: you said “Reaction rate is an **intensive property**” (slide 6), not a function of the volume/size/scale of the system





# The general mole balance equation

- ▶ If all the system variables (temperature, pressure, concentration, *etc.*) are uniform throughout the volume,  $V$ , **only then** can the reaction rate be taken out:
- ▶ More correct to write:  $r_j(V)$

$$G_j = \int_V r_j(V) dV = r_j \int_V dV = r_j \cdot V$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{(\text{time})(\text{volume})} \cdot \text{volume}$$

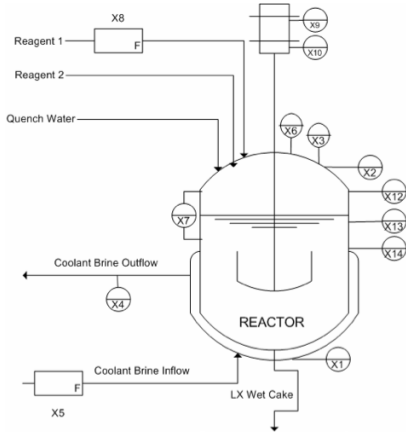
# The general mole balance equation

- ▶ Now, let's apply the balance equation to various reactor types

# Batch reactors

- ▶ No inflow or outflow.
- ▶ Charge reactors with reactants, then close up.
- ▶ What then?

# Batch systems



[From Cecilia Rodrigues' M.A.Sc thesis, 2006, McMaster

[Flickr: [#2516220152](#)]

University, used with permission]

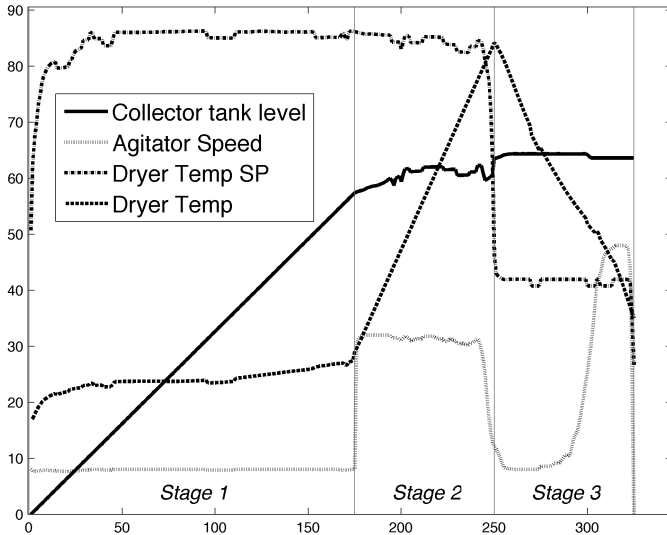
# Batch systems

See illustration at

<http://woodmoorbeer.org/Pages/sierra.html>

# Batch systems

Recorded values from a single batch



# Batch reactors

Where are they used?

- ▶ small scale products (low volumes)
- ▶ usually extremely high value product: medicines, speciality chemicals
- ▶ hard-to-make products
- ▶ multiple steps in the “recipe”

# Batch reactors

- ▶ Typically perfectly mixed, so  $\int_V r_j(V) dV$  can be replaced by  $r_j \cdot V$
- ▶ The mole balance: start with the general equation, then simplify:

$$F_{j0} - F_j + \int_V r_j(V) dV = \frac{dN_j}{dt}$$

$$\cancel{F_{j0}^0} - \cancel{F_j^0} + r_j \cdot V = \frac{dN_j}{dt}$$



# Batch reactors

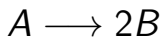
$$\frac{dN_j}{dt} = r_j \cdot V$$

**Note:**  $V$  is *not* assumed to be constant here. It could be a function of time or of the extent of reaction (and indirectly a function of time).

So for batch reactors:

$$\frac{dN_j(t)}{dt} = r_j(t) \cdot V(t)$$

# Batch example problem



with  $-r_A = kC_A$  and  $k = 0.23\text{min}^{-1}$  in a constant volume batch reactor.

We are also given the inlet concentration and volume:  $C_{A0} = 2\text{mol/L}$ ,  $V = 10\text{L}$ .

How long does it take to reduce the concentration of  $A$  in reactor to 10% of its initial value (i.e. a 90% conversion)?

# Batch example problem

# Batch example problem

# Continuous-Stirred Tank Reactor

- ▶ CSTR's: are assumed to be well mixed
- ▶ System properties constant throughout reactor.
- ▶ This implies the product concentrations, temperatures, and other **intensive** properties *leaving the tank* are the same as that *within* tank.

# Continuous-Stirred Tank Reactor (CSTR)



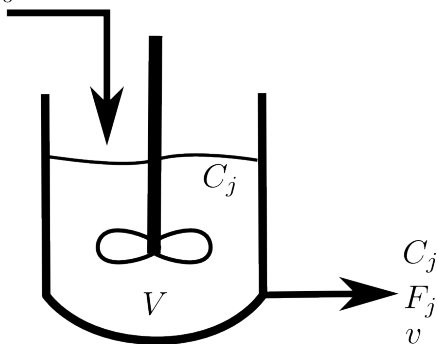
[[Flickr #6240399099](#)]

# Continuous-Stirred Tank Reactor

- ▶ Where are CSTRs used? When we want entire system to be operated:
  - ▶ at the same concentration
  - ▶ at the same temperature
- ▶ where we require good agitation to contact the reactants
- ▶ e.g. emulsion polymerization
- ▶ a catalyst is suspended in a liquid product
- ▶ leaching gold from crush ore (rock); crushed particles  $\sim 50\mu m$  with gold particles exposed
- ▶ Leaching:  $4\text{Au} + 8\text{NaCN} + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{Na}[\text{Au}(\text{CN})_2] + 4\text{NaOH}$

# Continuous-Stirred Tank Reactor (CSTR)

$C_{j0}$   
 $F_{j0}$   
 $v_0$



- ▶ At any given time,  $t$
- ▶  $F$ : molar flow rate
- ▶  $C$ : concentration
- ▶  $v$ : volumetric flow
- ▶ subscript  $j$ ,  $j^{\text{th}}$  species
- ▶ subscript 0, inlet stream

$C_j$ : Concentration of species  $j$  in the reactor of liquid volume  $V$

- ▶  $V$  is **not** the total physical reactor volume



# Continuous-Stirred Tank Reactor (CSTR)

- ▶ General mole balance equation:

$$F_{j0} - F_j + \int_V r_j(V) dV = \frac{dN_j}{dt}$$

- ▶  $\frac{dN_j}{dt} = 0$ , (often analyzed at steady state, **but not necessarily**).
- ▶ No spatial variation with reactors

$$\Rightarrow \int_V r_j(V) dV = r_j V \Rightarrow \boxed{V = \frac{F_{j0} - F_j}{-r_j}}$$

# Continuous-Stirred Tank Reactor (CSTR)

We can relate to concentration via

**Awkward Fogler notation**

$$F_j = C_j v$$

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

$$V = \frac{v_0 C_{A0} - v C_A}{-r_A} \quad (1-9)$$

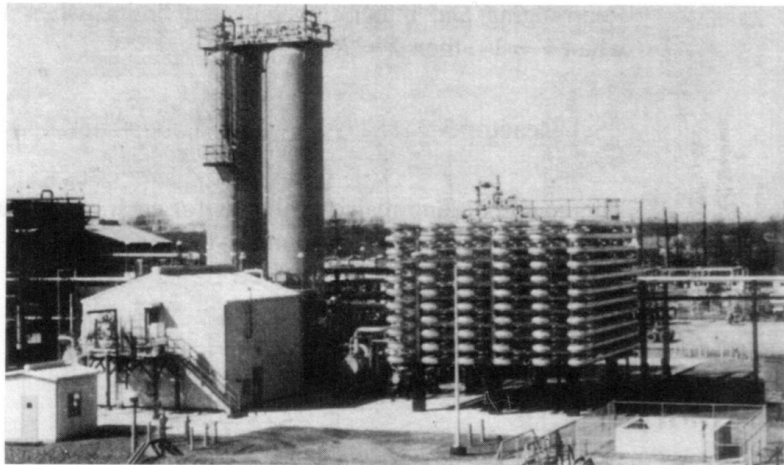
**Improved (?) notation**

$$F_j = C_j q$$

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

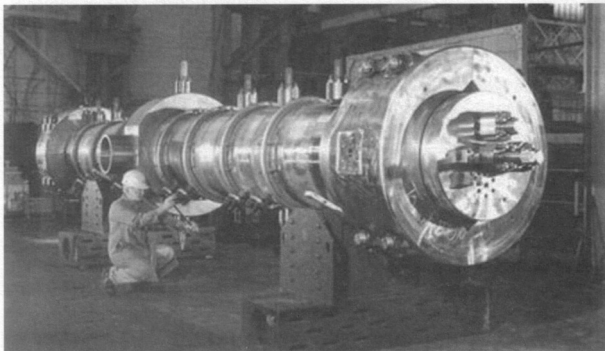
$$V = \frac{q_0 C_{A0} - q C_A}{-r_A}$$

# Tubular reactors



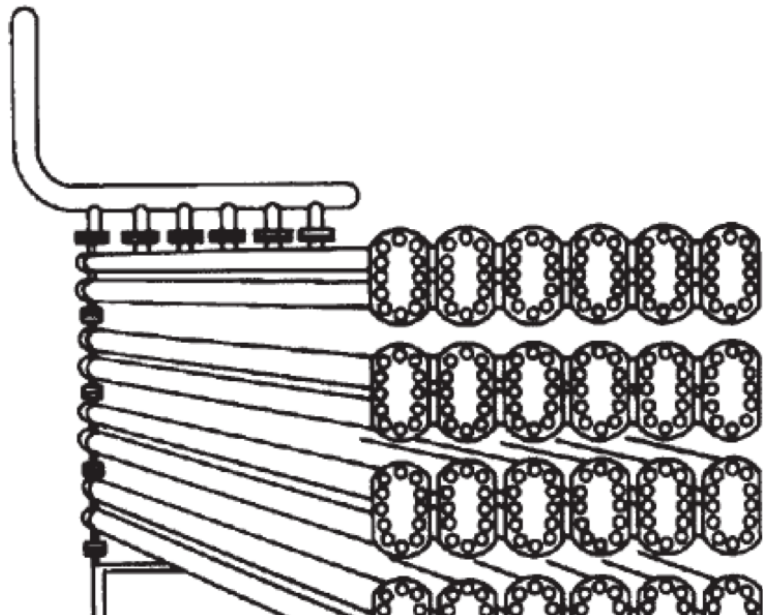
Dimersol G (an organometallic catalyst) unit (two CSTRs and one tubular reactor in series) to dimerize propylene into isohexanes. Institut Français du Pétrole process. [Photo courtesy of Editions Technip (Institut Français du Pétrole).]

# Tubular reactors



Polyethylene reactor; this 16-in inner-diameter reactor is designed to operate at 35,000 psi and 600°F; in operation, this reactor is in a vertical configuration. Courtesy of Autoclave Engineers, Division of Snap-tite, Inc.

# Tubular reactors



# Tubular reactors (covered on the board in class)

- ▶ Assume turbulent flow  $\Rightarrow$  modelled as plug (no radial variation in concentration)
- ▶ Referred to as plug-flow reactor (PFR).
- ▶ Starting point - general mole balance.

$$F_{j0} - F_j + \int_V r_j(V) dV = \frac{dN_j}{dt} = 0$$

Apply to differential volume:

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

# Tubular reactors (covered on the board in class)

Rearranging and dividing by  $\Delta V$ ,

$$\left[ \frac{F_j|_{V+\Delta V} - F_j|_V}{\Delta V} \right] = r_j$$

Taking limit as  $\Delta V \rightarrow 0$

$$\boxed{\frac{dF_j}{dV} = r_j}$$

Integral form:

$$V = \int_0^V dV = \int_{F_{j0}}^{F_{jf}} \frac{dF_j}{r_j}$$

# Tubular reactors (covered on the board in class)

**Remark 1:** Analysis does not assume constant cross-sectional area.

⇒ applicable also to other geometries

End up with same design equation.

**Remark 2:** Furthermore, for liquids (why not for gases?) at steady state the volumetric flow rate is equal throughout the reactor, i.e.,  $v_o = v$



## PFR example

$A \longrightarrow B$  in a tubular reactor. Feed enters at constant volumetric rate  $q = 10 \text{ L}\cdot\text{min}^{-1}$ . The reaction follows first-order kinetics with rate constant  $k = 0.23 \text{ min}^{-1}$ .

1. Determine the volume required to reduce the exiting concentration to 10% of the entering value, i.e.  $C_A = 0.1 C_{A0}$ ?
2. As above, but for 99% conversion, i.e.  $C_A = 0.01 C_{A0}$ ?
3. What happens to the conversion if we halve the volumetric flow rate  $q_{\text{new}} \leftarrow q_{\text{previous}}$ . Intuitively, what do we expect?

## PFR example

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

Express design equation in terms of concentration:

$$\frac{dF_A}{dV} = \frac{d(C_A q)}{dV} = q \frac{dC_A}{dA}$$

$$q \frac{dC_A}{dV} = r_A = -kC_A$$

# PFR example

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

$$\Rightarrow -\frac{q}{k} \ln \left( \frac{C_A}{C_{A0}} \right) = V$$

$$\Rightarrow V = -\frac{10}{0.23} \ln \left( \frac{0.1 C_{A0}}{C_{A0}} \right) = -\frac{10}{0.23} (-2.3) = 100 \text{ L}$$

Note: Plug in the numbers at the very last step

2. For 99% conversion: 200L

3. For half input flow: 99% conversion (increased!)

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See F2006 example 1.1 or F2011 example 1.2 for similar problem

# Packed-bed reactor (PBR)

Analogous development, except

- ▶ we use  $W$  (mass of catalyst) instead of  $V$  as independent variable, and
- ▶  $r'_j = \left[ \frac{\text{moles } j}{(\text{time})(\text{mass catalyst})} \right]$  instead of  $r_j = \left[ \frac{\text{moles } j}{(\text{time})(\text{volume})} \right]$

# Comparison

## Plug flow reactor

- ▶ PFR
- ▶ Mole balance at steady state:

$$F_{j0} - F_j + \int_V r_j dV = 0$$

- ▶ Differentiate:

$$\boxed{\frac{dF_j}{dV} = r_j}$$

## Packed bed reactor

- ▶ PBR
- ▶ Mole balance at steady state:

$$F_{j0} - F_j + \int_W r'_j dW = 0$$

- ▶ Differentiate:

$$\boxed{\frac{dF_j}{dW} = r'_j}$$

# Summary

General mole balance equation:

$$F_{j0} - F_j + \int_V r_j(V) dV = \frac{dN_j}{dt}$$

# Summary

a) Batch reactor Differential form  $\frac{dN_j}{dt} = r_j V$

- ▶ Can we ever make a steady-state assumption for batch?

b) CSTR

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

# Summary

## c) PFR

Differential form:  $\frac{dF_j}{dV} = r_j$

Integral form  $V = \int_{F_{j0}}^{F_{jf}} \frac{dF_j}{r_j}$

Given initial and final concentrations, we expressed equations in terms of  $C_A$  and solved.