ChE 344
Reaction Engineering and Design

Lecture 11: Tues, Feb 15, 2022

Example PBMR, **collection and analysis of rate data**

Reading for today’s Lecture: Chapter 7

Reading for Lecture 12: Chapter 8

Lecture 11: Collecting and Analyzing Rate Data
Related Text: Chapter 7

Thus far we have always assumed we already know the rate law, but sometimes to design a reactor you must first determine the rate law from doing experiments yourself, or interpreting experiments that someone else did.

Steps to deriving kinetic parameters from experimental data.

0. **Gather data**, noting given or assumed knowledge about its collection

1. **Postulate a form of the rate law**. A common form will be a power law expression:

$$r = kC_A^{\alpha}C_B^{\beta}$$

2. **Mole balance on the type of reactor used** (usually either constant volume batch, or differential PFR or PBR).

3. **Process data** in terms of measured variables

4. **Simplify equations** as appropriate for the problem (for example, using method of excess where you assume pseudo-orders).

5. **Calculate rate law** using appropriate methods for your data

i. Integral method, assume a reaction order, solve the design equation and plot your data to see if it matches the expression (useful if you expect whole/integer order dependence on concentration).

ii. Differential method (differentiate the experimental data to allow comparison with a differential rate law). For batch reactors this requires determining $\frac{dC_A}{dt}$ through graphical, numerical, or fitting to a polynomial and taking its derivative wrt time. For example:

$$\ln\left[-\frac{dC_A}{dt}\right] = \ln[-r_A] = \ln[k] + \alpha\ln[C_A]$$

The slope of $\ln\left[-\frac{dC_A}{dt}\right]$ vs. $\ln[C_A]$ will be α **iff** the intercept is constant for all the data. Here that would mean the rate constant *k* would need to be constant, usually by operating at the same temperature.

iii. Non-linear regression. Minimize the difference between your calculated values and the measured values for your proposed rate law and parameters. Use an Excel Solver or regression tool to determine the parameters that give the best fit.

$$s^2 = \sum_{i=1}^{N}\left(t_{i,measured} - t_{i,calculated}\right)^2$$

6. **Check** "goodness of fit", for example through a correlation coefficient. If your rate law cannot fit the data, you may need to propose another rate law, for example in heterogeneous catalysis we often see rate laws of the form:

$$r = \frac{kP_A}{1 + K_AP_A}$$

The molar flow out of the **membrane** will be related to the surface area of the membrane (surface area of cylinder):

$$W_B = k_C'\left(C_B - C_{B,sweep}\right) = \frac{\text{molar flow rate through membrane}}{\text{surface area of membrane}}\left[\frac{mol}{m^2 s}\right]$$

$$F_{B,membrane} = W_B \pi D \Delta L = k_C'\left(C_B - C_{B,sweep}\right)\pi D \Delta L$$

$$R_B \equiv \frac{F_{B,membrane}}{\Delta V}$$

$$a = \frac{\pi D L}{\frac{\pi D^2}{4} L} = \frac{4}{D} = \frac{\text{membrane surface area}}{\text{reactor volume}}\left[\frac{m^2}{m^3}\right]$$

$$k_C \equiv k_C' a$$

$$R_B = W_B a = k_C' a\left(C_B - C_{B,sweep}\right)$$

$$R_B = k_C\left(C_B - C_{B,sweep}\right)$$

If flow rate of inert sweep gas is sufficiently high,

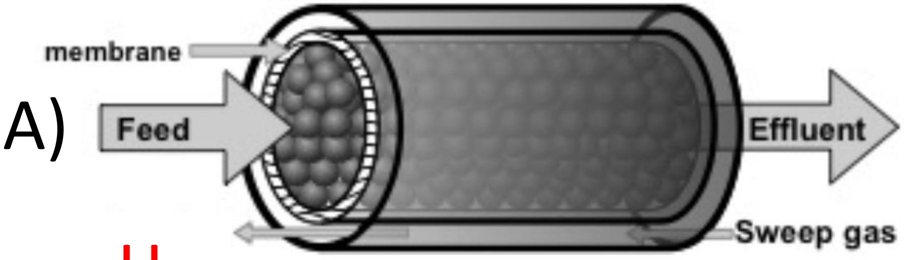
$C_{B,sweep} \approx 0$

$$R_B = k_C C_B$$

k_C mass transfer coefficient wrt $V_{reactor}$, here units 1/time

Example problem: Membrane reactor, isothermal, gas-phase but no pressure drop. Membrane is permeable to H_2 only. Elementary as written, and only A is fed into the reactor.

C_6H_{12} (A)



C_6H_6 (B) + H_2 (C)

H_2

$$C_6H_{12} \rightleftarrows C_6H_6 + 3H_2$$

$$A \rightleftarrows B + 3C$$

Remove C to help equilib.

Need to work out with our molar flow rates F_A, F_B, F_C:

$$r_A' = \frac{dF_A}{dW};\ r_B' = \frac{dF_B}{dW};\ \frac{dF_C}{dW} = r_C' - R_C\rho_{bed}^{-1} = r_C' - (k_C C_C)\rho_b^{-1}$$

$$r_A = \rho_b r_A'$$

Derivation from class

PFR + Membrane Design equation: $$\frac{dF_C}{dV} = r_C - R_C$$

Definitions:

$$W = V\rho_{bed} = V\rho_c(1-\phi_b) \qquad r_C = \rho_b r_C'$$

$$\frac{dW}{dV} = \rho_{bed} \equiv \rho_b$$

Rearranging:

$$\frac{dF_C}{dV} = \frac{dF_C}{dW}\frac{dW}{dV} = \frac{dF_C}{dW}\rho_b \qquad r_C - R_C = \rho_b r_C' - \frac{\rho_b}{\rho_b}R_C$$

$$\frac{dF_C}{dW}\rho_b = \rho_b r_C' - \frac{\rho_b}{\rho_b}R_C$$

$$\frac{dF_C}{dW} = r_C' - \frac{1}{\rho_b}R_C$$

Rate law (for elementary, reversible reaction): $A \rightleftarrows B + 3C$

$$\boldsymbol{r} = -r_A' = k\left[C_A - \frac{C_B C_C^3}{K_C}\right]$$

$$\frac{r_A'}{-1} = \frac{r_B'}{+1} = \frac{r_C'}{+3}$$

Stoichiometry: Recall definitions (here not using conversion, but same concept). Here we have isothermal, no pressure drop reactor.

$$C_A = \frac{P_0}{RT_0}\frac{F_A}{F_T} \qquad C_B = \frac{P_0}{RT_0}\frac{F_{\boldsymbol{B}}}{F_T} \qquad C_C = \frac{P_0}{RT_0}\frac{F_{\boldsymbol{C}}}{F_T}$$

$$F_T = F_A + F_B + F_C$$

Can solve using Polymath if we have some parameters

$C_{total,0} = P_0/(RT_0) = 0.2$ M

$k = 10$ L kg_{cat}^{-1} s^{-1}

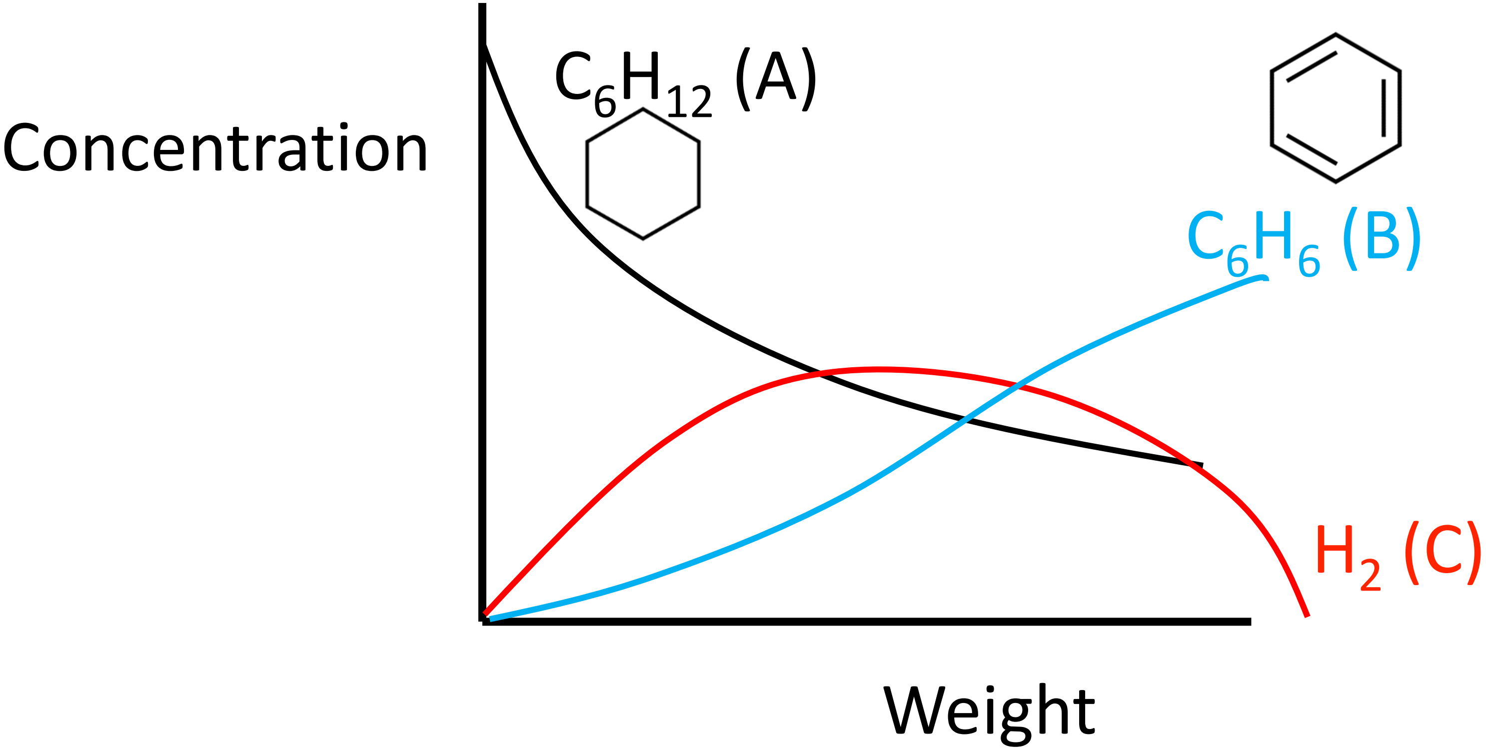
$F_{A0} = 10$ mol/s

$K_C = 200$ M^2 Equilibrium constant!

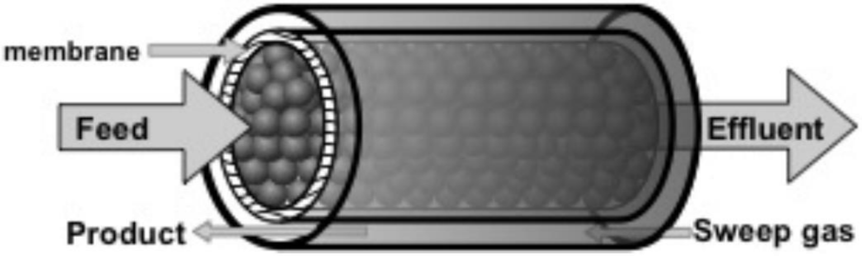
k_C $[s^{-1}]$ Mass transfer constant

$k_C\rho_b^{-1} = 0.5$ L kg_{cat}^{-1} s^{-1}

$$A \rightleftarrows B + 3C$$



Summary for membrane reactors



Can help with equilibrium limited reactions (R_C = +) or controlling concentration of reactant (R_C = -)

Molar Flow Rate Mole Balance (here written for PFR)

$$r_A = \frac{dF_A}{dV};\; r_B = \frac{dF_B}{dV};\; \frac{dF_C}{dV} = r_C - R_C = r_C - k_C(C_C - C_{Cs})$$

sweep

Rate laws

$$A \rightleftarrows B + 3C \qquad \boldsymbol{r} = -r_A = k\left[C_A - \frac{C_B C_C^3}{K_C}\right] \qquad \frac{r_A}{-1} = \frac{r_B}{+1} = \frac{r_C}{+3}$$

Stoichiometry: Here using molar flow rates because species are being removed in a method not accounted for in conversion $C_A = F_A/v$

$Pv = F_T RT$

$P_0 v_0 = F_{T0} RT_0$

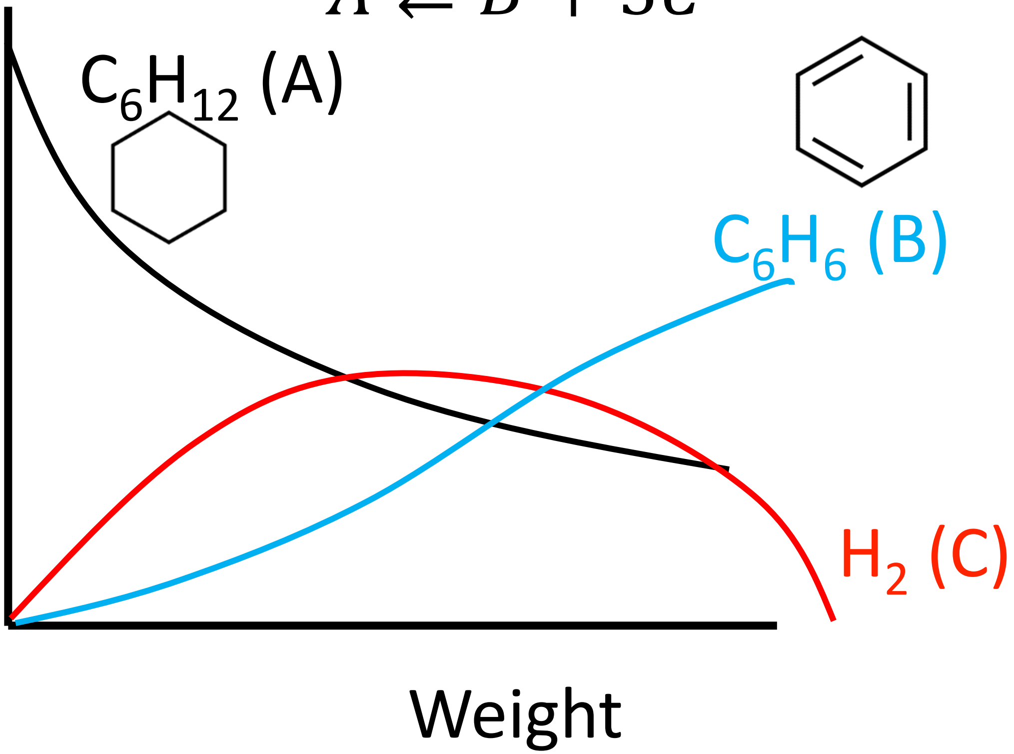
$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0 \frac{F_T}{F_{T0}} \frac{T}{T_0} \frac{P_0}{P}}$$

Lecture 4

Discuss with your neighbors:

If we wanted to remove H_2 at a faster rate, what would do that? Note I am not saying have a lower H_2 concentration, although they are interrelated

$$A \rightleftarrows B + 3C$$



A) Larger k_C

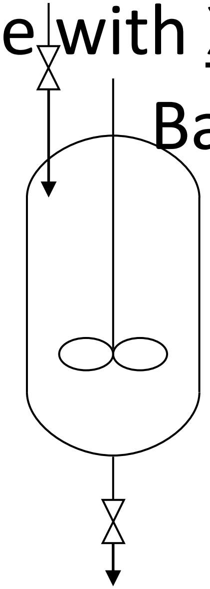
B) Faster forward rxn

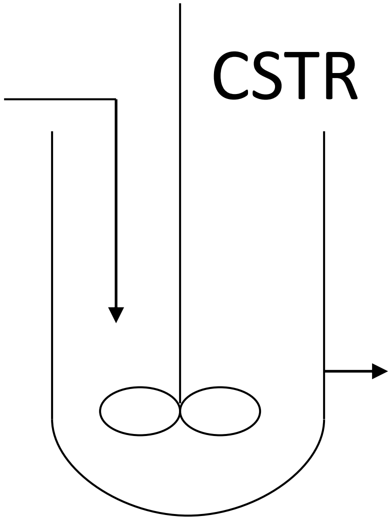
C) Slower flowing sweep gas

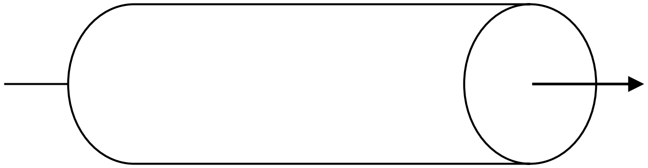
[✓ D) A and B both]

What can we do so far? Design several diff. reactor types!

Can solve with X


Batch


CSTR


Plug flow

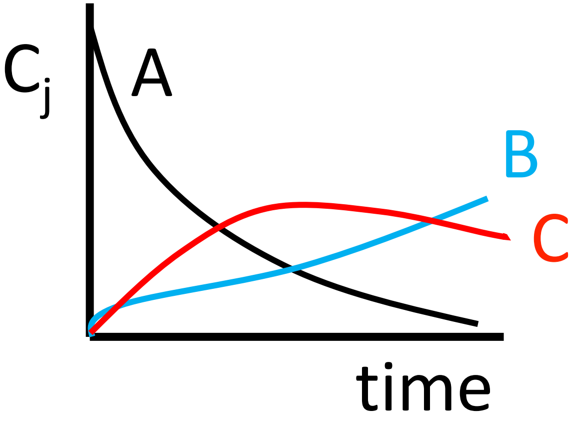
Packed bed

Pressure drop

Should solve with moles/molar flow rate

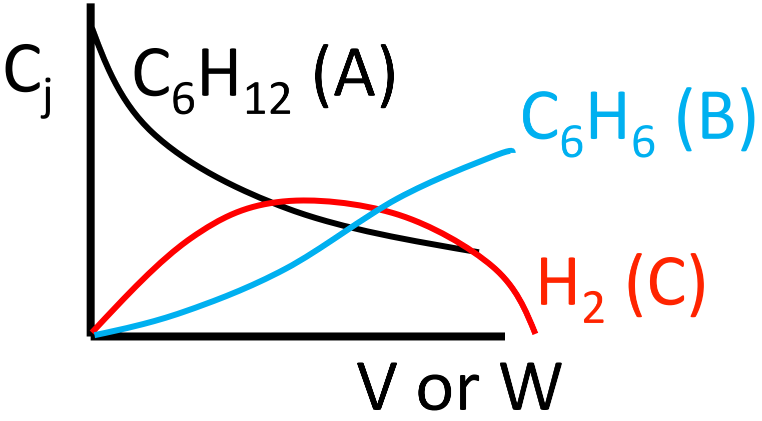
Semi-batch

$$A + B \rightarrow C$$



Membrane

$$A \rightarrow B + 3C$$



Discuss with your neighbors:

You have a desired elementary reaction A + B → D and an undesired elementary reaction A + 2B → U. To get high $S_{D/U}$, which process should you use?

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2}\frac{C_A {C_B}^1}{C_A {C_B}^2} = \frac{k_1}{k_2}{C_B}^{-1}$$

A) High concentrations of A, C_B won't matter

[✓ B) Semi-batch feeding B into a reactor with pure A initially]

C) Semi-batch feeding A into a reactor with pure B initially

D) Selectivity won't depend on the reactor configuration

Reactor design for chemical processes/plants

- Wastewater treatment
- Food production
- Plastics
- Pharmaceuticals/medicines
- Fuels
- Environmental cleanup

Mole balance
(selecting reactor)

Rate law

Stoichiometry

Pressure drop?

Combine

Evaluate

So far we have been assuming that someone will give us the rate law. But what if we have to get that information ourselves?

Reactor design to get information

$$r_A = -k \times f(C_j) \; or - k \times f(P_j); \qquad k = A\exp(-E_A/(RT))$$

If we are interested in a reaction, how do we

- determine reaction orders? or complex rate expression?
- find the rate constant?

In almost all cases, we have to do experiments.

Batch reactor (const. V)

$$r_A = \frac{dC_A}{dt}$$

'Differential'* flow reactor

$$r_A = \frac{dF_A}{dV} \longrightarrow r_A = \frac{\Delta F_A}{\Delta V}$$

$$r_A' = \frac{dF_A}{dW} \longrightarrow r_A' = \frac{\Delta F_A}{\Delta W}$$

*Run under conditions where r_A is constant

Steps to analyze data

1. Postulate a rate law: power law? or $r = \frac{kP_A}{1+KP_A}$
2. Select reactor and corresponding mole balance
   - i. Batch
   - ii. Differential PFR/PBR

3. Process data in terms of measured variables (N_A, C_A, P_A)

4. Look for simplifications (e.g., excess, $\varepsilon \approx 0$)

5. Calculate rate using appropriate method for your data

i. Integral method

ii. Differential analysis

iii. Non-linear regression

6. Check "goodness of fit"

Batch reactor i) integral method to determine reaction orders

7.3

Constant volume batch reactor (measure concentration of A as a function of time)

$$A \rightarrow Products$$

Propose rate law, here we guess a power law: $r_A = -kC_A^{\alpha}$

Mole balance: $$r_A = \frac{dC_A}{dt}$$ Only for const. V

Zero order

$$\frac{dC_A}{dt} = r_A = -k$$

$$C_A = C_{A0} - kt$$

First order

$$\frac{dC_A}{dt} = r_A = -kC_A$$

$$\ln\left(\frac{C_{A0}}{C_A}\right) = kt$$

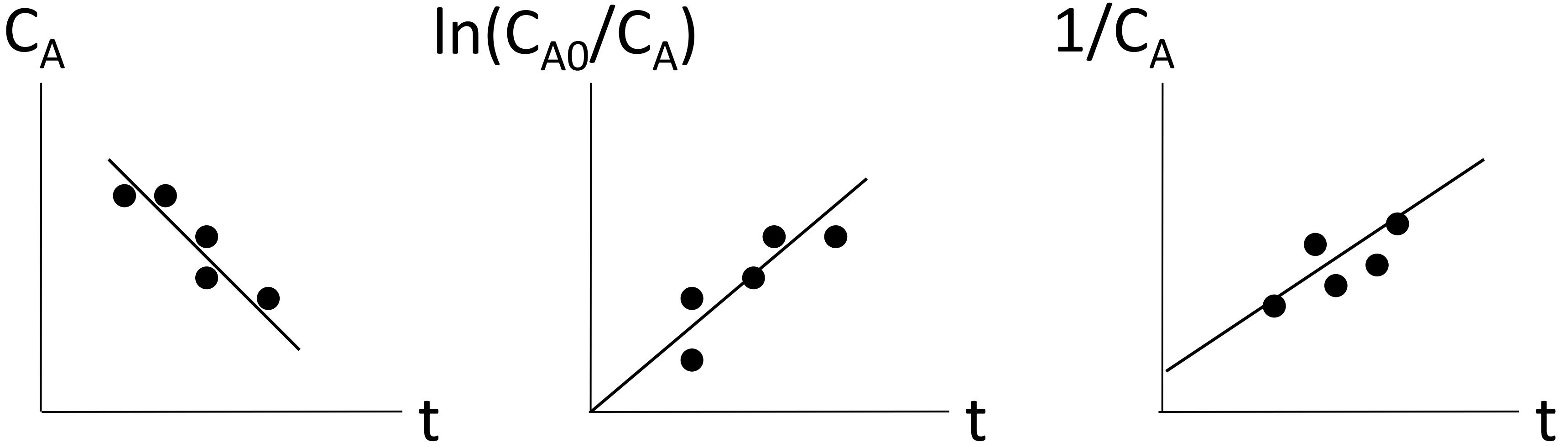
Second order

$$\frac{dC_A}{dt} = r_A = -kC_A^2$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

Take experimental measurements (in batch reactor) of concentrations as a function of time and plot to see if data is linear:

If $\alpha = 0$ If $\alpha = 1$ If $\alpha = 2$



$$C_A = C_{A0} - kt \qquad \ln\left(\frac{C_{A0}}{C_A}\right) = kt \qquad \frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

This works well if we have integer orders

<u>Discuss with your neighbors</u>:

You run the reaction A + B → D in a constant V batch reactor and get the following info. What is the reaction order in B?

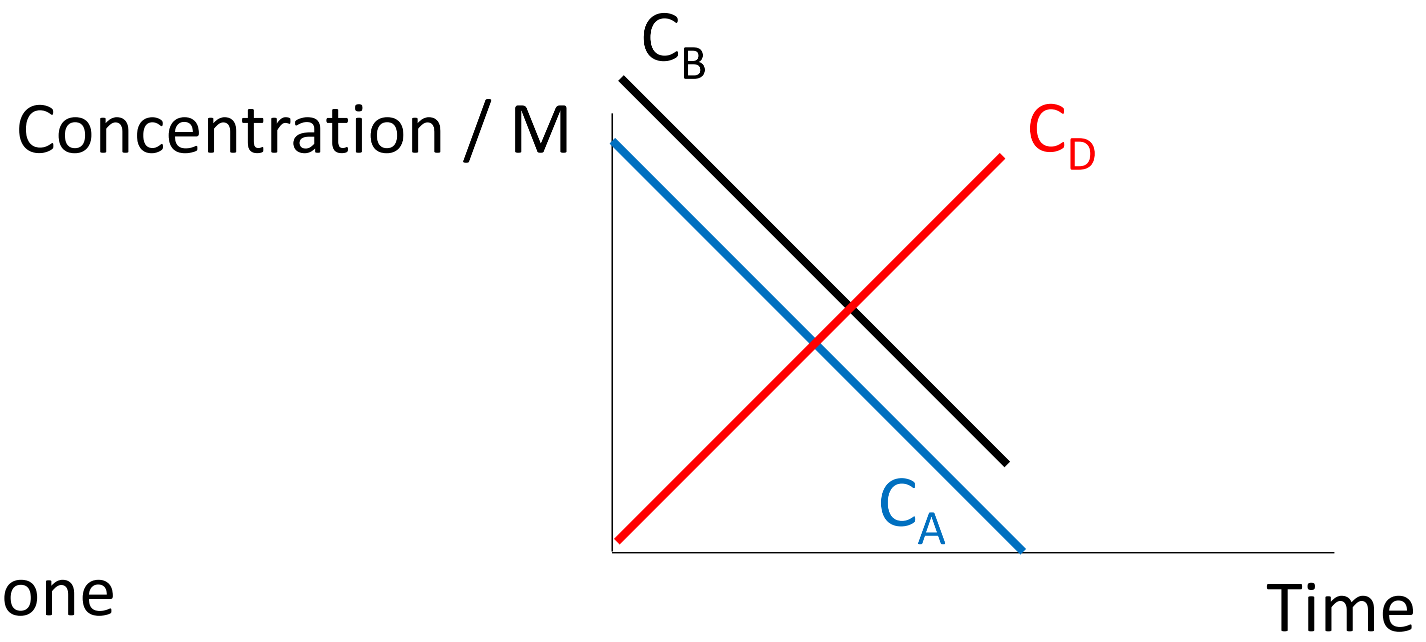
Time/s	**0**	**100**	**200**	**300**	**400**
C_A / M	1	0.8	0.6	0.4	0.2
C_B / M	1.2	1.0	0.8	0.6	0.4
C_D / M	0	0.2	0.4	0.6	0.8

[✓ A) Zero]

B) +1

C) ½

D) Negative one



ii) Differential method (applied to batch reactors). Chap 7.4

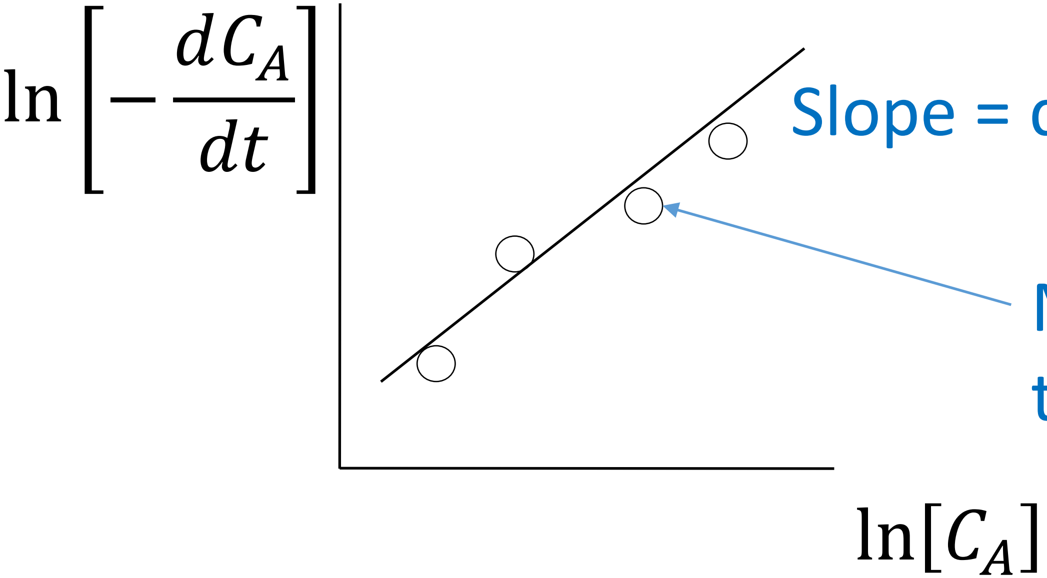
$$-\frac{dC_A}{dt} = -r_A = kC_A^{\alpha}$$

If we have $r_A(C_A)$ already we can directly do this

Take the natural log of both sides

$$\ln\left[-\frac{dC_A}{dt}\right] = \ln[-r_A] = \ln[k] + \alpha\ln[C_A]$$

Get k once we have reaction order

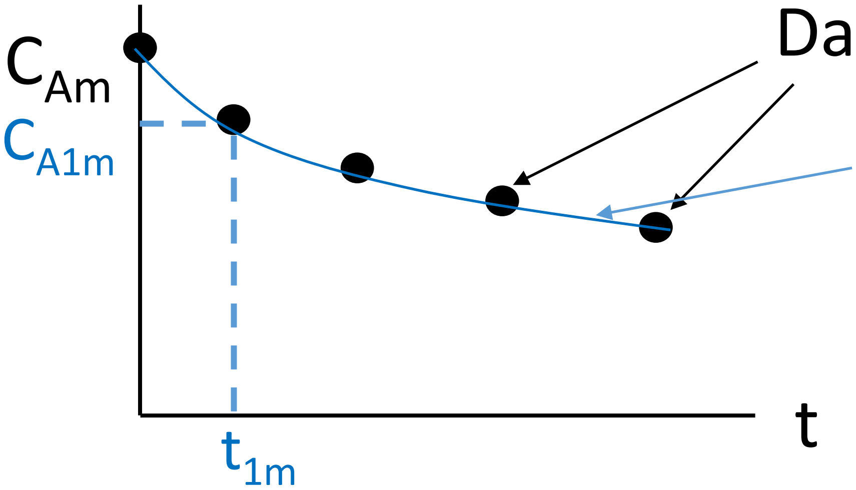


Slope = α

Measured C_A at a given time

How do you extract $-\frac{dC_A}{dt}$?

- Graphical (7.4.1)
- Numerical methods (7.4.2)
- Differentiation of polynomial fit to the data



Data points

Fitted polynomial e.g.

$C_A = at^2+bt+c$ such that

$\frac{dC_A}{dt}$=2ta+b

C_{Am} = measured

Time/s	t_{0m}	t_{1m}	t_{2m}	t_{3m}	t_{4m}
C_A / M	C_{A0m}	C_{A1m}	C_{A2}	C_{A3}	C_{A4}
dC_A/dt	$\left(-\frac{dC_A}{dt}\right)_0$	$\left(-\frac{dC_A}{dt}\right)_1$	$\left(-\frac{dC_A}{dt}\right)_2$	$\left(-\frac{dC_A}{dt}\right)_3$	$\left(-\frac{dC_A}{dt}\right)_4$

Additional method: iii) Nonlinear and linear regression (7.5)

$$\frac{dC_A}{dt} = r_A = -kC_A^{\alpha}$$

Integrating for the case $\alpha \neq 1$

$$C_A = [C_{A0}^{1-\alpha} - (1-\alpha)kt]^{1/(1-\alpha)}$$

Then, we take our measured values C_{A0m}, C_{A1m} , etc. and compare them to the calculated values from our equation above C_{A0c}, C_{A1c}, at the same times and minimize error between our measured values and our calculated values. We could do the same thing using the calculated times:

$$\boxed{t_c = \frac{C_{A0}^{1-\alpha} - C_A^{1-\alpha}}{k(1-\alpha)}}$$

Specified conc. of A

We can use regression to derive parameters (e.g., α and k) that give us the best agreement between our measured data and our calculated values.

That is, find the values of α and k that minimize:

$$s^2 = \sum_{i=1}^{N}(t_{im} - t_{ic})^2 = \sum_{i=1}^{N}\left(t_{im} - \frac{C_{A0}^{1-\alpha} - C_{Ai}^{1-\alpha}}{k(1-\alpha)}\right)^2$$

Measured   Calculated from rate law

Can do this with "Solver" in Excel, regression in Polymath, etc.

The goal is to have a rate law that fits your data the best.

You can also use this method for more complex rate laws.

Polymath regression tutorials:

http://www.umich.edu/~elements/5e/software/polymath.html

Simplifying the system: Method of excess

Determine order of a given reactant while keeping the other reactants the same concentration.

This is similar to when we solved our pseudo-first order problem.

$$-r_A = kC_A^{\alpha}C_B^{\beta}$$

$$\theta_B - X \approx \theta_B$$

$$-r_A \approx \left(kC_{B0}^{\beta}\right)C_A^{\alpha}$$

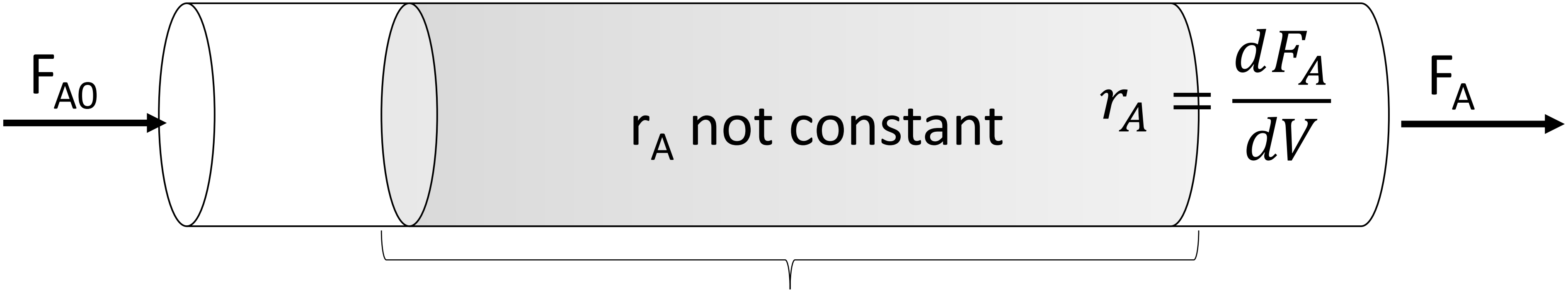
Find α

$$C_{A0} \gg C_{B0}$$

$$-r_A \approx (kC_{A0}^{\alpha})C_B^{\beta}$$

Find β

PFRs/PBRs



F_{A0}

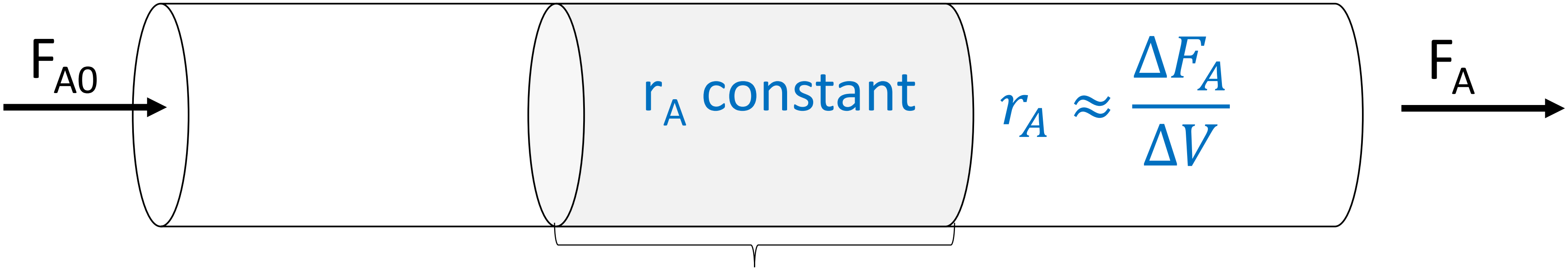
r_A not constant

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

F_A

Changing conditions moving down reactor
Tougher to model/extract rate parameters

Differential reactors for extracting reaction rates



F_{A0}

r_A constant

$$r_A \approx \frac{\Delta F_A}{\Delta V}$$

F_A

Low conversion (~ <5%), similar C_j everywhere
Get by high flow rate, low catalyst, etc.

Choosing experimental conditions to measure reaction orders

$$rate = k\prod C_i^{\alpha_i}$$

Caution: Order can change based on conditions

$$Reaction\ order = \left(\frac{\mathrm{d}\ln r}{\mathrm{d}\ln C_i}\right)_{C_{j\neq i},T}$$

Generally, measure the rate at a few different concentrations and plot to get the order. Make sure to keep other variables constant

In practice, better to measure the flow of your products than the disappearance of reactants (in case of reactant leaks/evaporation)

Discuss with your neighbors:

You are running a liquid-phase differential reactor (i.e., low conversions, X < 5%). You have the following rate laws and assumptions you are making:

$$-r_A = kC_A^2 \approx kC_{A0}^2 \approx kC_{A0}^2(1-X)^2$$

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

Which assumption of diff. conditions will lead to a larger error (at the same low conversion)?

A) There will be no error

B) Larger error for the second order reaction

C) Larger error for the first order reaction

D) The errors will be equal

Review: **Selectivity and yield** (instantaneous vs. overall)

$$A + B \xrightarrow{k_1} D$$

$$A + 2B \xrightarrow{k_2} U$$

Instantaneous selectivity $$S_{D/U} = \frac{r_D}{r_U}$$

Overall selectivity $$\tilde{S}_{D/U} = \frac{F_D}{F_U} \; or \; \frac{N_D}{N_U}$$

Instantaneous yield $$Y_{D/A} = -\frac{r_D}{r_A}$$

Overall yield $$\tilde{Y}_{D/A} = \frac{F_D}{F_{A0} - F_A} \; or \; \frac{N_D}{N_{A0} - N_A}$$

Will start using it more with multiple reactions next Lecture