ChE 344
Reaction Engineering and Design

Lecture 12: Thursday, February 17, 2022

Multiple reactions

Reading for today's Lecture: Chapter 8

Reading for Lecture 13: Chapter 11 (skipping ahead a bit, but we will be back!)

Lecture 12: Multiple Reactions
Related Text: Chapter 8

Updating the chemical reaction engineering algorithm/menu.

<table>
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0. Assumptions
- Isothermal?
- Isobaric?
- Rate law elementary as written?

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1. Mole balance (for multiple reactions in terms of number of moles or molar flow rates)
Example for packed bed flow reactors with A, B, and C:

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

$$\frac{dF_B}{dW} = r'_B$$

$$\frac{dF_C}{dW} = r'_C$$

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2. Rate law(s), for example elementary reactions

$$A \rightarrow B$$
$$A \rightarrow C$$
$$r'_1 = k_1 C_A;\ r'_2 = k_2 C_A$$
$$r'_{1A} = -r'_1;\ r'_{2A} = -r'_2$$
$$r'_{1B} = +r'_1;\ r'_{2B} = 0$$
$$r'_{1C} = 0;\ r'_{2C} = r'_2$$

$$\boxed{r'_A = -k_1 C_A - k_2 C_A}$$
$$\boxed{r'_B = k_1 C_A}$$
$$\boxed{r'_C = k_2 C_A}$$

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3. Stoichiometry on molar flow rate or number of moles:

$$C_j = N_j/V$$
$$C_j = F_j/v$$

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<tr><td>4. Any remaining required equations? For example, Ergun equation for pressure drop, etc.</td></tr>
<tr><td>5. Combine equations</td></tr>
<tr><td>6. Evaluate</td></tr>
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Note: To optimize selectivity, can look at the effect of different parameters on selectivity, for example does increasing the concentration of species *j* increase or decrease selectivity:

$$\left(\frac{dS_{D/U}}{dC_j}\right)_{C_{i\neq j},T}$$

Steps to **analyze rate data**

1. Postulate a rate law:

Power law $$rate = kC_A^{\alpha}C_B^{\beta}$$

Langmuir-Hinshelwood type: $$r = \frac{kP_A}{1 + K_AP_A}$$

2. Select reactor and corresponding mole balance
   i. Constant volume batch

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

   ii. Differential PFR/PBR

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

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

5. Calculate rate using appropriate method for your data

i. Integral method (useful for whole orders)

ii. Differential analysis $\ln(r_A)$ vs. ln(one changing variable)

iii. Non-linear regression minimizing error

$$r_A = kC_A^{\alpha} C_B^{\beta} C_C^{\gamma}$$

$$\ln[r_A] = \ln[k] + \alpha \ln[C_A] + \beta \ln[C_B] + \gamma \ln[C_C]$$

Differential or non-linear regression could work

$$r_A = k \frac{K_A P_A K_B P_B}{(1 + K_A P_A + K_B P_B)^2}$$

Differential won't work without simplification

Non-linear regression can work

6. Check "goodness of fit" R^2 value or correlation coefficient

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:

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

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 (t_{im})   Calculated from rate law (t_{ic})

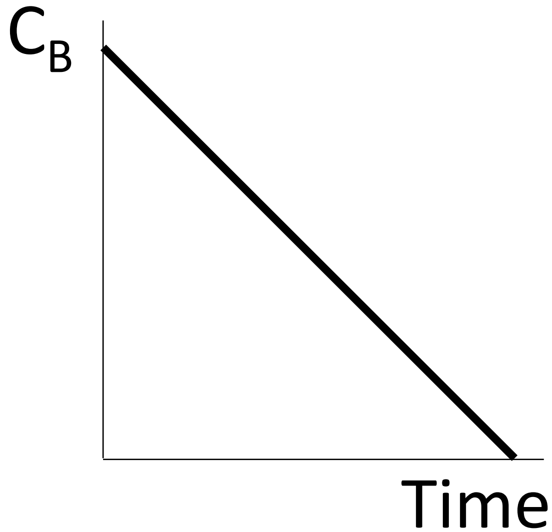
Can do this with "Solver" in Excel, regression in Polymath, etc.
The goal is to have a rate law that fits your data the best.
You can also use this method for more complex rate laws.

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

Discuss with your neighbor:

Which of the following plots for a constant volume batch reactor best matches a first order rate law for A → B?

A)



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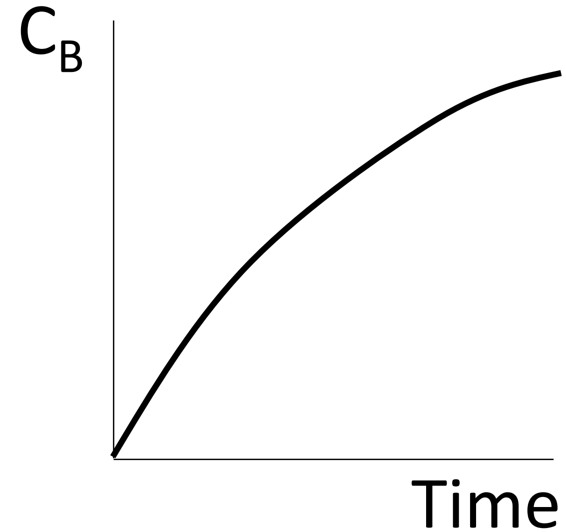

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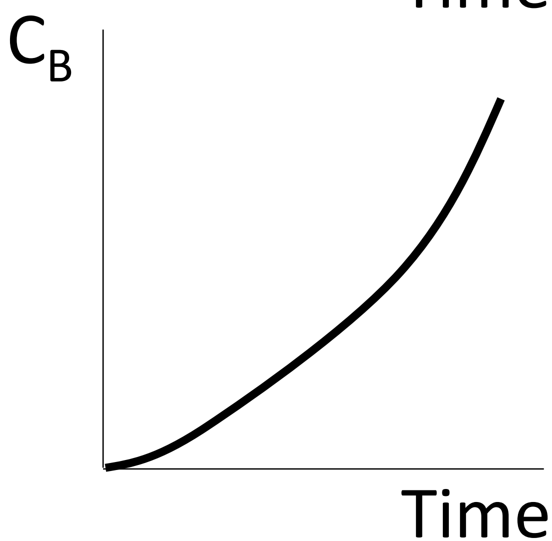

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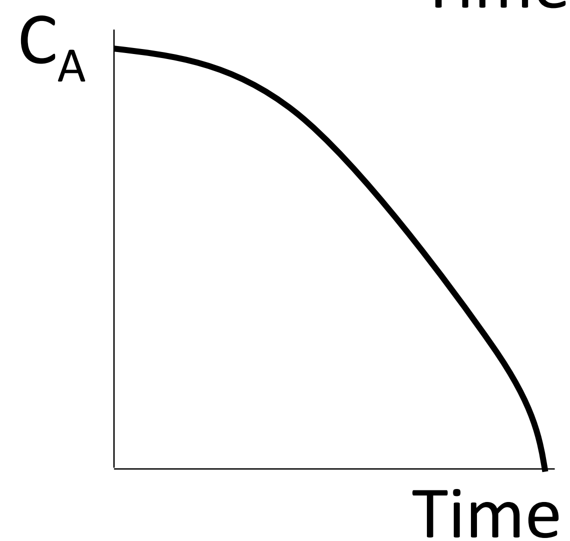


Simplifying the system: Method of excess

Determine the 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.

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

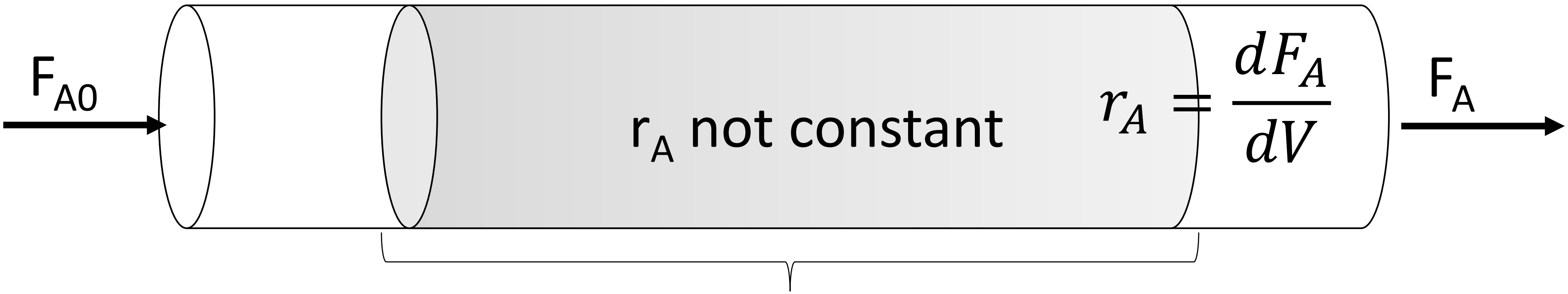
If $\theta_B - X \approx \theta_B$

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

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

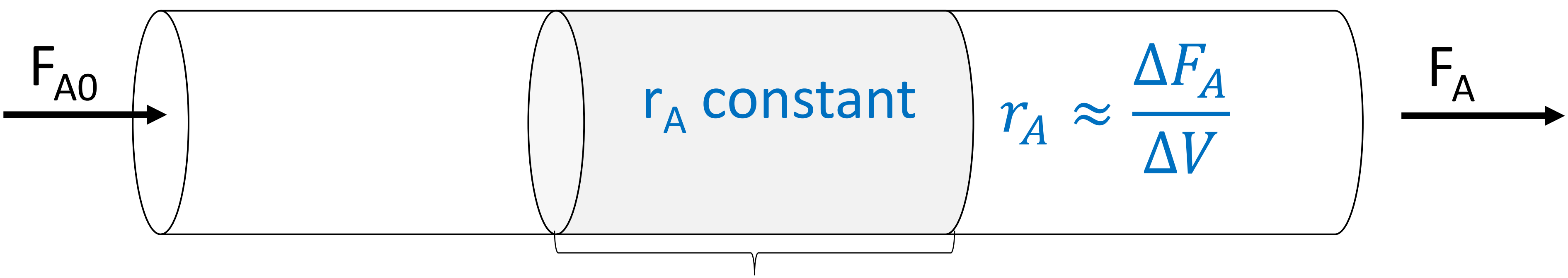
$$-r_A \approx (kC_{A0}^{\alpha}) C_B^{\beta}$$ Find β

PFRs/PBRs



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

Differential reactors for extracting reaction rates



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

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

Choosing experimental conditions to measure reaction orders

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

Caution: Order can change based on conditions

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

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)

So far we have been operating under the assumption that in a reactor only a single reaction is occurring. This is rarely the case in reality.

Catalytic converter

- CO, NO_x, HC oxidation (3-way cat. converter)

$$CO + 1/2\, O_2 \rightarrow CO_2$$

$$NO + CO \rightarrow CO_2 + N_2$$

$$hydrocarbon + xO_2 \rightarrow yCO_2 + zH_2O$$

Determining conversions are possible here, but they get a bit trickier! For example, was CO converted by the first or second reaction? Instead we'll use mole or concentration balances.

Rate laws for **multiple reactions**:

Let's start with something that is conceptually similar, reversible reactions! $A \rightleftarrows B$

Forward reaction (reaction 1): $A \overset{k_f}{\rightarrow} B$

Backward reaction (reaction 2): $B \overset{k_r}{\rightarrow} A$

If these are elementary as written: (from expt analysis)

$$r_1 = k_f C_A \qquad r_2 = k_r C_B$$

The reaction of A from reaction 1 only?

$$-r_{1A} = r_1 = k_f C_A \qquad \nu_{1A} = -1$$

From reaction 2 only?

$$+r_{2A} = r_2 = k_r C_B \qquad \nu_{2A} = +1$$

Total?

$$r_A = r_{1A} + r_{2A} = -r_1 + r_2 = -k_f C_A + k_r C_B$$

Let's apply the same concept for multiple reactions:

Desired product (reaction 1): $A \xrightarrow{k_1} D$

Undesired product (reaction 2): $A \xrightarrow{k_2} U$

If these are elementary as written:

$$r_1 = k_1 C_A \qquad\qquad r_2 = k_2 C_A$$

How about the reaction of A from reaction 1 only?

$$\frac{r_{1A}}{-1} = r_1 = k_1 C_A \qquad \nu_{1A} = -1$$

How about the reaction of D from reaction 1 only?

$$r_{1D} = r_1 = k_1 C_A \qquad \nu_{1D} = +1$$

U is not involved in reaction 1: $r_{1U} = 0$

What is the reaction of A from reaction 2 only?

$$-r_{2A} = r_2 = k_2 C_A$$

What is the reaction of U from reaction 2 only?

$$r_{2U} = r_2 = k_2 C_A \qquad r_{2D} = 0$$

What is the total reaction of A?

$$r_A = r_{1A} + r_{2A} = -r_1 - r_2 = -k_1 C_A - k_2 C_A$$

What is the total reaction of D?

$$r_D = r_{1D} + r_{2D} = r_1 + 0 = k_1 C_A + 0$$

What is the total reaction of U?

$$r_U = r_{1U} + r_{2U} = 0 + r_2 = 0 + k_2 C_A$$

Recall for instantaneous selectivity

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2}\frac{C_A^{\alpha_D}}{C_A^{\alpha_U}} = \frac{k_1}{k_2}C_A^{a} \qquad \text{where } a = \alpha_D - \alpha_U$$

If a > 0, in order to get higher selectivity for D over U want to:

Maximize C_A

1. Use a PFR for flow (higher C_A)
2. $C_A = P_A/RT$, so operate at high pressure
3. Batch reactor
4. Do not use diluents

If a < 0, want to: minimize C_A

1. Use a CSTR (all is at the outlet concentration)
2. Maintain low pressure
3. Use diluents

How would temperature affect selectivity?

For two parallel reactions

$$k_1 = A_1 \exp\left[-\frac{E_{a,D}}{RT}\right]$$

$$k_2 = A_2 \exp\left[-\frac{E_{a,U}}{RT}\right]$$

$$S_{D/U} \propto \frac{k_1}{k_2} = \frac{A_1}{A_2} \exp\left(-\frac{1}{RT}\left[E_{a,D} - E_{a,U}\right]\right)$$

If $E_{a,D} > E_{a,U}$, $S_{D/U} \propto \exp\left(-\frac{1}{T}\right)$

So want to run at high temperature to increase selectivity.

If $E_{a,D} < E_{a,U}$, $S_{D/U} \propto \exp\left(\frac{1}{T}\right)$

So want to run at lower temperature to increase selectivity.

$$A \overset{k_1}{\rightarrow} D \qquad A \overset{k_2}{\rightarrow} U$$

This was an example of a reaction in parallel. We can also have independent reactions:

$$A \overset{k_1}{\rightarrow} D \qquad B \overset{k_2}{\rightarrow} U$$

We can also have reactions in series:

$$A \overset{k_1}{\rightarrow} D \overset{k_2}{\rightarrow} U$$

Also: Complex

$$A + B \rightarrow C + D$$

$$A + C \rightarrow E$$

$$E \rightarrow G$$

Which I would like to rewrite as:

$$A \overset{k_1}{\rightarrow} D$$

$$D \overset{k_2}{\rightarrow} U$$

$$r_{\boldsymbol{U}} = r_{1U} + r_{2U} = 0 + k_2 C_D$$

$$r_A = r_{1A} + r_{2A} \qquad r_D = r_{1D} + r_{2D}$$

Discuss with neighbors:

For reactions in series:

$$A \xrightarrow{k_1} 2D \qquad r_1 = k_1 C_A$$

$$D \xrightarrow{k_2} U \qquad r_2 = k_2 C_D$$

What are r_A, r_D, and r_U? Recall how we get relative rates

$$\nu_{1A} = -1 \quad \nu_{1D} = +2 \quad \nu_{1U} = 0$$

$$\nu_{2A} = 0 \quad \nu_{2D} = -1 \quad \nu_{2U} = +1$$

A) $r_A = -r_1;\quad r_D = r_1 - r_2;\quad r_U = r_2$

B) $r_A = -r_1;\quad r_D = 2r_1 - r_2;\quad r_U = r_2$

C) $r_A = -r_1 - r_2; r_D = 2r_1 - r_2;\quad r_U = r_2$

D) $r_A = -r_1 - 2r_2; r_D = 2r_1 + r_2;\quad r_U = r_2$

Notice selectivity can become a bit more complicated for series reactions…

$$A \overset{k_1}{\rightarrow} 2D \qquad r_1 = k_1 C_A$$

$$D \overset{k_2}{\rightarrow} U \qquad r_2 = k_2 C_D$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{2r_1 - r_2}{r_2} = \frac{2k_1 C_A - k_2 C_D}{k_2 C_D}$$

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

Not as straightforward to determine by just cancelling terms (but still doable). Take derivative wrt species you would vary and see if positive or negative slope.

Reactor design with multiple reactions:

Mole balances of all species

In terms of molar flow rates or moles, not using conversion

Rate laws for every reaction, applied to each species

Rate laws may be more complex, because species may be reactants/products in multiple reactions

Stoichiometry

Again, using moles/molar flows rather than conversion (like we did for membrane reactors/semi-batch)

Example: Batch reactor where we want to maximize N_B:

1) $A \xrightarrow{k_1} B$

2) $B \xrightarrow{k_2} C$

We test the reactions separately and determine reaction 1 is first order in A, and reaction 2 is first order in B, so these are elementary as written

Mole balance on each species

$$\frac{dN_A}{dt} = r_A V \qquad \frac{dN_B}{dt} = r_B V \qquad \frac{dN_C}{dt} = r_C V$$

Rates on each species

$$r_A = r_{1A} + r_{2A} \qquad r_B = r_{1B} + r_{2B} \qquad r_C = r_{1C} + r_{2C}$$

$$-r_{1A} = r_1 = k_1 C_A \qquad r_{1B} = r_1 = k_1 C_A \qquad r_{1C} = 0$$

$$r_{2A} = 0 \qquad -r_{2B} = r_2 = k_2 C_B \qquad r_{2C} = r_2 = k_2 C_B$$

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

If we assume our batch reactor is constant volume: $C_j = N_j/V_0$

<u>Stoich.</u> $$C_A + C_B + C_C = C_{A0} + C_{B0} + C_{C0}$$

<u>Combine</u>: Constant V batch design and rate laws

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B$$

Can replace with mole balance

First equation:

$$\frac{1}{-k_1 C_A} dC_A = dt$$

$$C_A = C_{A0} e^{-k_1 t}$$

Can plug this into balance for B:

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t}$$

Can solve to get (through Laplace transform or integrating factor)

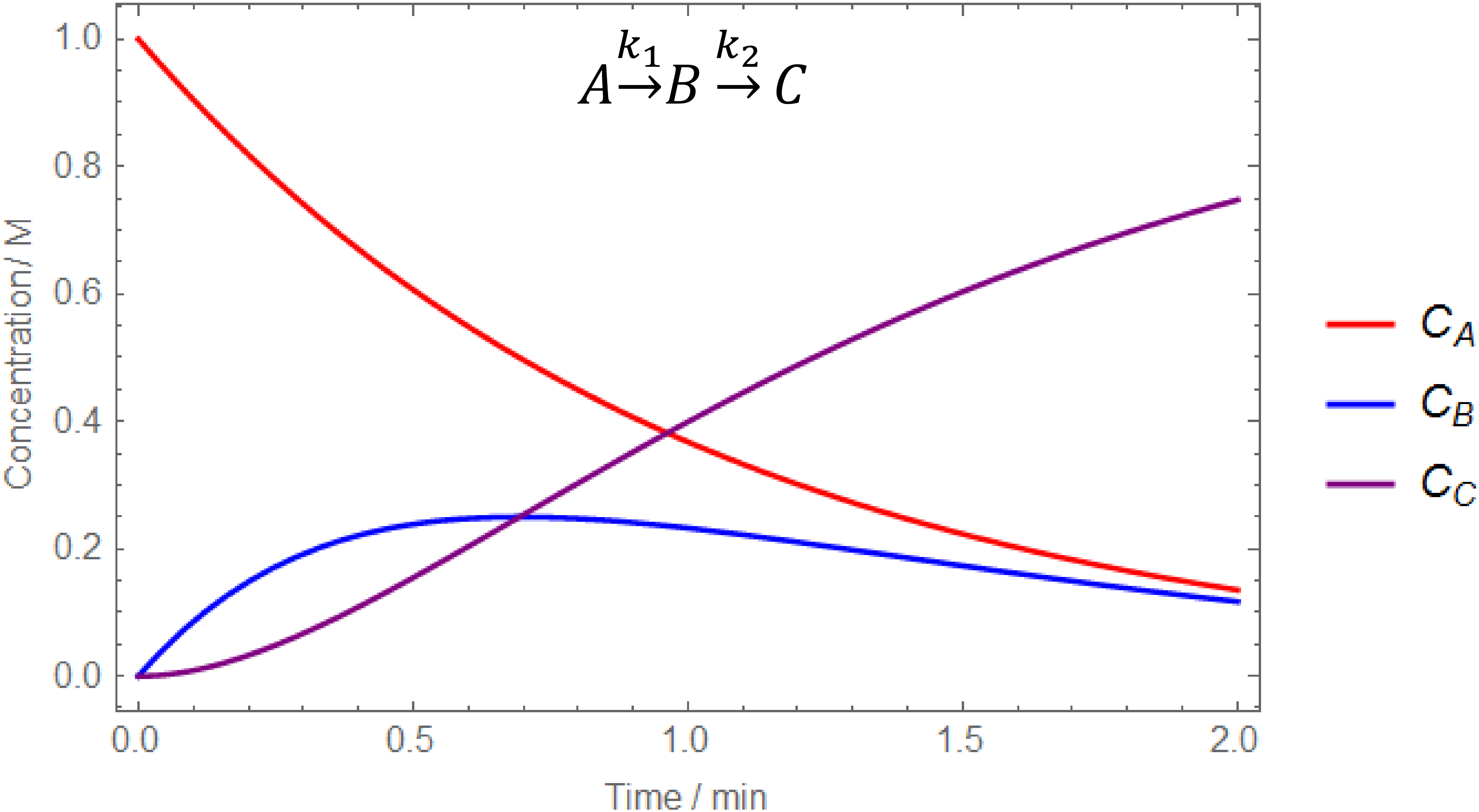
$$C_B = \left(\frac{C_{A0} k_1}{k_1 - k_2} + C_{B0}\right) e^{-k_2 t} - \frac{C_{A0} k_1}{k_1 - k_2} e^{-k_1 t}$$

And by mass balance:

$$C_C = C_{A0} + C_{B0} + C_{C0} - C_A - C_B$$
$$= C_{A0} + C_{B0} + C_{C0} - C_{A0} e^{-k_1 t}$$
$$- \left[\left(\frac{C_{A0} k_1}{k_1 - k_2} + C_{B0}\right) e^{-k_2 t} - \frac{C_{A0} k_1}{k_1 - k_2} e^{-k_1 t}\right]$$

If C_{A0} = 1 M, $C_{B0} = C_{C0}$ = 0 M, k_1 = 1 min^{-1}, k_2 = 2 min^{-1}

Series reaction



Then have:

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$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t}$$

Can solve by taking Laplace transform

$$F(s) = \int_0^\infty f(t) e^{-st} dt$$

$$\widehat{C_B}(s) = \mathcal{L}\{C_B(t)\} = \int_0^\infty C_B(t) e^{-st} dt$$

$$\mathcal{L}\left\{\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t}\right\}$$

$$\int_0^\infty \frac{dC_B}{dt} e^{-st} dt + k_2 \widehat{C_B}(s) = k_1 C_{A0} \int_0^\infty e^{-k_1 t} e^{-st} dt$$

$$\int_0^\infty \frac{dC_B}{dt} e^{-st} dt + k_2 \widehat{C_B}(s) = k_1 C_{A0} \frac{1}{k_1 + s}$$

Recall for Laplace transforms:

Skipped in class

$$\mathcal{L}\{f'(t)\} = sF(s) - f(0)$$

$$s\widehat{C_B}(s) - C_{B0} + k_2\widehat{C_B}(s) = k_1 C_{A0}\frac{1}{k_1 + s}$$

$$\widehat{C_B}(s) = \frac{sC_{B0} + k_1(C_{A0} + C_{B0})}{(s + k_1)(s + k_2)}$$

$$\mathcal{L}^{-1}\left\{\widehat{C_B}(s) = \frac{sC_{B0} + k_1(C_{A0} + C_{B0})}{(s + k_1)(s + k_2)}\right\}$$

$$C_B = \mathcal{L}^{-1}\left\{\frac{sC_{B0} + k_1(C_{A0} + C_{B0})}{(s + k_1)(s + k_2)}\right\}$$

$$= \mathcal{L}^{-1}\left\{\frac{k_1 C_{A0}}{(s + k_1)(s + k_2)}\right\} + \mathcal{L}^{-1}\left\{\frac{C_{B0}}{s + k_2}\right\}$$

Some definitions:

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$$\mathcal{L}^{-1}\left\{\frac{1}{s-a}\right\} = e^{at}$$

$$C_B = k_1 C_{A0}\mathcal{L}^{-1}\left\{\frac{1}{(s+k_1)(s+k_2)}\right\} + C_{B0}e^{-k_2 t}$$

$$\mathcal{L}^{-1}\left\{\frac{b}{(s-a)^2-b^2}\right\} = e^{at}\sinh(bt)$$

$$\mathcal{L}^{-1}\left\{\frac{b}{s^2-2as+a^2-b^2}\right\} = e^{at}\sinh(bt)$$

$$\mathcal{L}^{-1}\left\{\frac{1}{s^2+(k_2+k_1)s+k_2k_1}\right\} = \frac{e^{at}\sinh(bt)}{b}$$

$$k_2+k_1 = -2a; a = -\frac{k_2+k_1}{2}$$

$$a^2 - b^2 = k_2 k_1; b = \frac{k_1 - k_2}{2}$$

Skipped in class

$$C_B = k_1 C_{A0} \left[\frac{2}{k_1 - k_2} e^{-\frac{k_2 + k_1}{2} t} \frac{e^{\frac{k_1 - k_2}{2} t} - e^{-\frac{k_1 - k_2}{2} t}}{2} \right] + C_{B0} e^{-k_2 t}$$

$$C_B = \left(\frac{C_{A0} k_1}{k_1 - k_2} + C_{B0} \right) e^{-k_2 t} - \frac{C_{A0} k_1}{k_1 - k_2} e^{-k_1 t}$$