ChE 344
Reaction Engineering and Design

Lecture 21: Thursday, March 31, 2022

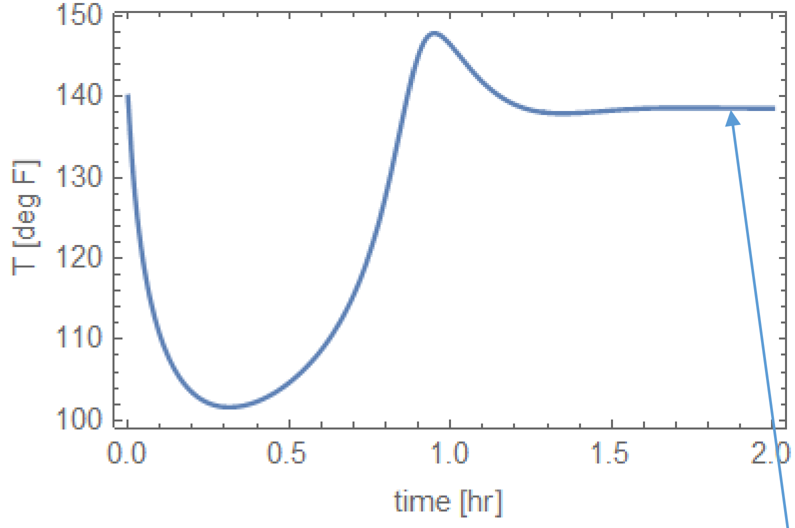
Postulating rate laws, reaction mechanisms,
pseudo-steady-state hypothesis

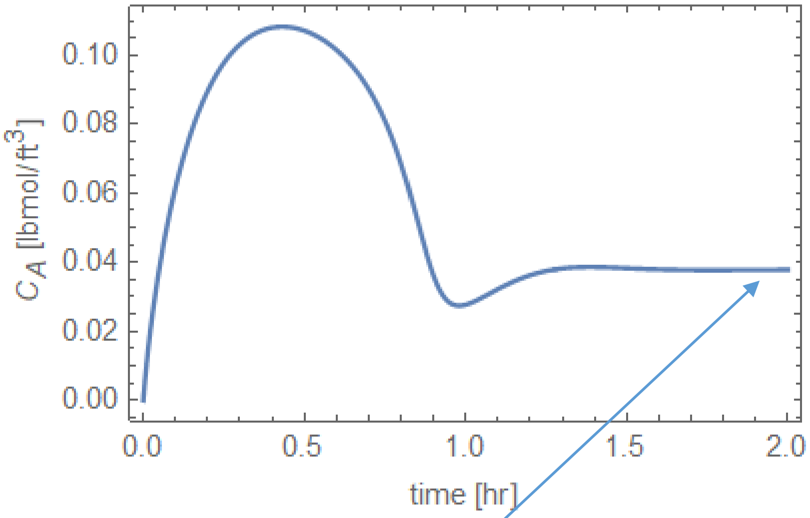
Reading for today’s Lecture: Chapter 9.1

Reading for Lecture 22: Chapter 9.2-9.3

Last time: Unsteady state CSTR (CSTR startup)

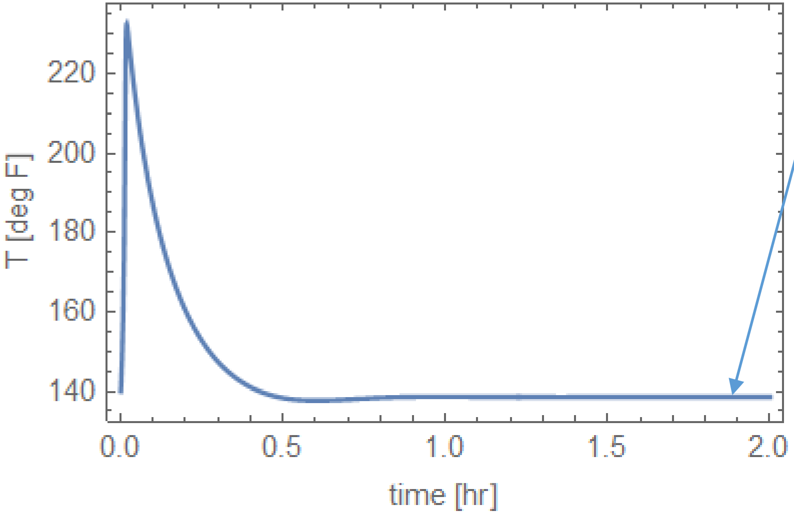
Initial conditions: $T(t=0) = 140$ °F, $C_A(t=0) = 0$

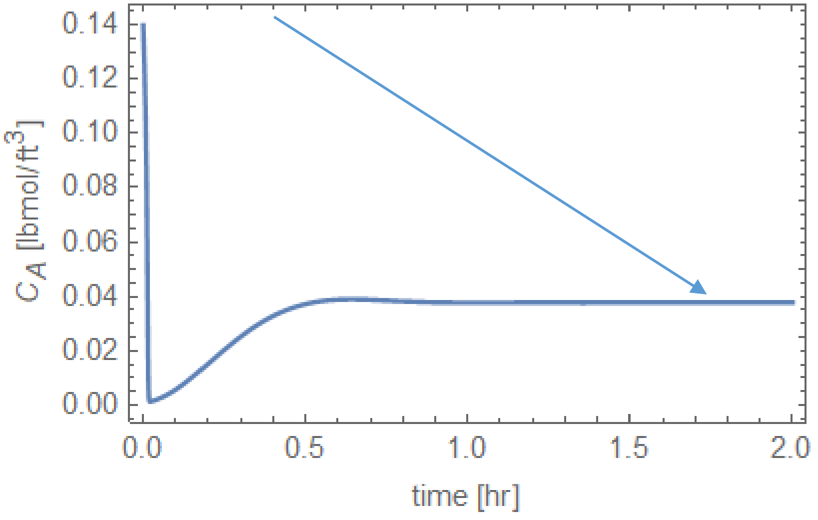




Initial conditions: $T(t=0) = 140$ °F, $C_A(t=0) = 0.14$ lbmol/ft^3

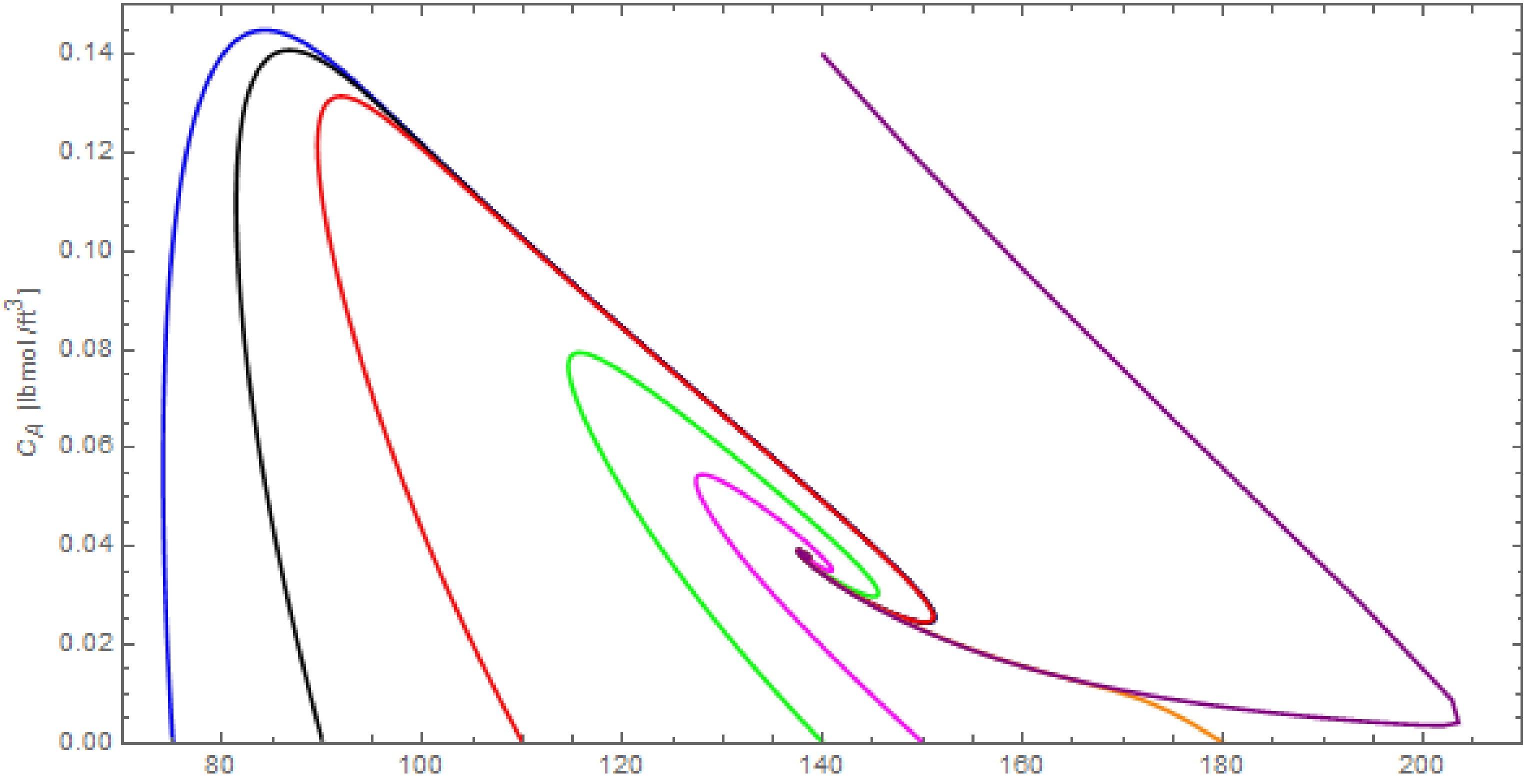
Same steady state, $T = 138.54$°F, $C_A = 0.038$ lbmol/ft^3





Discuss with your neighbors:

Which set of initial conditions for CSTR startup result in a temperature at some point that is greater than 200?



A) T(t=0) = 75 °F C_A (t=0) = 0

B) T(t=0) = 180 °F C_A (t=0) = 0

[✓ C) T(t=0) = 140 °F
C_A (t=0) = 0.14 lbmol/ft^3]

D) None of them

Lecture 21: Reaction mechanisms and pseudo steady-state hypothesis
Related Text: Chapter 9

Clarifying some definitions:

- **Reaction mechanism**: sequence of events (elementary reactions) that converts reactant molecules into product molecules
- **Elementary step/reaction**: reaction that occurs in one step with one transition state, follows elementary rate law
    - Reactions that follow an elementary rate law are not necessarily elementary steps/reactions, but all elementary reactions will follow elementary rate law
- **Active intermediate**: chemical species that reacts as fast as it is formed, generally not observed or measured. As a result its concentration is typically very low.
- **PSSH**: pseudo-steady-state hypothesis, which assumes that the net rate for an active intermediate is zero

Postulating rate law:

1. Start with the overall balanced reaction based on experiment
2. Postulate elementary steps to form your reaction mechanism, trying to minimize the number of simultaneous collisions
    a. Avoid elementary steps where more than 2 molecules react together
    b. Make use of experimental clues
    c. Ensure that the elementary steps lead to the overall reaction from Step 1
3. Postulate whether any species are active intermediates
4. Use the PSSH hypothesis to simplify/remove variables
5. Check whether the resulting rate law from your reaction mechanism is consistent with experiment, if not, use the experimental data to postulate a different set of elementary steps (back to Step 2)

Example reaction and reaction mechanism:

Overall reaction:

$$2NO + O_2 \rightarrow 2NO_2$$

Three step reaction mechanism (each step is an elementary reaction, step 2 is just the reverse of step 1):

$$NO + O_2 \rightarrow NO_3$$

$$NO_3 \rightarrow NO + O_2$$

$$NO_3 + NO \rightarrow 2NO_2$$

Summing up reaction 1 and 3 (don't include reaction 2 b/c it is the reverse of reaction 2) will give overall reaction.

Notes on safety (ICP 19):

Chain reactions consist of initiation, where radicals form from a molecule, propagation, and termination steps. Generally they are exothermic so can be very dangerous as we have noted before.

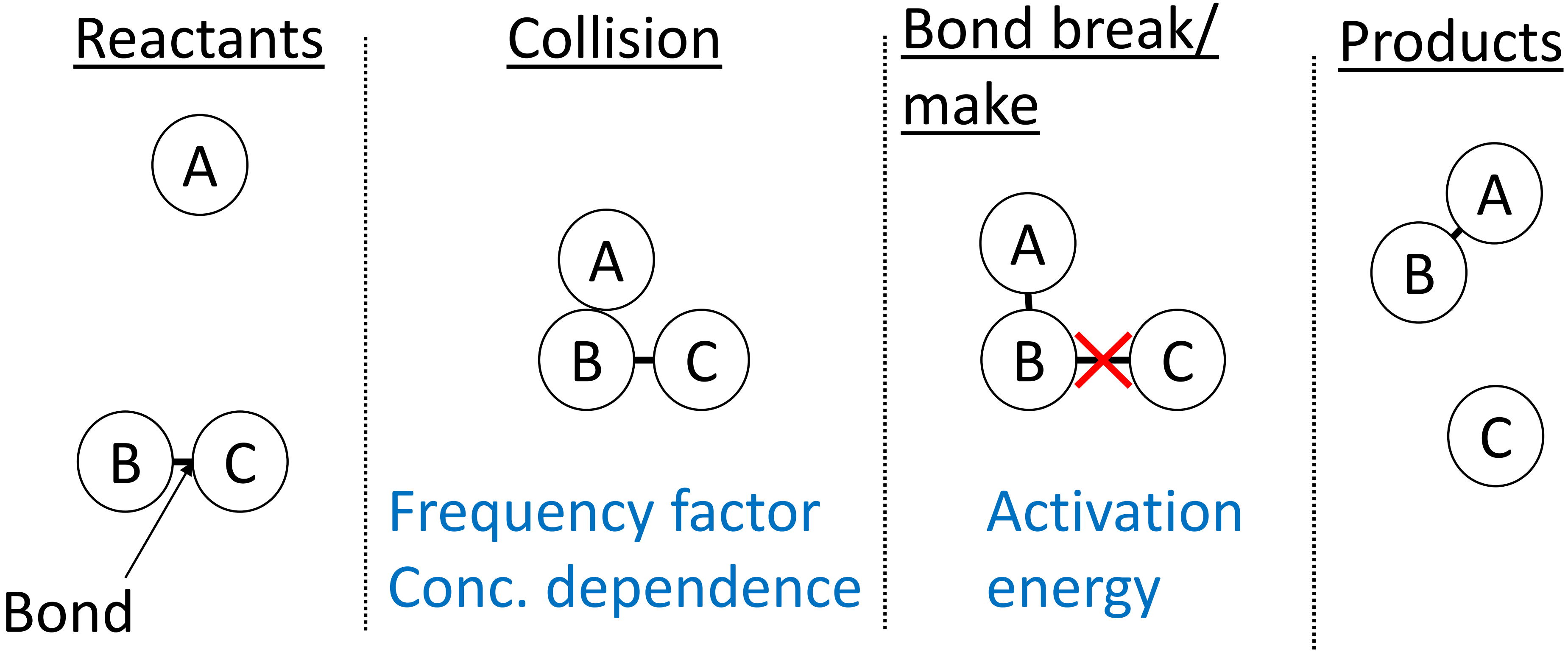
A branching step is a step where more reactive intermediates are formed than consumed.

Today: Revisiting rate laws from Lecture 3 and experimental rate data from Lecture 11

From Lecture 3, the reactants must (from "collision theory"):

1. collide (higher concentration = more chance for collisions)
2. break/make new bonds which takes energy (E_a)!

$$A + BC \longrightarrow AB + C$$

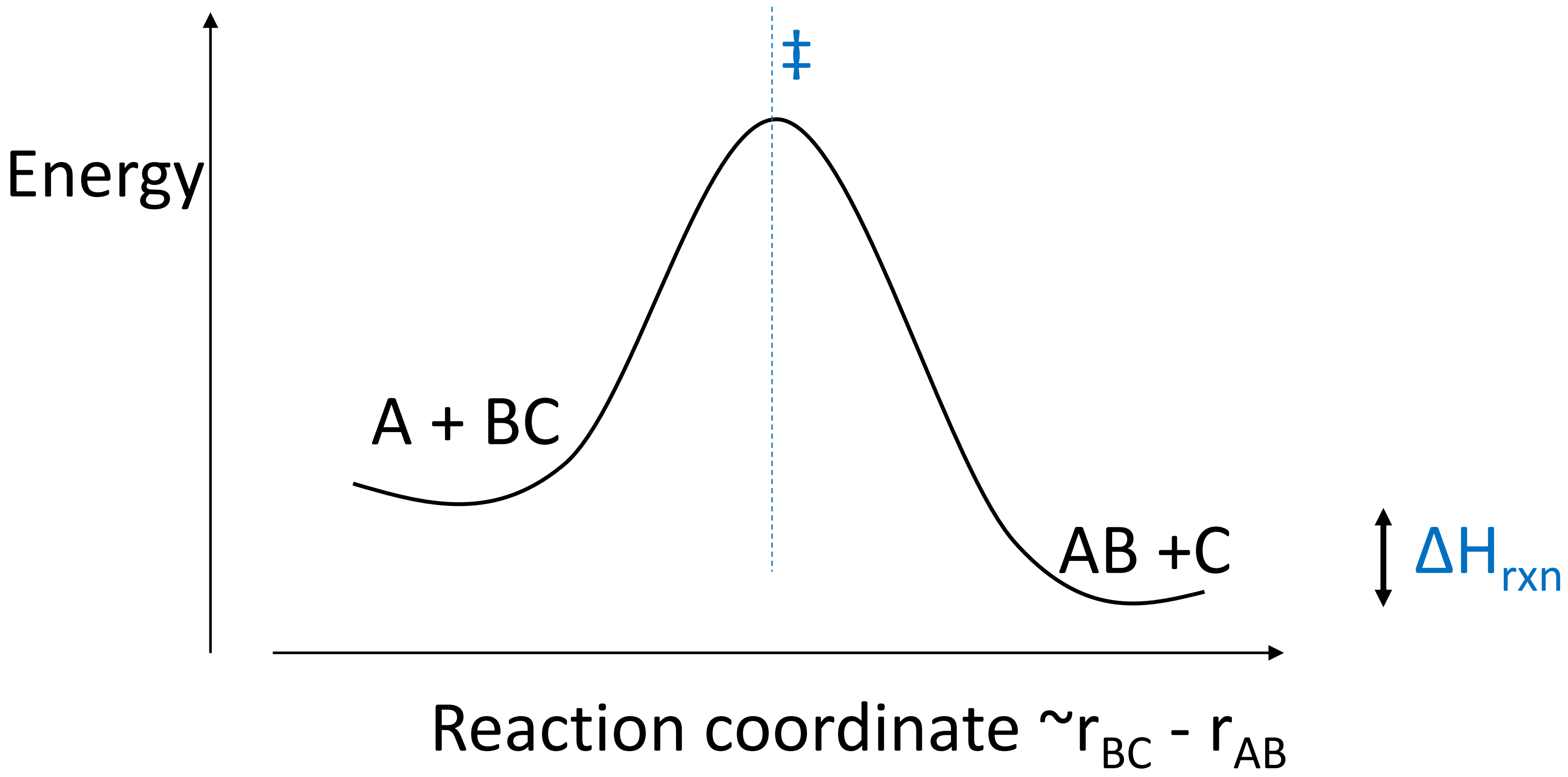


Reactants | Collision | Bond break/make | Products

Frequency factor
Conc. dependence

Activation energy

Another way we thought of this was to consider the "transition state" going from a reactant to a product.



Thinking about both of these, we expect the rate to be proportional to concentration of A and BC (elementary).

From Lecture 11 we learned that rate laws can have different dependencies on concentration (or pressure), and we can identify the rate law empirically (by doing experiments, and then fitting to the data).

Power law:

$$-r_A = k C_A^{\alpha} C_B^{\beta}$$

More complex expressions (e.g. Langmuir-Hinshelwood)

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

Why do these reactions have these dependencies? Another way of asking, why don’t all reactions have elementary rate laws?

The reason for this is that most reactions don’t occur in a single step. In Lecture 12, we talked about reactions in series.

$$A \rightarrow B \rightarrow C$$

Recall we broke this down into individual reactions:

$$A \rightarrow B$$

$$B \rightarrow C$$

But if we didn’t know that B was ever formed (maybe it is so short lived we could never detect it), we may think the reaction was only:

$$A \rightarrow C$$

Then B is some intermediate on the way of A converting to C

Let’s think about a reaction:

$$\mathrm{A + BC \longrightarrow AB + C}$$

If this reaction occurs via a single elementary step (A and BC reacting together), we might expect the rate law to just be:

$$-r_A = kC_A C_{BC}$$

But what if that is not the full picture? What if, in order to react, BC needs to first do an isomerization:

$$\mathrm{BC} \xrightarrow{k_1} \mathrm{BC'} \qquad r_{\mathbf{1},BC'} = k_1 C_{BC}$$

Then A can react with BC’

$$\mathrm{A + BC'} \xrightarrow{k_2} \mathrm{AB + C} \qquad -r_A = k_2 C_A C_{BC'}$$

We see now that we have multiple steps (reactions) to deal with, and our rate law will not be the same as for a single elementary step

We call this a two step **reaction mechanism**

Note: Elementary steps involving >2 molecules essentially never occur

<u>Discuss with your neighbors</u>: For the overall reaction:

$$A_2 + B \rightarrow A_2B$$

We break it down into 5 elementary steps

(1) $A_2 \rightarrow 2A$

(2) $2A \rightarrow A_2$

(3) $A + B \rightarrow AB$

(4) $AB \rightarrow A + B$

We'll write reversible rxns as two separate steps

What is the fifth step to complete the overall reaction?

[✓ A) $AB + A \rightarrow A_2B$]

B) $A_2B \rightarrow AB + A$

Trimolecular

C) $B + 2A \rightarrow A_2B$

Wrong stoich

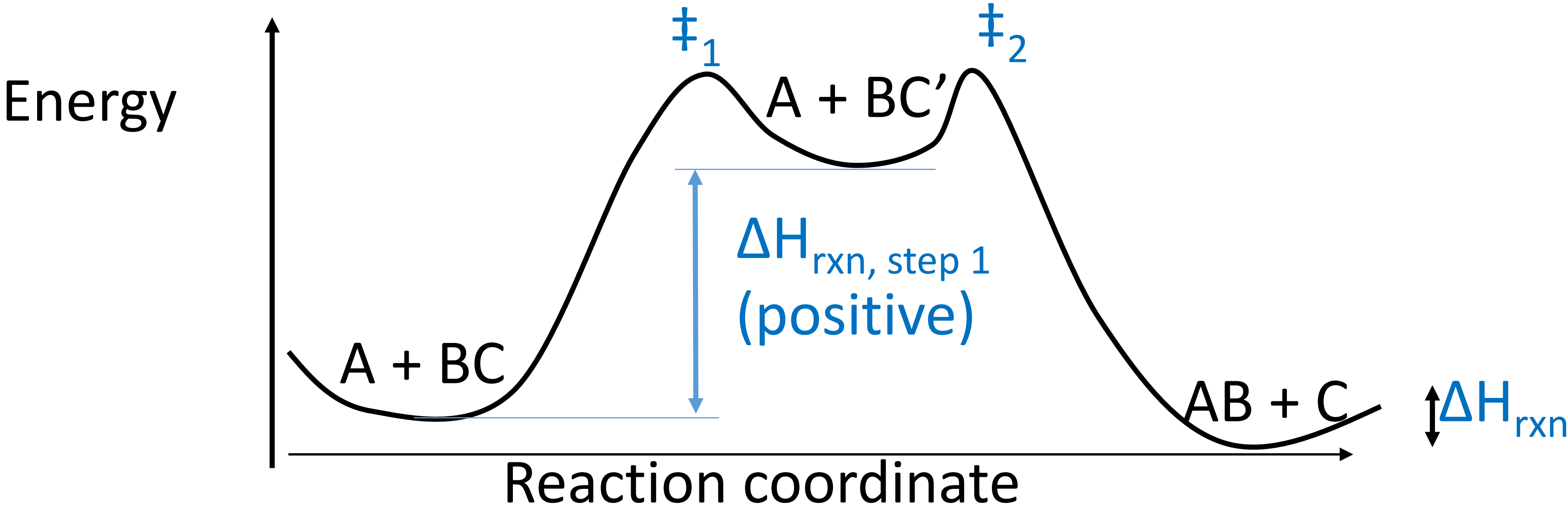
D) $A_2 + AB \rightarrow A_2B$

If elementary $A + BC \longrightarrow AB + C$ $-r_A = kC_AC_{BC}$

If 2 elementary steps $BC \xrightarrow{k_1} BC'$ $r_{\mathbf{1},BC'} = k_1C_{BC}$

$A + BC' \xrightarrow{k_2} AB + C$ $-r_A = k_2C_AC_{BC'}$

If we could accurately measure $C_{BC'}$ as an intermediate, we could just treat this as two individual elementary reactions. But, if $C_{BC'}$ cannot be determined, perhaps because it is so short lived, we call it an active intermediate



An active intermediate is a molecule that is in a highly energetic and reactive state.
Generally, we assume it disappears (reacts) as fast as it is formed, such that its net rate of reaction is zero. That is, active intermediate species are assumed to be at steady state. This assumption is called the **Pseudo Steady State Hypothesis (PSSH)**. Applying PSSH to B in $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ in a batch reactor:

Say that B is at a pseudo steady state, which is not necessarily true, as A and C are not at steady state, so B cannot be at steady state. But result is:

1. Assume $r_B = 0$, and eliminate B from overall rate equations
2. When the PSSH is applied, algebra is simplified starting from the last intermediate species
3. The overall rates can be converted to have less independent parameters

For PSSH, individual steps of reaction and formation of intermediate are much faster than net rate of that intermediate, so we assume net rate of species is zero.

Limitations:

- Rate laws do not accurately describe behavior at short times using PSSH
- When reactive intermediates are generated through branching steps, can build up to high levels. Example:

$$H + O_2 \rightleftarrows OH + O$$

$$O + H_2 \rightleftarrows OH + H$$

Each branching step creates reactive radicals and so the radical population is not small, and so PSSH is in general not appropriate for branching reactions

Utility of PSSH: Lets try our series reaction in a batch reactor:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

We had the analytical solution of:

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

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

If initial concentration of B is zero:

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

$$= C_{A0}\frac{k_1}{k_2\left(1 - \frac{k_1}{k_2}\right)}\left(e^{-k_1 t}\right)\left(1 - e^{-k_2\left(1 - \frac{k_1}{k_2}\right)t}\right)$$

How to rewrite:

Skipped in class

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

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

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

$$= C_{A0}\frac{k_1}{k_2\left(1 - \frac{k_1}{k_2}\right)}\left(e^{-k_1 t}\right)\left(1 - e^{-k_2(1 - \frac{k_1}{k_2})t}\right)$$

When you write it this way you can see there is an important term k_1/k_2. If k_1/k_2 << 1 then B are quickly converted to C as soon as they are formed from A. Under these conditions:

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

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

$$C_B \overset{k_1/k_2 \ll 1}{\approx} C_A \frac{k_1}{k_2} \left(1 - e^{-k_2 t}\right)$$

So evident that C_B is much less than C_A, and after time k_2^{-1} that is less than k_1^{-1}, get:

$$C_B \approx C_A \frac{k_1}{k_2}$$

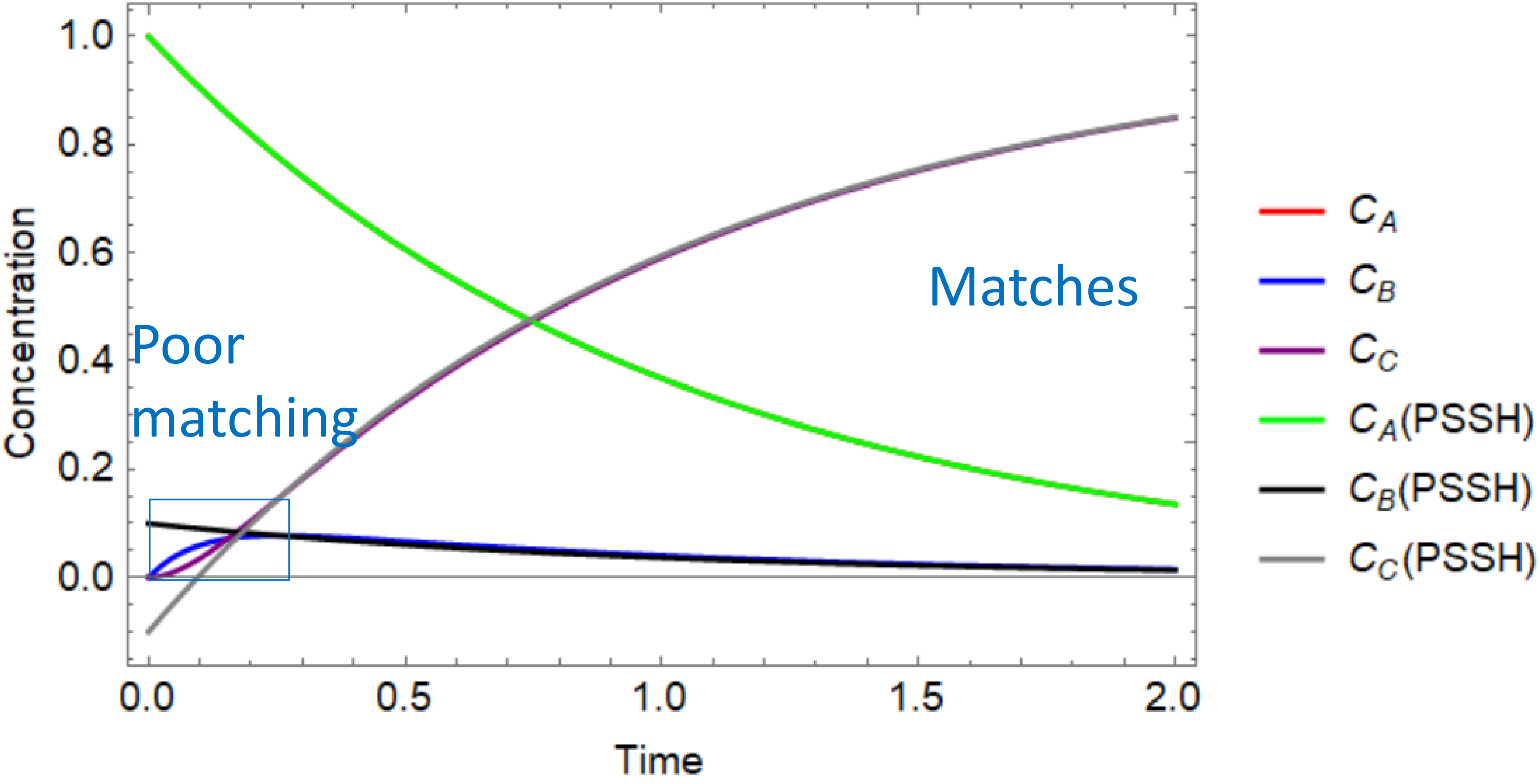
This would be what you would get from assuming steady state on B based on the PSSH:

$$r_B = \frac{dC_B}{dt} = k_1 C_A - k_2 C_B \approx 0$$

$$C_B \approx C_A \frac{k_1}{k_2}$$

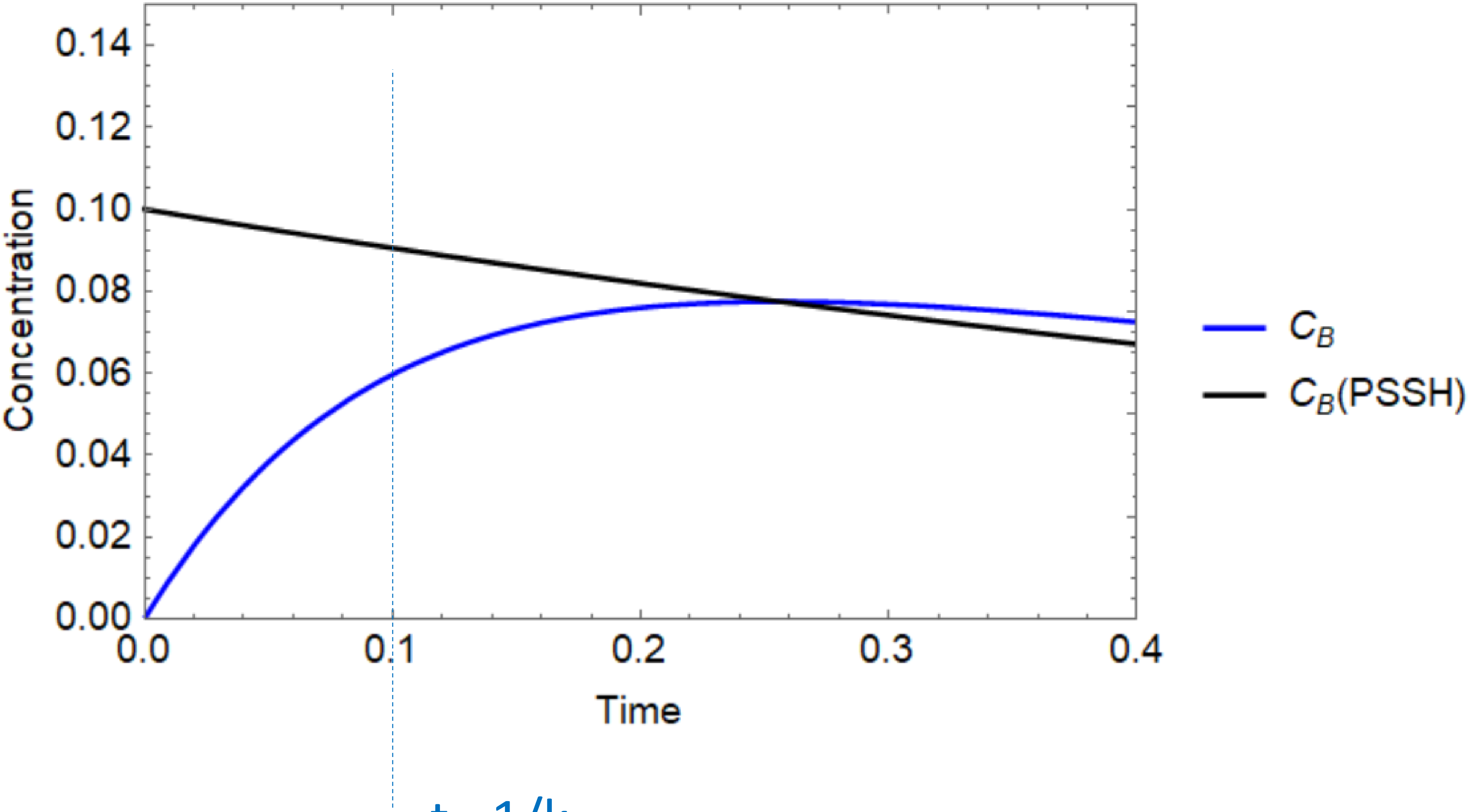
But clearly since $C_A = C_{A0} e^{-k_1 t}$ this cannot be a real steady state (time dependent).

PSSH matches the analytical solution at longer times (when r_B is smaller)



Matches

Poor matching


0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Concentration
0.0
0.1
0.2
0.3
0.4
Time
C_B
C_B(PSSH)

$t = 1/k_2$

Algorithm for **identifying a rate mechanism** (Table 9-1, pg 370 in book)

1. Propose an active intermediate (AI)
2. Propose a mechanism, utilizing the rate law from experimental data
3. Model each reaction in mechanism as elementary reaction
4. Write rate laws for each AI
5. Write net rate of formation for AI and use PSSH
6. Eliminate concentrations of intermediate species by solving equations from Steps 4 and 5
7. If rate law does not agree, assume a new mechanism/intermediates and go back to Step 3

Rules of thumb for mechanism development (Table 9-2, pg 374 in book). Not inclusive! But may be of some help…

1. Species having concentration in the denominator of rate law probably collide with active intermediate

$$\mathrm{M} + \mathrm{AI} * \rightarrow [\mathrm{Products}]$$

2. Constant appearing in denominator may mean spontaneous decomposition of active intermediate

$$\mathrm{AI} * \rightarrow [\mathrm{Products}]$$

3. Species having concentration appear in numerator of rate law probably produce active intermediate in one of the steps

$$[\mathrm{Reactants}] \rightarrow \mathrm{AI} * + [\mathrm{Other\ products}]$$

Lets use an example, nitric oxide oxidation to NO_2

$$2NO + O_2 \rightarrow 2NO_2$$

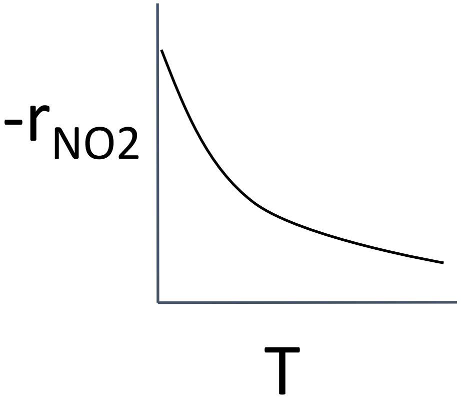
This reaction is very unlikely to happen in one step

What is the empirical rate law? Elementary rate law

$$r_{NO_2} = k_{empirical} C_{NO}^2 C_{O_2}$$

But unlikely to occur in a single elementary step

Also, we observe that the rate of reaction decreases with increasing temperature (non-Arrhenius behavior). Why is this?



Discuss with your neighbors:

$$2NO + O_2 \rightarrow 2NO_2 \quad r_{NO_2} = k_{empirical} C_{NO}^2 C_{O_2}$$

Using the rules of thumb from above:
Constant in denominator, NO and O_2 in numerator

Based on this, which of the following may be a reasonable elementary step to assume is part of the mechanism? Note these are not definitive rules, but I'm asking you using the rules of thumb, which are imperfect.

[✓ A) $NO + O_2 \rightarrow NO_3$

AI = NO_3]

B) $NO + 2O_2 \rightarrow NO_5$

AI = NO_5

C) $NO_3 + NO \rightarrow 2NO_2$

AI = NO_3

D) $NO + N_2 \rightarrow N_3O$

AI = N_3O

Reaction mechanism broken down into elementary steps.

Each elementary step obeys an elementary rate law

1) $NO + O_2 \rightarrow NO_3$

2) $NO_3 \rightarrow NO + O_2$

3) $NO_3 + NO \rightarrow 2NO_2$

We will see why
in a moment

$$r_{1NO_3} = k_1 C_{NO} C_{O_2}$$

$$r_{2NO_3} = -k_2 C_{NO_3}$$

$$r_{3NO_3} = -k_3 C_{NO_3} C_{NO}$$

$$r_{NO_2} = -2r_{3NO_3}$$

Lets consider the intermediate NO_3, and apply the PSSH to it such that the net reaction rate of NO_3 is zero

$$r_{1NO_3} = k_1 C_{NO} C_{O_2};\ r_{2NO_3} = -k_2 C_{NO_3}; r_{3NO_3} = -k_3 C_{NO_3} C_{NO}$$

$$r_{NO_3} = r_{1NO_3} + r_{2NO_3} + r_{3NO_3} \approx 0$$

$$r_{NO_3} = k_1 C_{NO} C_{O_2} - k_2 C_{NO_3} - k_3 C_{NO_3} C_{NO} \approx 0$$

$$k_1 C_{NO} C_{O_2} - C_{NO_3}(k_2 + k_3 C_{NO}) = 0$$

$$C_{NO_3} = \frac{k_1 C_{NO} C_{O_2}}{(k_2 + k_3 C_{NO})}$$

We can use this to get the rate of NO_2 formation

$$r_{NO_2} = -2r_{3NO_3} \qquad r_{3NO_3} = -k_3 C_{NO_3} C_{NO}$$

From PSSH on NO_3: $C_{NO_3} = \dfrac{k_1 C_{NO} C_{O_2}}{(k_2 + k_3 C_{NO})}$

$$r_{NO_2} = -2r_{3NO_3} = -2\left(-k_3 C_{NO_3} C_{NO}\right)$$

$$r_{NO_2} = 2k_3 C_{NO} \frac{k_1 C_{NO} C_{O_2}}{(k_2 + k_3 C_{NO})} = 2\frac{k_1 k_3 C_{NO}^2 C_{O_2}}{(k_2 + k_3 C_{NO})}$$

If $k_2 >> k_3 C_{NO}$

Actually does appear in denominator!

$$r_{NO_2} \approx 2\frac{k_1 k_3}{k_2} C_{NO}^2 C_{O_2} = k_{effective} C_{NO}^2 C_{O_2}$$

But this “effective” rate constant is not a true elementary rate constant.

$$k_{effective} = 2\frac{k_1 k_3}{k_2} = 2\frac{A_1 A_3}{A_2}\exp\left[\frac{-\left(\overbrace{-E_{a2} + (E_{a1} + E_{a3})}^{E_{a,\mathrm{eff}}}\right)}{RT}\right]$$

If $E_{a2} > (E_{a1} + E_{a3})$, our effective activation energy is negative

This is why the rate decreases with increasing temperature for our rate of NO_2 production. A negative activation energy is a flag that a reaction is not a single elementary step.

Note: Often you’ll see concentrations written as $[NO_2]$ rather than C_{NO_2}, especially when dealing with reaction mechanisms and kinetics