

Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

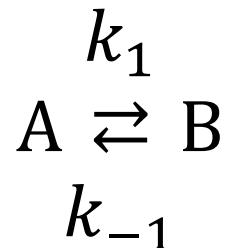
Recap from last session

- Macroscopic kinetics vs microscopic dynamics
- Elementary vs complex reactions
- Molecularity vs order of a reaction
- Rate equations vs
- Integrated reaction rate laws (0th, 1st, 2nd)
- Arrhenius equation (& its useful plot!)

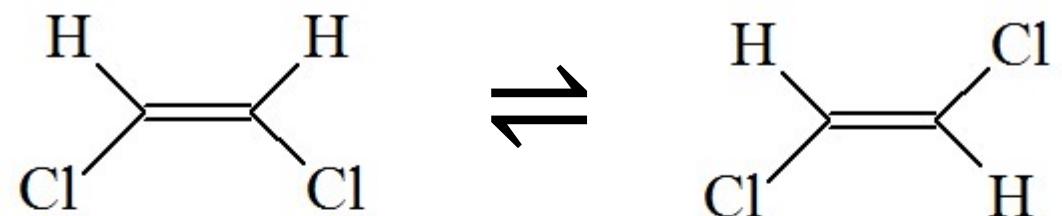
Chapter 2

Complex Reactions

2.1 Reversible Reactions



e.g.



- Obtain two linear ODEs:
- $\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$
- $\frac{d[B]}{dt} = k_1[A] - k_{-1}[B]$
- Use extent of reaction: $x = [A]_0 - [A] = [B] - [B]_0$

- yields $\frac{dx}{dt} = k_1([A]_0 - x) - k_{-1}([B]_0 + x)$

$$= \underbrace{-(k_1 + k_{-1})x}_{(k_1[A]_0 - k_{-1}[B]_0)}$$

- Substitute k to simplify to

$$\frac{dx}{dt} = -kx + c$$

- $\int_0^{x_t} \frac{dx}{-kx+c} = \int_0^t dt$

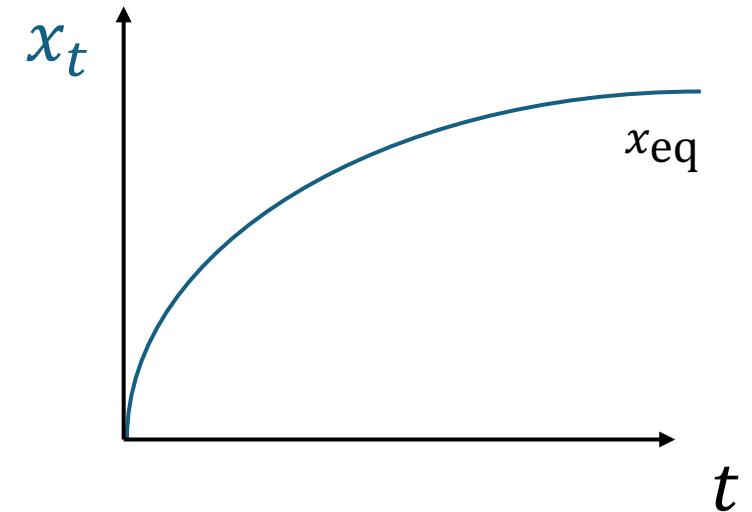
- $$-\frac{1}{k} \int_0^{x_t} \frac{dx}{x - \frac{c}{k}} = -\frac{1}{k} \ln \left| \frac{x_t - \frac{c}{k}}{-\frac{c}{k}} \right| = t$$

$$\underbrace{}_{>0}$$

- We find that $x_t = \frac{c}{k} (1 - e^{-kt})$ -What happens at late times?

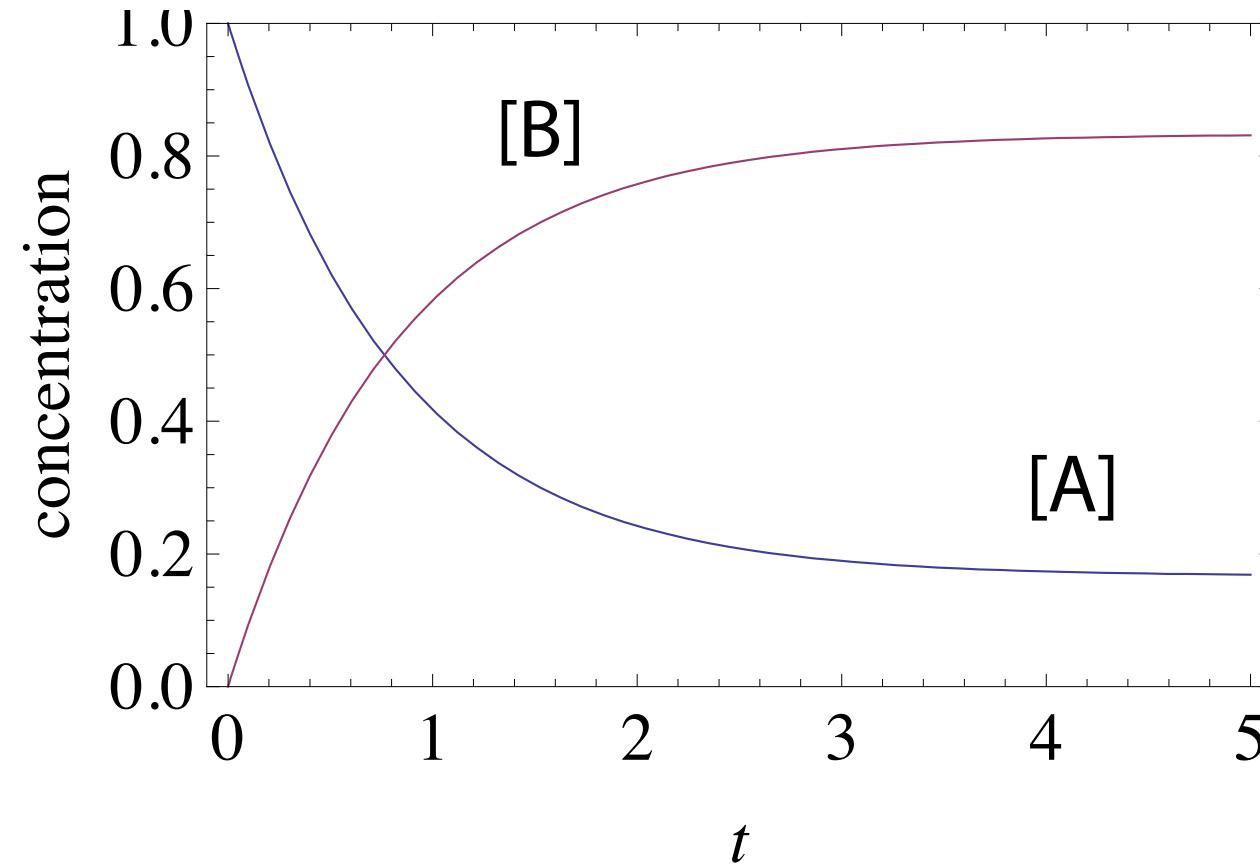
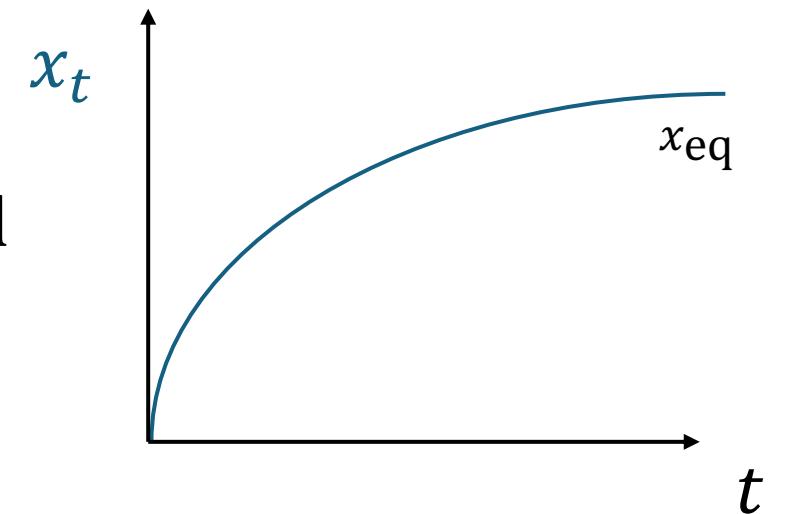
- $x_{\text{eq}} = \lim_{t \rightarrow \infty} x_t = \frac{c}{k} = \frac{k_1[A]_0 - k_{-1}[B]_0}{(k_1 + k_{-1})}$

- Meaning $x_t = x_{\text{eq}}(1 - e^{-kt})$



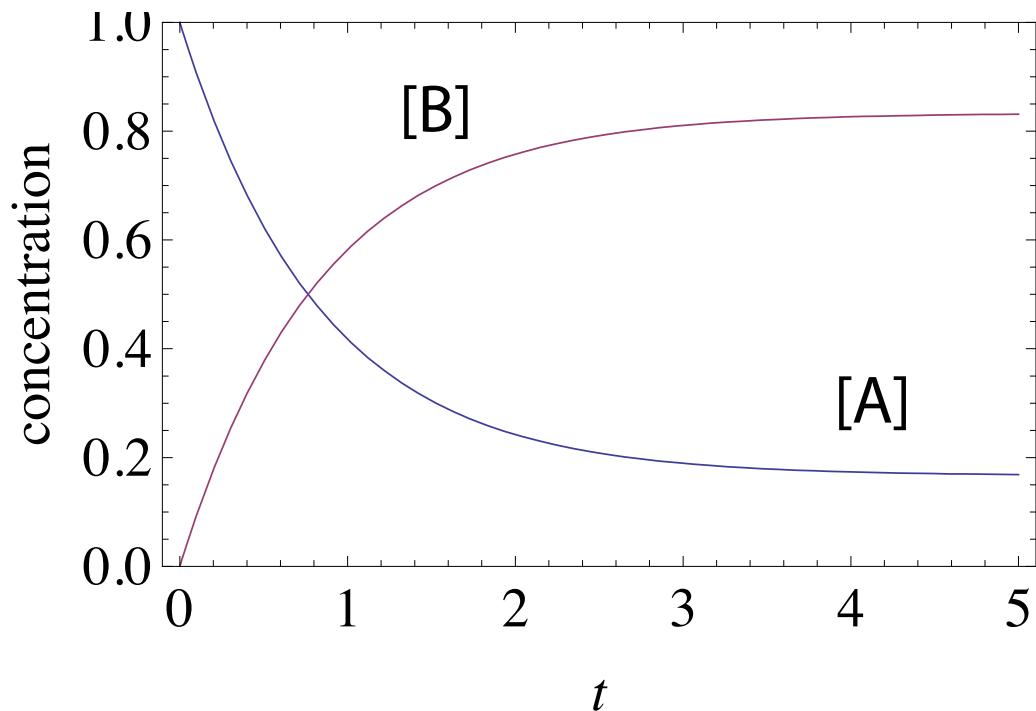
- Over time, we reach the equilibrium value x_{eq}
- And also equil. concentrations for A and B:
- $[A]_{\text{eq}} = [A]_0 - x_{\text{eq}}$ and $[B]_{\text{eq}} = [B]_0 + x_{\text{eq}}$

- $[A] = [A]_{\text{eq}} + x_{\text{eq}}e^{-kt}$
- $[B] = [B]_{\text{eq}} - x_{\text{eq}}e^{-kt}$



- Remember: *reversible* reaction, so detailed balance holds! So
- $k_1[A]_{\text{eq}} = k_{-1}[B]_{\text{eq}}$
- and equilibrium constant:

$$K_{\text{eq}} = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_1}{k_{-1}}$$



2.2 Consecutive Reactions

A first order consecutive reaction with 2 steps: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

- E.g. radioactive decay: $^{239}_{92}\text{U} \rightarrow ^{239}_{93}\text{Np} \rightarrow ^{239}_{94}\text{Pu}$

- $$\frac{d[A]}{dt} = -k_1[A]$$



easiest one to solve:

$$[A] = [A]_0 e^{-k_1 t}$$

- $$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

- $$\frac{d[C]}{dt} = k_2[B]$$



- $\frac{d[B]}{dt} = k_1[A] - k_2[B]$

- Insert solution for $[A] = [A]_0 e^{-k_1 t}$

- $\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$

- Rearrange to $\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t}$

an *inhomogeneous* linear ODE

...How to solve this?



- $\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t}$

an inhomogeneous linear ODE

- General solution:

= general solution of the homogeneous ODE 1

+ a particular solution of the inhomogeneous ODE 2

1 • For the general solution of the homogeneous ODE we find

$$\frac{d[B]}{dt} + k_2[B] = 0$$

- So, $[B]_h = [B]_{h,0} e^{-k_2 t}$



- $\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t}$

an inhomogeneous linear ODE

- General solution:

= general solution of the homogeneous ODE 1

+ a particular solution of the inhomogeneous ODE 2

2 • For the particular solution of the inhom. ODE, we guess

$[B]_p = [B]_{p,0} e^{-k_1 t}$ Then substitute into inhom. ODE:

$$-k_1[B]_{p,0} e^{-k_1 t} + k_2[B]_{p,0} e^{-k_1 t} = k_1[A]_0 e^{-k_1 t} \quad \rightarrow [B]_{p,0} = \frac{k_1[A]_0}{k_2 - k_1}$$



- General solution:
 - = general solution of the homogeneous ODE
 - + a particular solution of the inhomogeneous ODE
- Add the general homogeneous and the particular inhomogeneous solutions $\underline{1} + \underline{2}$
- $[B] = [B]_{h,0} e^{-k_2 t} + \frac{k_1 [A]_0}{k_2 - k_1} e^{-k_1 t}$
- Using boundary condition: $[B]_0 = [C]_0 = 0$ we get
- $[B] = \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$

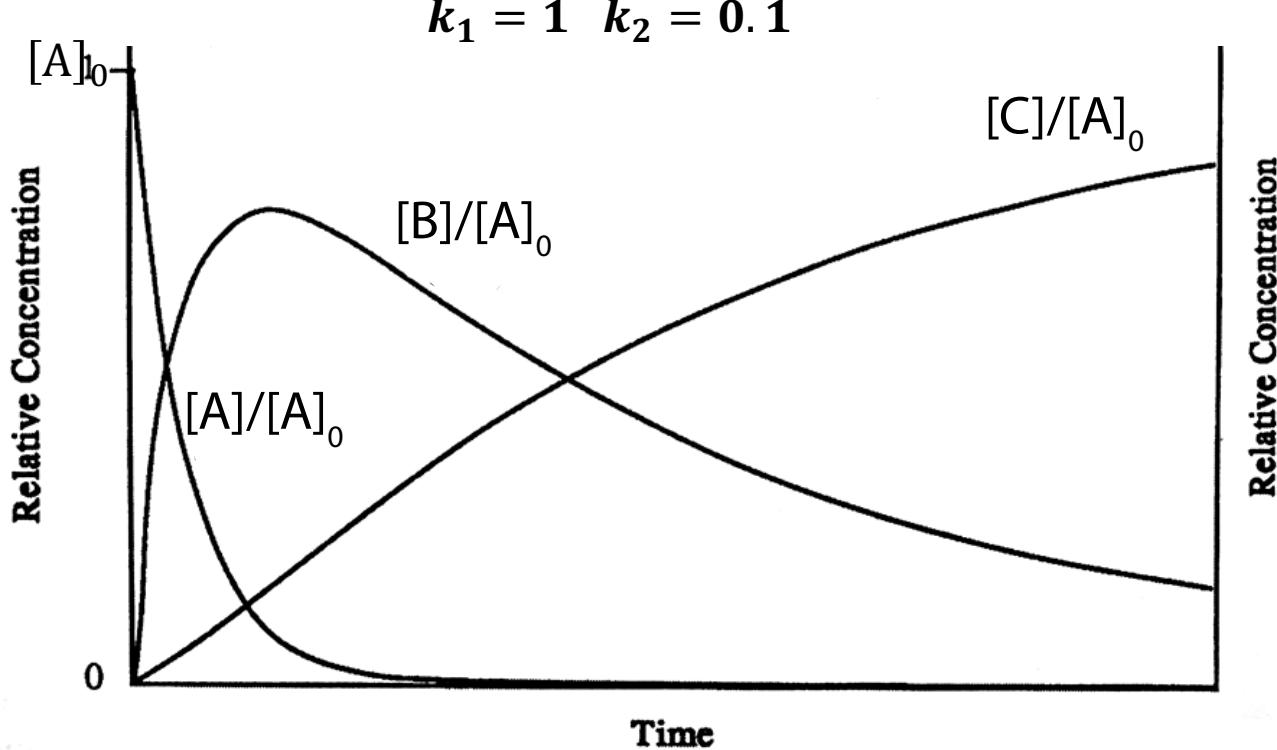
- And with $[A] + [B] + [C] = [A]_0$ we find
- $[C] = [A]_0 - [A] - [B]$
- $[C] = [A]_0 \left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right)$



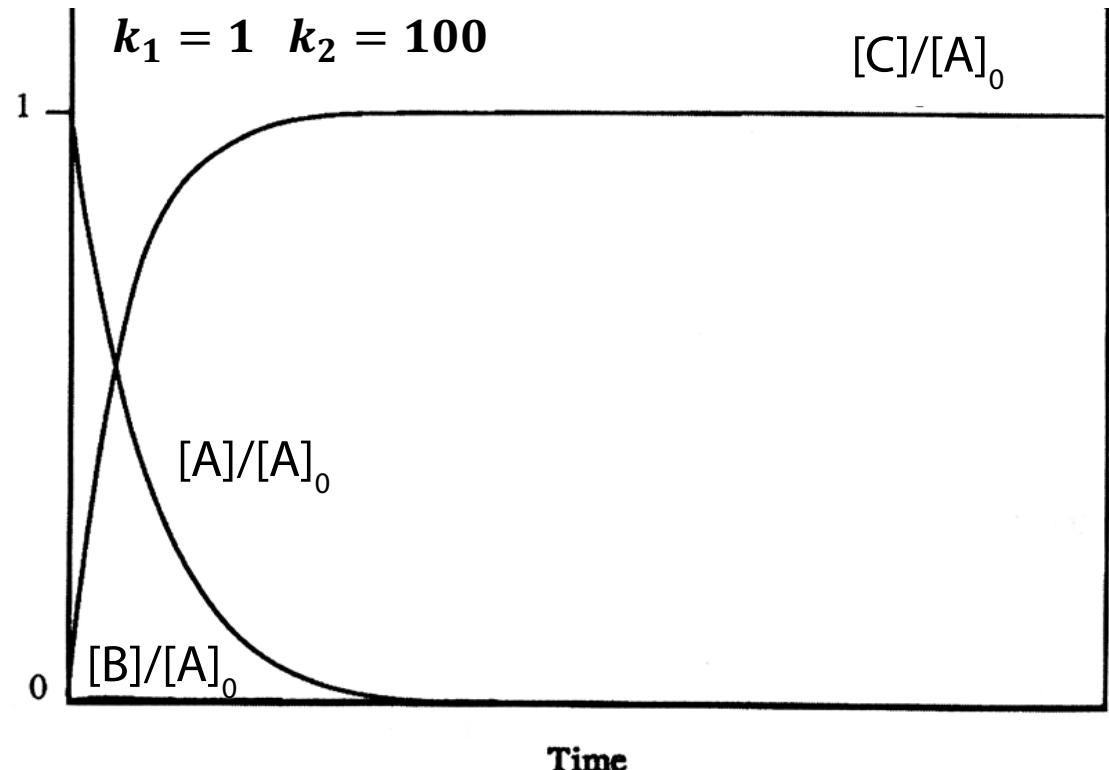
Two cases:

for $k_1 \gg k_2$

$$k_1 = 1 \quad k_2 = 0.1$$



for $k_2 \gg k_1$ $[C] \approx [A]_0(1 - e^{-k_1 t})$

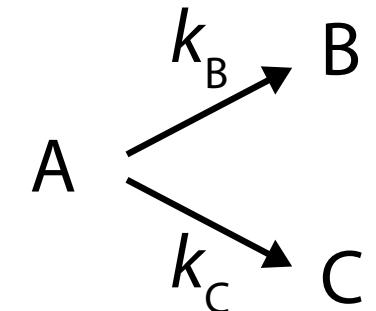


2.3 Parallel Reactions

Case 1: First-order decay to different products

What are the rate laws for the components?

- $[A] = [A]_0 e^{-(k_B+k_C)t}$
- $\frac{d[B]_t}{dt} = k_B[A]_t = k_B[A]_0 e^{-(k_B+k_C)t}$ and with $[B]_0 = [C]_0 = 0$
- $[B]_t = \frac{k_B}{(k_B+k_C)} [A]_0 (1 - e^{-(k_B+k_C)t})$
- $[C]_t = \frac{k_C}{(k_B+k_C)} [A]_0 (1 - e^{-(k_B+k_C)t})$

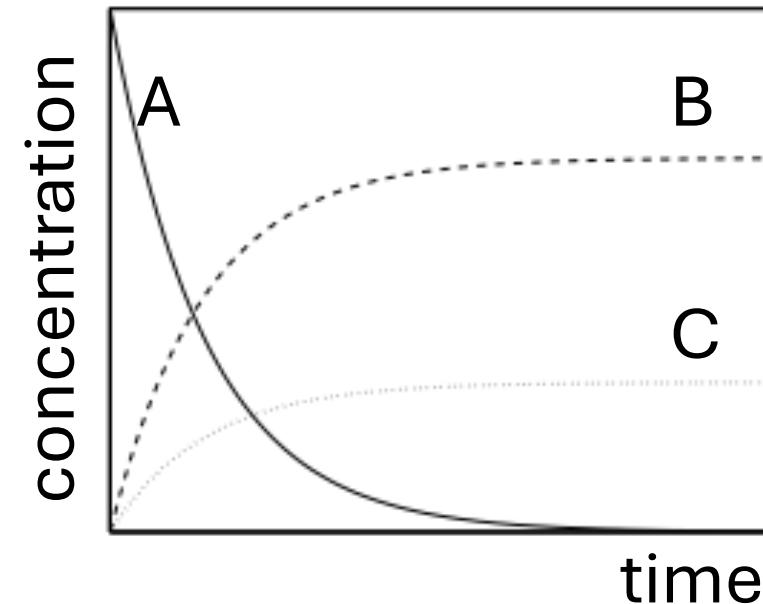
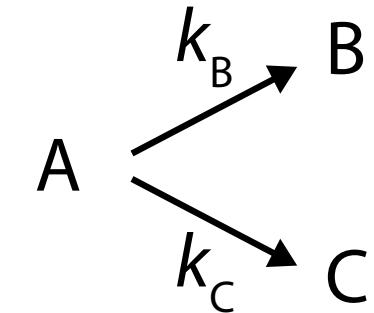


2.3 Parallel Reactions

Case 1: First-order decay to different products

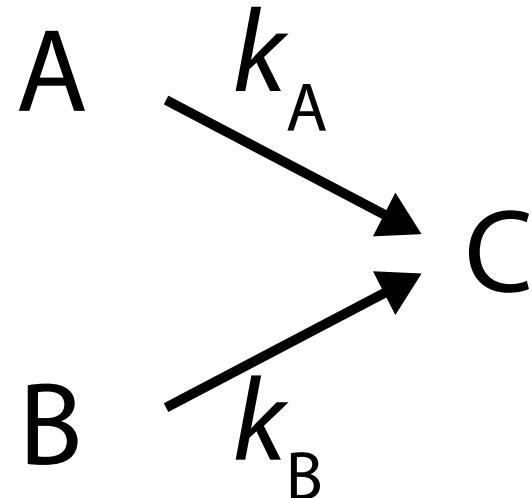
Note: The *branching ratio* is constant over time:

$$\text{B.R.} = \frac{[B]_t}{[C]_t} = \frac{k_B}{k_C}$$



2.3 Parallel Reactions

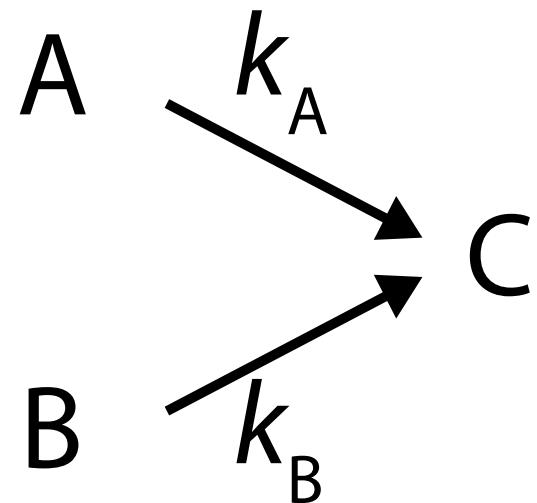
Case 2: First-order decay to the same product



Quiz: What are the integrated rate laws for all components?
In an exam, be able to also plot the concentrations over time.

A brief note on AI to enhance your learning experience – a very useful tool

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I am studying reaction kinetics.
What are the integrated rate laws for the individual components in a parallel reaction of A reacting to C and B reacting to C?

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I am studying reaction kinetics. What are the integrated rate laws for the individual components in a parallel reaction of A reacting to C and B reacting to C?



In a parallel reaction, two different reactants, A and B, independently react to form a common product C. The reactions can be represented as follows:



where k_1 and k_2 are the rate constants for the respective reactions.

To derive the integrated rate laws for the individual components A and B in this parallel reaction, we consider the kinetics of each reaction separately.

↓
1 Integrated Rate Law for A

1. Integrated Rate Law for A

Assuming the reaction of $A \rightarrow C$ is first-order with respect to A:

$$\frac{d[A]}{dt} = -k_1[A]$$

To find the integrated rate law for A, we separate the variables and integrate:

$$\int \frac{d[A]}{[A]} = - \int k_1 dt$$

This integration yields:

$$\ln[A] = -k_1 t + \ln[A]_0$$

Exponentiating both sides gives:

$$[A] = [A]_0 e^{-k_1 t}$$

where $[A]_0$ is the initial concentration of A.

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2. Integrated Rate Law for B

Similarly, assuming the reaction of $B \rightarrow C$ is first-order with respect to B:

$$\frac{d[B]}{dt} = -k_2[B]$$

Again, we separate the variables and integrate:

$$\int \frac{d[B]}{[B]} = - \int k_2 dt$$

This gives:

$$\ln[B] = -k_2 t + \ln[B]_0$$

Exponentiating both sides gives:

$$[B] = [B]_0 e^{-k_2 t}$$

Exponentiating both sides gives:

$$[B] = [B]_0 e^{-k_2 t}$$

where $[B]_0$ is the initial concentration of B.

Summary of Integrated Rate Laws

- For reactant A: $[A] = [A]_0 e^{-k_1 t}$
- For reactant B: $[B] = [B]_0 e^{-k_2 t}$

Integrated Rate Law for Product C

The formation of product C in a parallel reaction is the sum of the contributions from both reactions:

$$\frac{d[C]}{dt} = k_1[A] + k_2[B]$$

Substitute the integrated rate laws for [A] and [B]:

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Integrated Rate Law for Product C

The formation of product *C* in a parallel reaction is the sum of the contributions from both reactions:

$$\frac{d[C]}{dt} = k_1[A] + k_2[B]$$

Substitute the integrated rate laws for *[A]* and *[B]*:

$$\frac{d[C]}{dt} = k_1[A]_0 e^{-k_1 t} + k_2[B]_0 e^{-k_2 t}$$

To find the integrated form, integrate with respect to time:

$$C = [A]_0(1 - e^{-k_1 t}) + [B]_0(1 - e^{-k_2 t})$$

Summary of the Integrated Rate Law for Product *C*

$$C = [A]_0(1 - e^{-k_1 t}) + [B]_0(1 - e^{-k_2 t})$$



from both reactions:

$$\frac{d[C]}{dt} = k_1[A] + k_2[B]$$

Substitute the integrated rate laws for *[A]* and *[B]*:

$$\frac{d[C]}{dt} = k_1[A]_0 e^{-k_1 t} + k_2[B]_0 e^{-k_2 t}$$

To find the integrated form, integrate with respect to time:

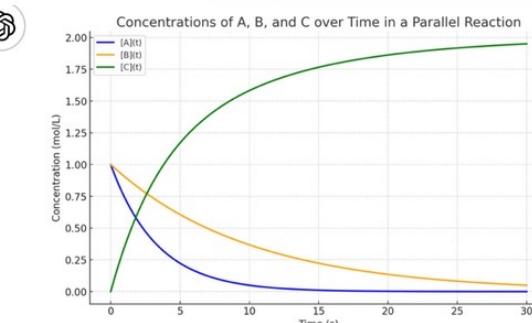
$$C = [A]_0(1 - e^{-k_1 t}) + [B]_0(1 - e^{-k_2 t})$$

Summary of the Integrated Rate Law for Product *C*

$$C = [A]_0(1 - e^{-k_1 t}) + [B]_0(1 - e^{-k_2 t})$$

These equations describe the concentrations of *A*, *B*, and *C* as functions of time in a parallel reaction system.

Plot A, B and C over time.



The plot above shows the concentrations of *A*, *B*, and *C* over time in a parallel reaction system where $A \rightarrow C$ and $B \rightarrow C$.

- **A** and **B** decrease exponentially over time as they are consumed in their respective reactions.
- **C** increases as the common product is formed from both *A* and *B*. Initially, the increase in *[C]* is rapid as both reactions contribute to its formation. As *A* and *B* deplete, the rate of increase in *[C]* slows down.

The shape of these curves is determined by the rate constants k_1 and k_2 , as well as the initial concentrations of *A* and *B*.

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2.4 Approximate Solutions

2.4.1 The Steady-State Approximation (SSA)

- **Condition:** **intermediates** A_i are only ever present in *small* concentrations
→ time derivative of this intermediate is negligible compared to other time derivatives, *i.e.*

$$\frac{d[A_i]}{dt} \approx 0$$

Careful, don't set $[A_i]$ itself to be =0! Why?

- **Example 1** (we solved this already): $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

Case: assume $k_2 \gg k_1$, so B reacts away faster than it is formed
 $\rightarrow [B]$ is small, can apply steady-state condition: $[B]_S$

- $\frac{d[B]_S}{dt} = k_1[A] - k_2[B]_S = 0$!
- $[B]_S = \frac{k_1}{k_2} [A] = \frac{k_1}{k_2} [A]_0 e^{-k_1 t}$ and therefore
- $[C] = [A]_0 (1 - e^{-k_1 t})$ same solution as before, slide 13! ☺
- C builds up as if B was not present and we simply had reaction $A \xrightarrow{k_1} C$

- **Example 1** (we solved this already): $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

with

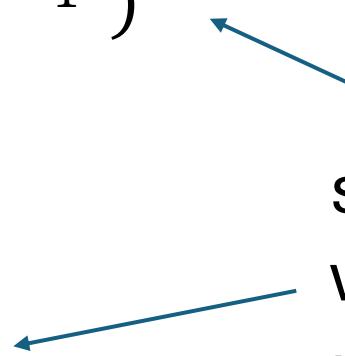
Case: assume $k_2 \gg k_1$

From previous slide:

$$[C] = [A]_0 \left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right) \approx [A]_0 (1 - e^{-k_1 t})$$

works equally well for inserting for B:

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \approx \frac{k_1}{k_2} [A]_0 e^{-k_1 t}$$



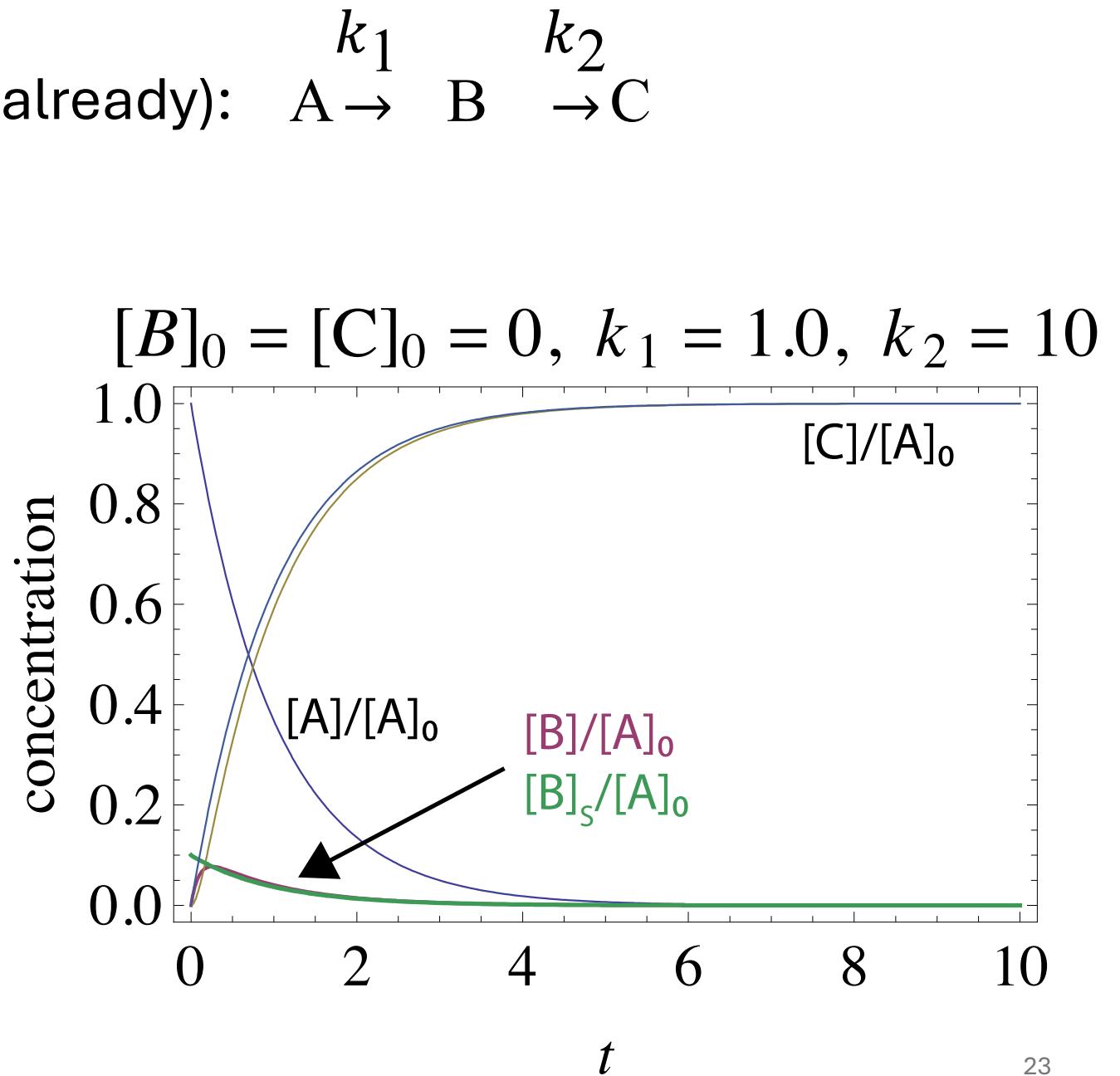
same results as
without having
made the SSA
before, for this
Case 1

- **Example 1** (we solved this already): $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

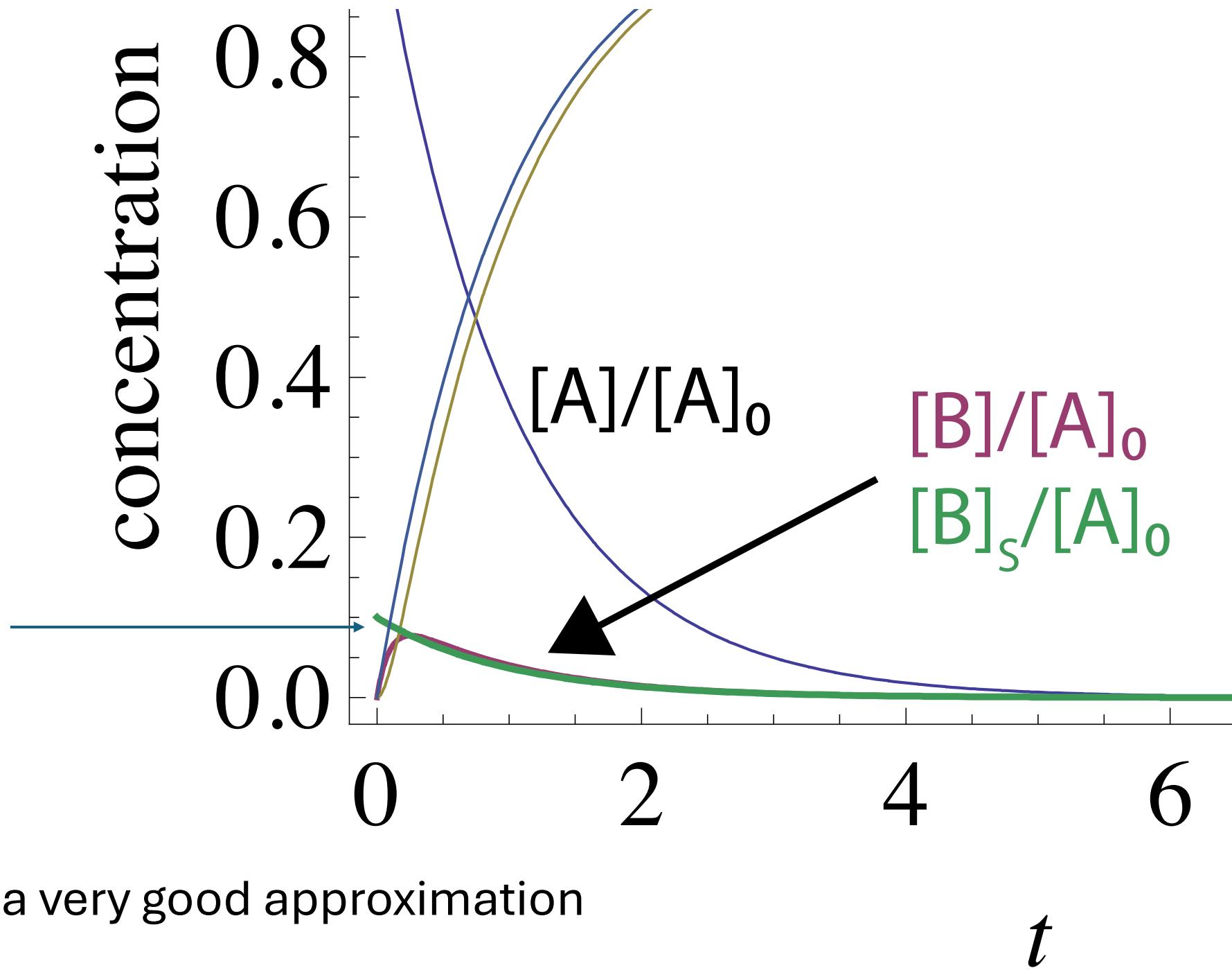
with

Case: assume $k_2 \gg k_1$

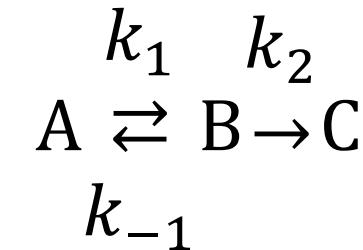
Exact solution (from before)
compared to
Steady-state approximation
 pretty good agreement! :)



...except
for this
early time
bit here:
B should
never be
this high...



- **Example 2: Consecutive reaction with reversible first step**



- e.g., in enzyme kinetics or therm. activated reactions
- Rate equations:
- $\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$
- $\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B]$
- $\frac{d[C]}{dt} = k_2[B]$
- Could solve these analytically, but let's use SSA!



- $\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B]$

- in SSA, B remains very small, so

- $\frac{d[B]_S}{dt} = k_1[A] - (k_{-1} + k_2)[B]_S \stackrel{!}{=} 0$

- $[B]_S = \frac{k_1}{k_{-1} + k_2} [A]$

- For applying this SSA, we need to assume: $k_1 \ll k_{-1} + k_2$
- Putting this solution in for the A and C rate equations, we find

- $\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]_S = \left(-k_1 + \frac{k_1 k_{-1}}{k_{-1} + k_2} \right) [A] = -\frac{k_1 k_2}{k_{-1} + k_2} [A]$

- $\frac{d[C]}{dt} = k_2[B]_S = \frac{k_1 k_2}{k_{-1} + k_2} [A]$

→

k_{eff}



- These results are like those gained for a much simpler $A \xrightleftharpoons[k_{-1}]{k_1, k_2} B \rightarrow C$ reaction, namely a simple first-order one:



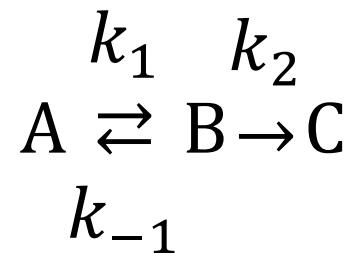
- Let's distinguish further between 2 cases within our initial assumption of $k_1 \ll k_{-1} + k_2$:

Case 1: $k_2 \gg k_{-1}$ (i.e. all B formed reacts straight to C)

- then $k_{eff} \approx k_1$ and the reaction behaves as if $A \rightarrow C$.

- $A \rightarrow B$ then is bottleneck of reaction, *i.e.* the **first step** is the *rate-limiting, rate-determining, or rate-controlling* step.

Case 2: Let's assume the **second step** $B \rightarrow C$ is **rate-limiting**!

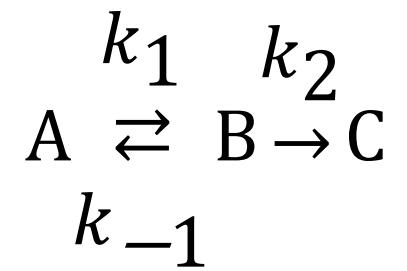


with the condition $k_{-1} \gg k_2$

Meaning:

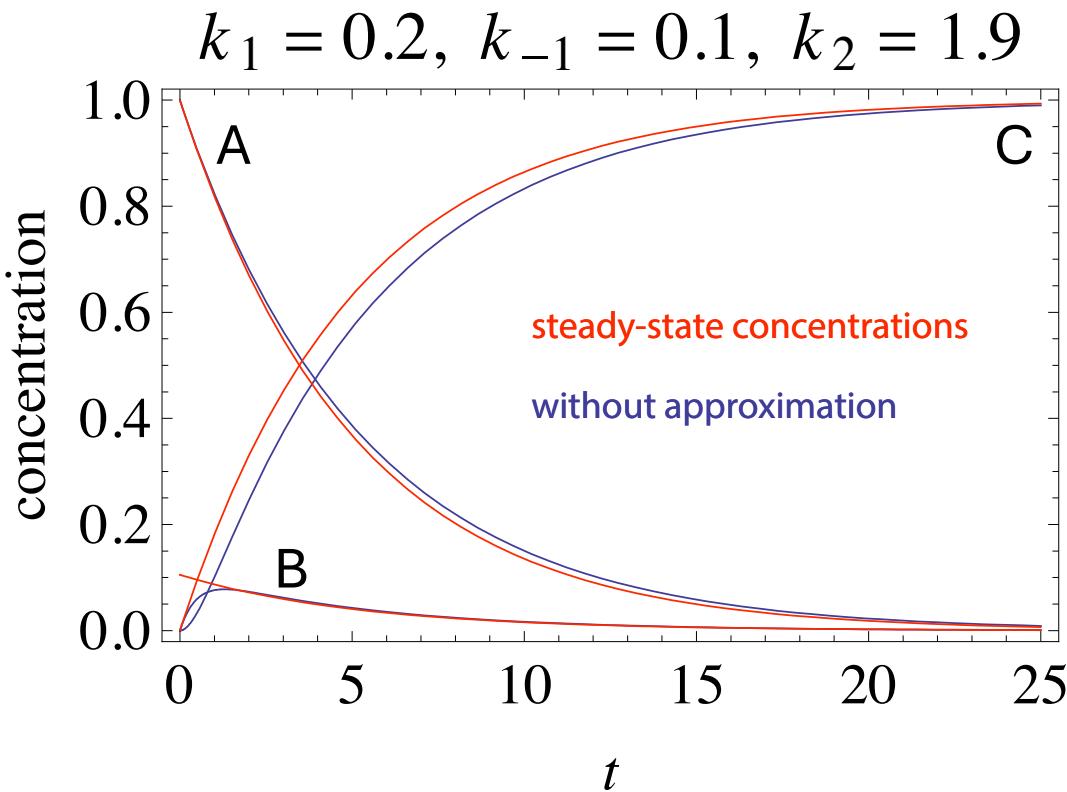
- $k_{eff} = \frac{k_1 k_2}{k_{-1}} = K k_2$ with $K = \frac{k_1}{k_{-1}}$
- Here, second step is so slow that A and B are in a *quasi-equilibrium*:

$$A \xrightleftharpoons[k_{-1}]{k_1} B$$
 with equilibrium const. $K = \frac{[B]}{[A]} = \frac{k_1}{k_{-1}}$
- This quasi-equilibrium is called ***pre-equilibrium***
- For C we find $\frac{d[C]}{dt} = k_{eff}[A] = \frac{k_1 k_2}{k_{-1}} [A] = K k_2 [A]$



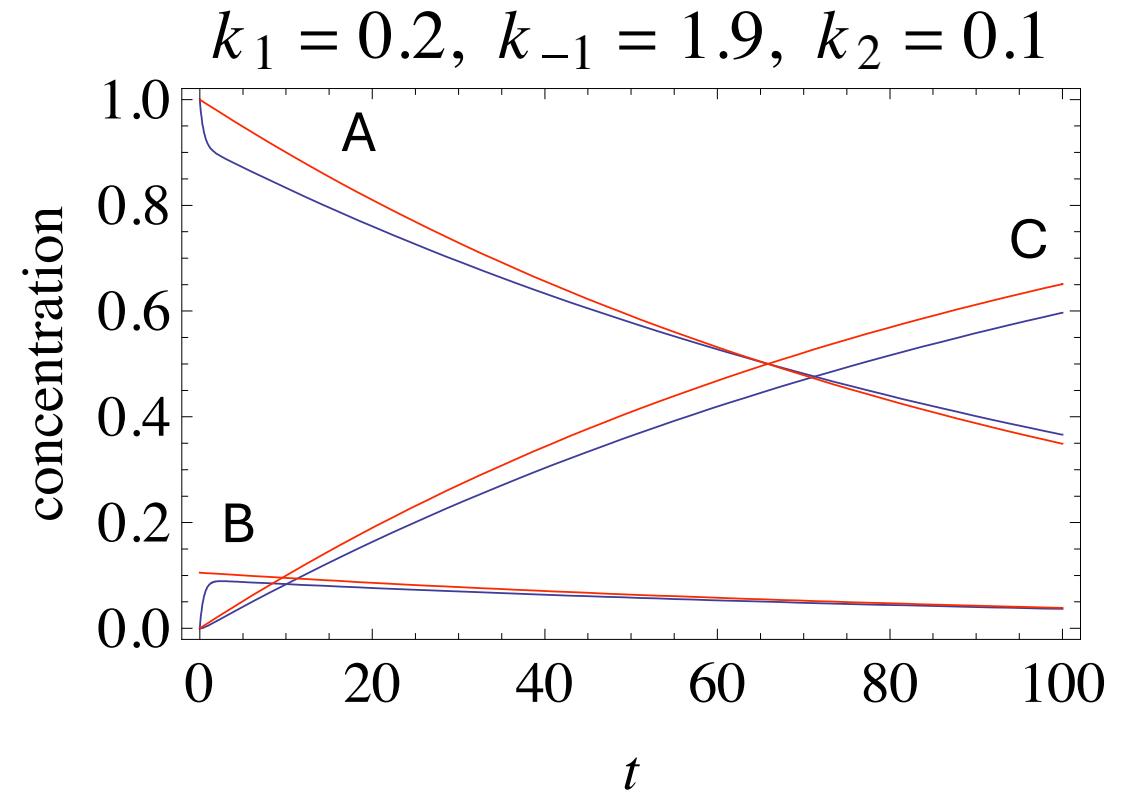
Case 1:

k_1
 $A \rightarrow B$ rate-limiting, $k_2 \gg k_{-1}$



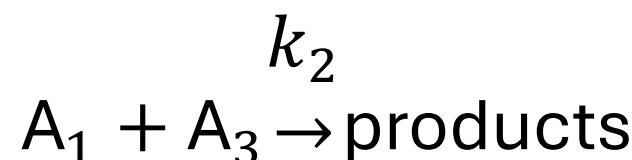
Case 2:

k_2
 $B \rightarrow C$ rate-limiting, $k_{-1} \gg k_2$



2.4.2 The Pseudo-First-Order Method

- Goal: do clever experiments to simplify analysis of complex reactions
- How? Flooding of the reaction with one reactant at a time

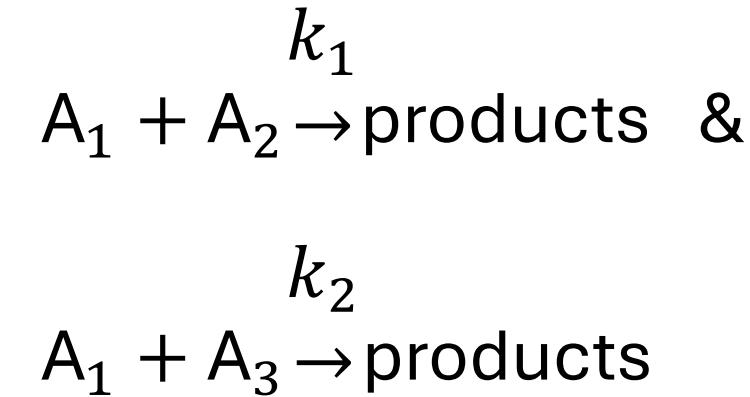


- Second order rate equations:

$$\frac{d[A_2]}{dt} = -k_1[A_1][A_2]$$

$$\frac{d[A_3]}{dt} = -k_2[A_1][A_3]$$

- Trick: supply $[A_1]$ in large excess in your reaction
- This results in $[A_1] \gg [A_2]$ and $[A_1] \gg [A_3]$
- What happens to $[A_1]$ over time?
- It stays essentially constant: $[A_1] \approx \text{const.}$
- Meaning effective rate constants can be used for
- $\frac{d[A_2]}{dt} = -k_1[A_1][A_2] \approx -\kappa_1[A_2]$
- $\frac{d[A_3]}{dt} = -k_2[A_1][A_3] \approx -\kappa_2[A_3]$
- reduced the complex problem to simple pseudo-1st-order ones! ☺
- Then just measure the monoexp. decays to get the κ 's, and from them calculate the k 's



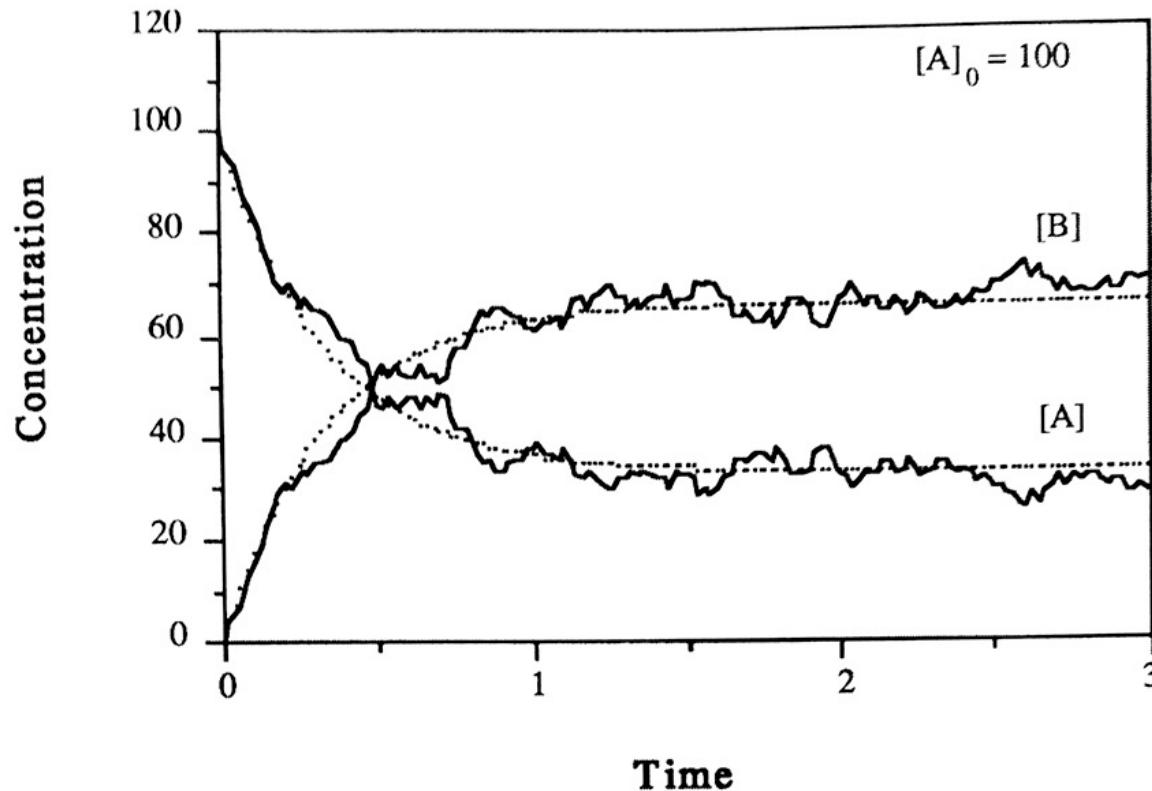
2.5 Exact Analytical Solution Methods

2.5.1 Matrix Method for Coupled Linear ODEs

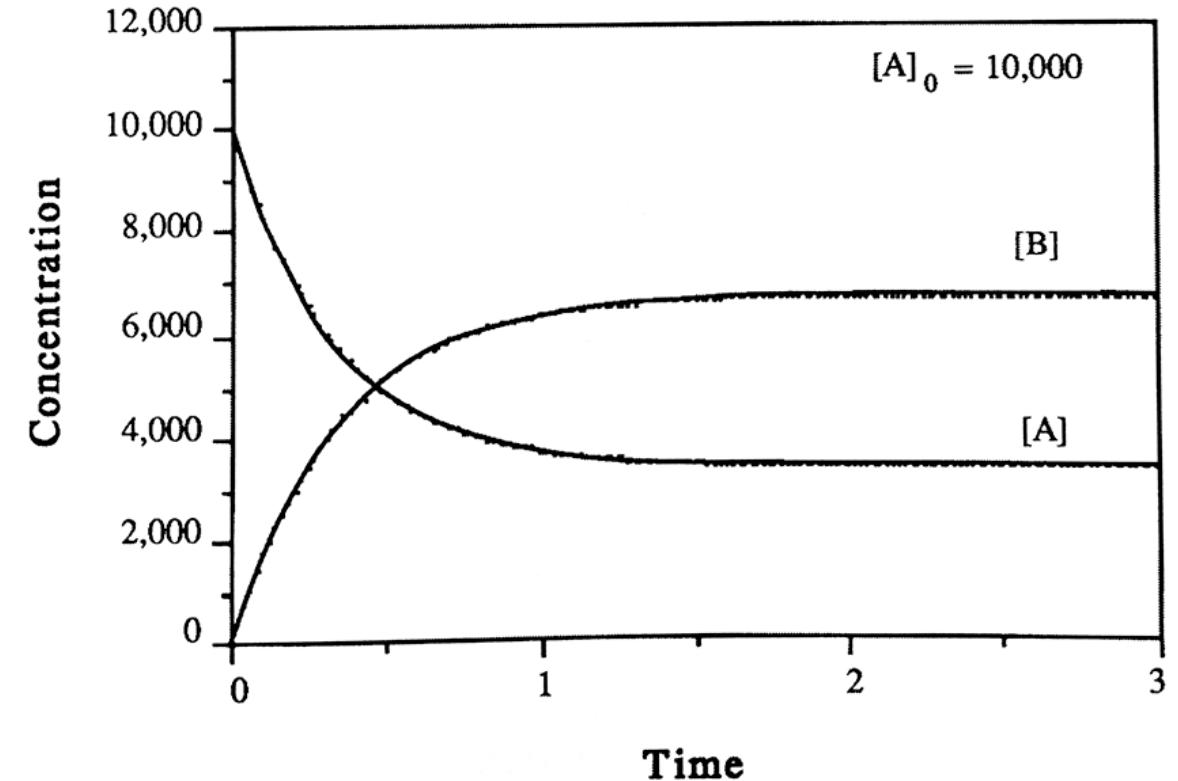
2.5.2 LaPlace Method for Coupled Linear ODEs

2.6 Numerical Solution Methods

2.6.1 The Stochastic Method



becomes important once number of collision partners small (e.g. in a cell)



compared to our *deterministic* approach so far (large numbers)