Week 10 Recitation

Chapter 9: Kinetics

Updates

- Exam II: Plan to upload grades by this Friday

- Assignment 8: Holding off on until after Exam II

- Veterans Day on November 11th

- November 25th: Last day of in-person lectures – that includes this recitation section

- As we near the end of the content for the course, considering adding office hours to help students (i.e. final exam prep)

- Lame duck period until January 20th, 2021

Questions?

What have we covered so far?

- Chapter 1: Molecular interpretation of energy and energy transfer
- Chapter 2: Energy is conserved
- Chapter 3: The Universe is fated to become boring
- Chapter 4: Will a process occur?
- Chapter 5: What is the probability of a process occurring?
- Chapter 8: Stuff moves y'all
- Chapter 9: If it moves, it can collide, and "productive" collisions make chemistry happen
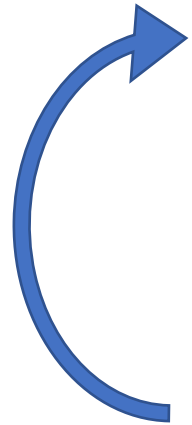
Kinetics

Kinetics: The study and understanding of the rate of change of anything

Chemical kinetics: The study of the rates of reactions

What can we study using kinetics?

- Reactions

- Macromolecular folding

- Isotopic decay

Why do we study kinetics?

Kinetics is the natural complement to thermodynamics – if what we have studied up to this point are descriptions of state, then this section will cover how quickly a system completes a process + considering competing processes.
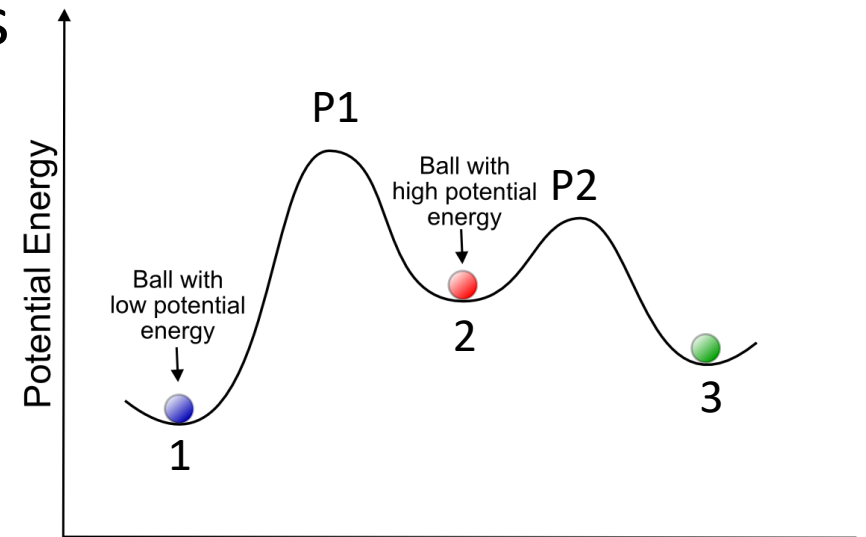
Points to clarify and topics to cover

- Rate law expressions ($v = k[A]^n[B]^m$) describe velocity (rate) of reaction with respect to the species of interest

- Order = n + m

- Units of k depend on the order the reaction ($M^x\ s^{-1}$) such that $v = M\ s^{-1}$

- Reactants **decrease** w/ time; products **increase** w/ time (dc/dt)

- Many systems are not just A → B:
  - We need to consider intermediates
  - Assumptions about intermediates (e.g. steady-state)
  - Other components of the system matter (catalysts, activities)

- Stoichiometry ≠ kinetic order

- For nA → mB: $v = -1/n * (dA/dt) = 1/m * (dB/dt)$

- A mechanism describes the series of steps that form the products

Reaction Order: 0

Order: The dependence of the rate on the concentration of a molecular species

Example: Zero-order expression

$$\frac{dc}{dt} = -k$$

- dc/dt is the change in **concentration** with respect to **time**
- k is a rate constant

Integrate the rate expression:

$$\int dc = -k \int dt = -k \int 1 \times dt$$

$$c(t) = -kt + C$$

- C is an integration constant corresponding to some initial condition
- Math note: If derivative of t w/ respect to t is 1, the integral of 1 is t

Reaction Order: 1

Order: The dependence of the rate on the concentration of a molecular species

Example: First-order expression

$$\frac{dc}{dt} = -k[c]$$

- [c] is the concentration of the species

Indefinite integral:

$$\int \frac{dc}{[c]} = -k \int dt$$

$$\ln([c]) = -kt + C$$

Definite integral:

$$\ln\left(\frac{[c]_2}{[c]_1}\right) = -k(t_2 - t_1) + C$$

Reaction Order: Decay

Order: The dependence of the rate on the concentration of a molecular species

$$\ln\left(\frac{[c]_2}{[c]_1}\right) = -k(t_2 - t_1) + C$$

To derive an equation for any [c] at t > 0:

Let $t_2 = t > 0$ and $t_1 = 0$,

$$\ln\left(\frac{[c]_t}{[c]_0}\right) = -k(t - 0)$$

Exponentiate and redistribute,

$$\frac{[c]_t}{[c]_0} = e^{-kt}$$

$$[c]_t = [c]_0 e^{-kt}$$

Applying the equations: Half-life

Half-life: An exponential decay process; for every period $t_{1/2}$, half of the species is lost to decay

$$[A]_{t_{1/2}} = [A]_0 e^{-kt_{1/2}}$$

$$\frac{[A]_0}{2} = [A]_0 e^{-kt_{1/2}}$$

Cancel $[A]_0$ and take natural log. to remove e,

$$-\frac{\ln\left(\frac{1}{2}\right)}{k} = t_{1/2} \equiv \frac{\ln(2)}{k}$$

Conclusion: We have determined a general formula for calculating the half-life when given the rate of decay for a first-order process.

Reviewing Dr. Foster's half-life decay fit

Data: Shelf life of penicillin
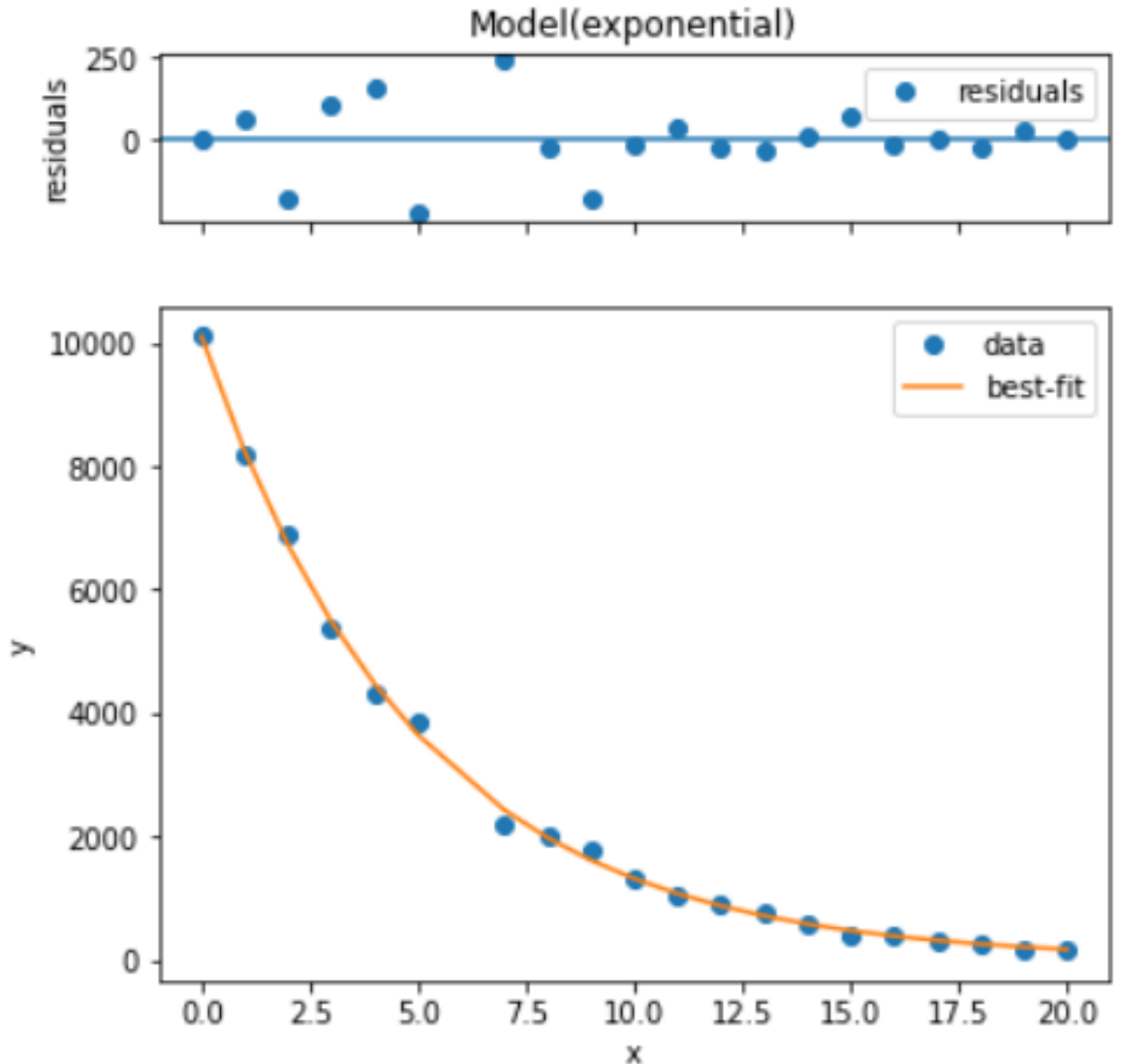
Check: Is this a decay process?

Plot: ln(penicillin_u) as f(time)

Check: Linear? If yes, exp() decay.

Fit: Take the equation derived on the previous slide and fit to data.

Assess: result.plot(), examine the residuals!

You want small and randomly distributed residuals – if this is not the result, reconsider the model used.

Reaction Order: 2

Order: The dependence of the rate on the concentration of a molecular species

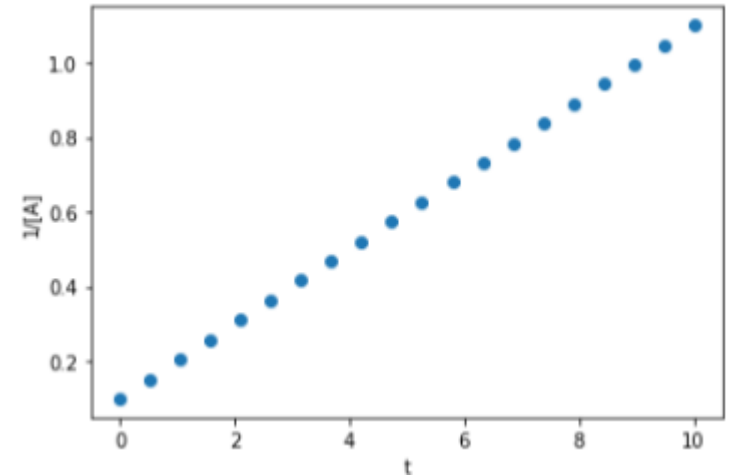Example: Second-order expression

$$\frac{dc}{dt} = -k[c]^2$$

Indefinite integral:

$$\int \frac{dc}{[c]^2} = -k \int dt$$

$$\frac{1}{[c]} = kt + C$$

Definite integral:

$$\frac{1}{[c]_2} - \frac{1}{[c]_1} = k(t_2 - t_1) + C$$

Reaction Order: Decay and Half-life

Order: The dependence of the rate on the concentration of a molecular species

$$\frac{1}{[c]_2} - \frac{1}{[c]_1} = k(t_2 - t_1) + C$$

To derive an equation for any [c] at t > 0:

Let t_2 = t > 0 and t_1 = 0,

$$\frac{1}{[c]_t} - \frac{1}{[c]_0} = k(t - 0)$$

Redistribute,

$$\frac{1}{[c]_t} = \frac{1}{[c]_0} + kt$$
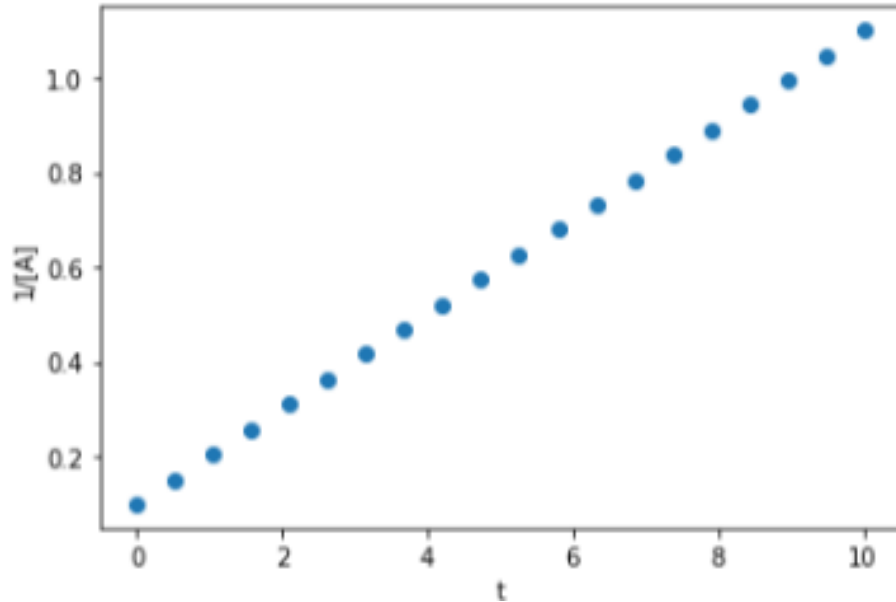
Half-life ($[c]_t = (1/2)[c]_0$):

$$\frac{1}{k[c]_0} = t_{1/2}$$

What about fitting second-order rxn data?

How can we tell if the reaction is second-order with respect to the reactant?

Examine the following:

- 1/[A] as f(time)

- Linear? Then second-order

- Also plot using derived model

This slide is a bit boring because this is a simple check – no big epiphanies to be had here.
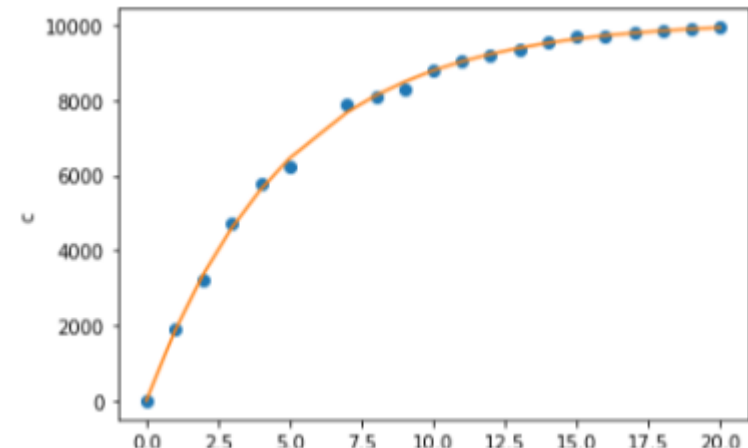
Applying the equations: Product Formation

Consider A → B, where reaction proceeds at some rate k:

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

$[B]_0 = 0$; $[A]_t$ decays; assume stoichiometric conversion from A to B:

$$[B] = [A]_0\left(1 - e^{-kt}\right)$$

- At t = 0, e^0 = 1 and [B] = 0
- As t → inf., [B] reaches eq. concentration
- If k is fast, then eq. achieved sooner
- If k is slow, then eq. achieved later

Concept Checks

What should be the units of reaction rate/velocity?

What linear plots indicate zero-, first-, and second-order reactions?

Is it a good idea to linearize data?

What sort of materials would be zero-order with respect to the reaction?

How does stoichiometry alter the rate expression? Why?

Concepts to be covered:

How do pseudo-order kinetics work? What are the advantages of this?

What does it mean to be a rate-limiting step?

Most processes are not stoichiometric conversions – how would we consider equilibria in kinetics?

Objectives for next lesson

Covering approximations and assumptions you can make about reactions

Initial rate approximation, steady-state, and pre-equilibrium kinetics

Arrhenius and temperature dependence + collision theory

Transition state theory

Any other questions about this or the trajectory of this recitation section?

Questions?