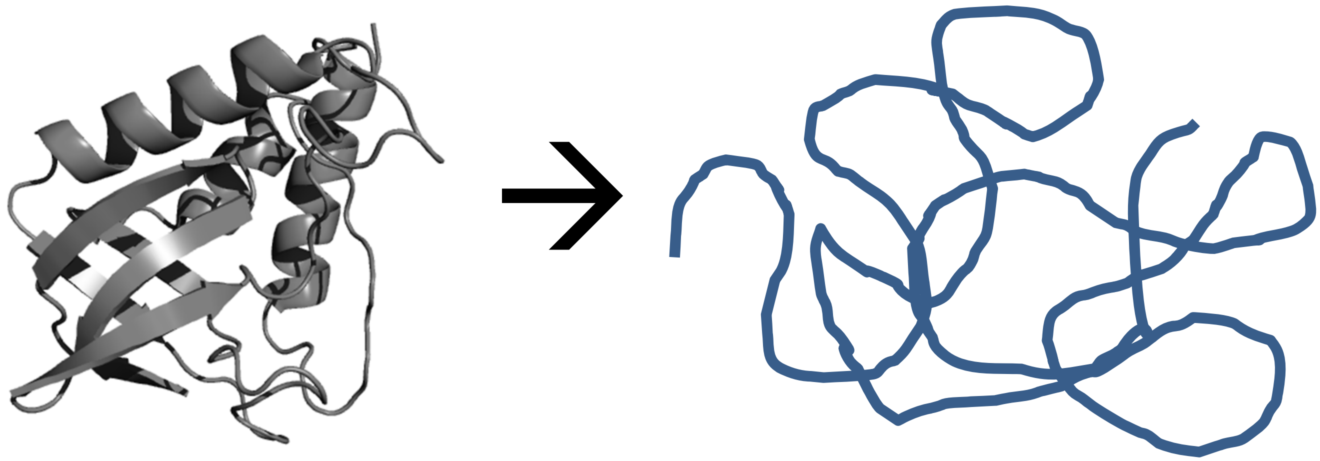
Chemical Kinetics



- **Question:** How fast much time does it take for a protein to unfold? *Why?*

- For that matter, how long does it take *any* reaction?

Chemical Kinetics: Concepts

- Any reaction (forward or reverse) will take a certain amount of time

- **Analogy:** Driving to Tupelo takes 1 hour

$$v_{avg} = \frac{\Delta x}{\Delta t} \text{ or } v = \frac{dx}{dt}$$

- Chemical reactions also have a “rate” at which they occur

Reaction Rates

- Instead of distance, reaction *velocities* measure the **change in concentration per unit time**

- Example:

$$v_{avg} = \frac{\Delta[A]}{\Delta t} \text{ or } v = \frac{d[A]}{dt}$$

- This is the change in [A] vs. time.

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Reaction Rates

- Consider a generic reaction:

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

- The *rate of formation* of C should probably depend on the concentrations (activities) of A, B, C, and D:

$$v_c = \frac{d[C]}{dt} = f([A],[B],[C],[D])$$

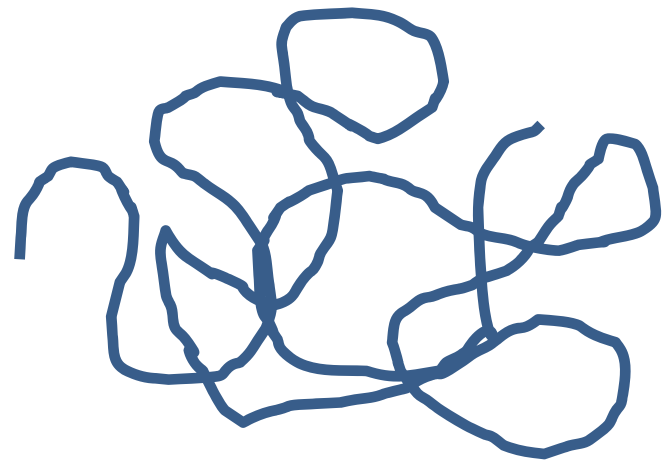
Thermodynamics *vs*. Kinetics

- **Thermodynamics:**
  - Will a reaction occur?
  - How much work can it do?

- **Kinetics:**
  - How quickly will a reaction occur?
  - What's the molecular mechanism?

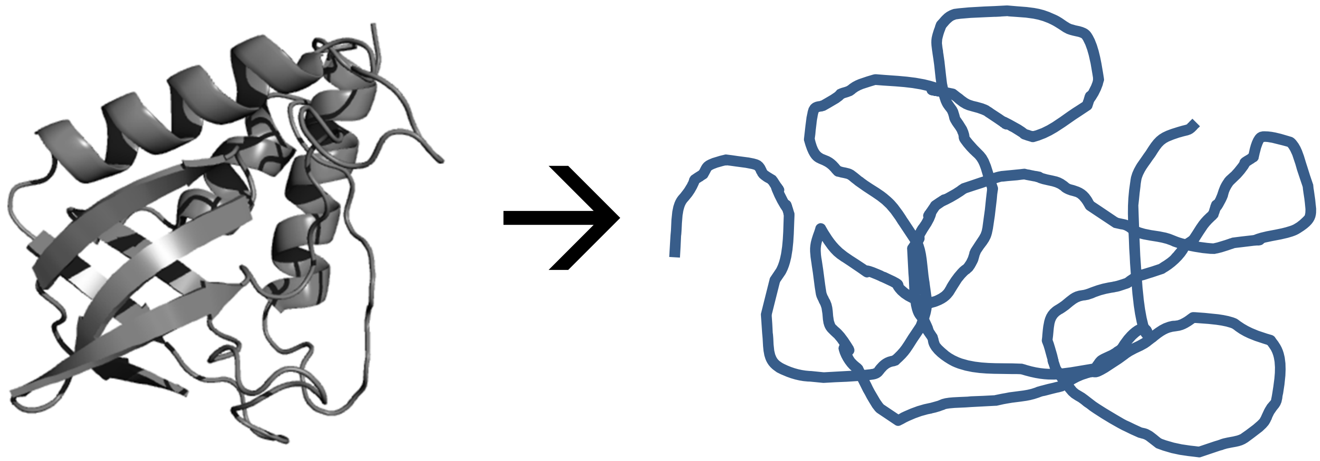
- **Both** involve creating and testing models!

Protein Folding Example



- If we're **not** at equilibrium, the *folded* state will change over time: $v_N = \frac{d[N]}{dt}$
- The *unfolded* state will also change: $v_U = \frac{d[U]}{dt}$
- **These rates should be related!**

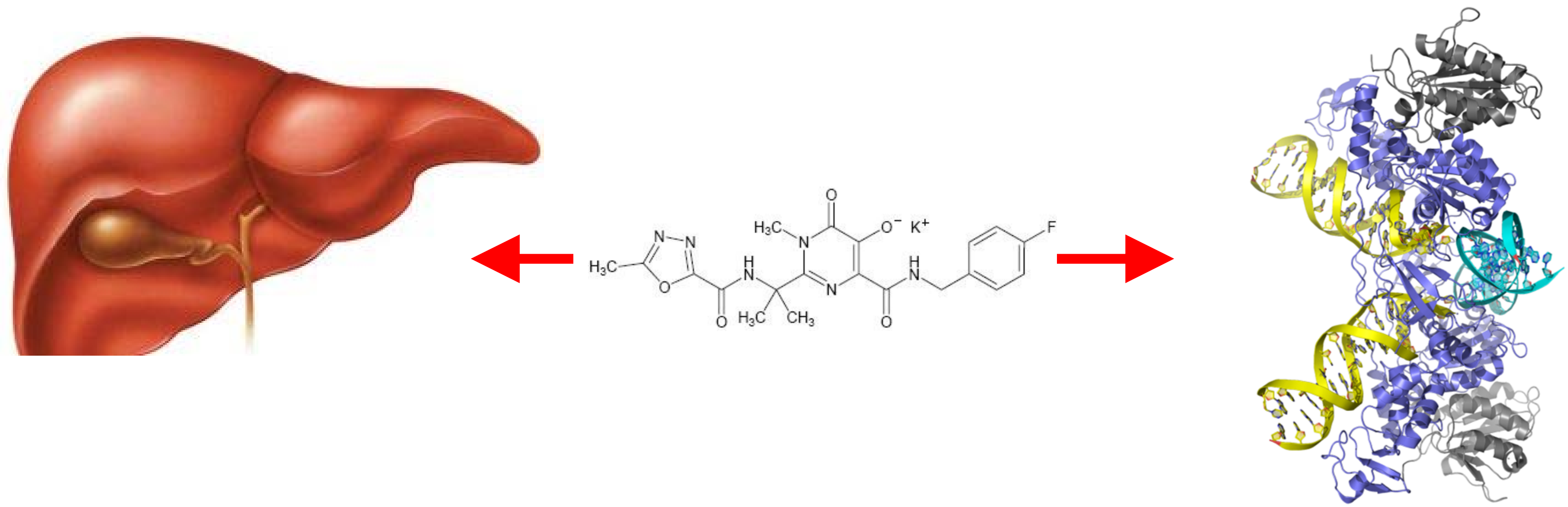
Protein Folding Example



- If we're **at** equilibrium, what happens to the *(actual)* velocities?

- What happens to the *measured* velocities?

Is Kinetics Important?



- Consider a drug which can bind your protein or be broken down
- Which pathway dominates?

How to Measure Kinetics?

- Given a generic chemical reaction:

$$A + B \rightarrow C$$

- Considerations:
  - A and B are colorless, C is bright green
  - You can purchase A and B (pure) from Sigma
  - C forms relatively slowly (minutes)

- **Think:** How could you measure [C] vs. time?

How to Measure Kinetics?

- Given a generic chemical reaction:

$$A + B \rightarrow C$$

- Considerations:
  - A, B and C are colorless
  - You can purchase A and B (pure) from Sigma
  - C forms relatively slowly (minutes)
  - $C + D \rightarrow E$ is very fast and irreversible, and E is bright green

- **Think:** How could you measure [C] vs. time?

How to Measure Kinetics?

- Ultimately, *it depends*
  - The rate itself (fast vs. slow)
  - Spectroscopic signal change (if any)
  - Whether chemistry can be “trapped”
  - Etc.

Kinetics Terminology

- **Stoichiometry:** Molar ratios of reactants and products

$$NO_2 + CO \rightarrow NO + CO_2$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

  – What produces what?

Kinetics Terminology

- **Reaction Mechanism:** A set of *elementary steps* that tell us exactly what's going on:

Stoichiometry { $NO_2 + CO \rightarrow NO + CO_2$

vs.

Overall mechanism {
$2NO_2 \rightarrow NO_3 + NO$ ⟵ Elementary step
$NO_3 + CO \rightarrow NO_2 + CO_2$

- If we know $\Delta \bar{G}_1^0$, do we know the mechanism?

Kinetics Terminology

- **Molecularity:** How many molecules are involved in (the first half) of an elementary step

Bimolecular reactions:

$$2NO_2 \rightarrow NO_3 + NO$$

$$NO_3 + CO \rightarrow NO_2 + CO_2$$

- Fundamentally, elementary steps are giving us more information than *just* stoichiometry

Kinetics Terminology

- **Rate Law:** A *model* that expresses the velocity of a reaction in terms of concentrations

$$v_A = \frac{d[A]}{dt} = k[A]^a[B]^b[C]^c$$

Rate constant

- It is **not possible** to deduce the rate law from stoichiometry alone!
  - Many rate law *models* are possible given one stoichiometry

Kinetics Terminology

- **Reaction Order:** An exponent in a rate law

$$v_A = \frac{d[A]}{dt} = k[A]^a[B]^b[C]^c$$

  - Reaction order of A is *a*
  - *Overall* reaction order is *a* + *b* + *c*

Chemical Kinetics and Differential Equations

- **Differential Equation:** An equation that relates a variable to a derivative of that variable

$$\frac{d}{dt}f(t) = f(t)$$

- DiffEQ's are the "bread and butter" of chemical kinetics:

$$\frac{d[A]}{dt} = k[A]^a$$

Zero Order Reactions

- **Rate Law:** The rate is constant

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