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

\[ \nu_{avg} = \frac{\Delta x}{\Delta t} \] or \[ \nu = \frac{dx}{dt} \]

• 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:

\[ \nu_{avg} = \frac{\Delta[A]}{\Delta t} \text{ or } \nu = \frac{d[A]}{dt} \]

• This is the change in [A] vs. time.
Reaction Rates

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• Example:

$$\nu_{avg} = \frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \nu = \frac{d[A]}{dt}$$

• This is the change in [A] vs. time.
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:

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

\[
\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2
\]

\[
2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}
\]

– What produces what?
Kinetics Terminology

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

\[
\begin{align*}
\text{NO}_2 + \text{CO} & \rightarrow \text{NO} + \text{CO}_2 \\
\text{vs.} \\
2\text{NO}_2 & \rightarrow \text{NO}_3 + \text{NO} \\
\text{NO}_3 + \text{CO} & \rightarrow \text{NO}_2 + \text{CO}_2
\end{align*}
\]

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

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

\[
\begin{align*}
2\text{NO}_2 & \rightarrow \text{NO}_3 + \text{NO} \\
\text{NO}_3 + \text{CO} & \rightarrow \text{NO}_2 + \text{CO}_2
\end{align*}
\]

• 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

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

• 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

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