Lecture 28  Chapt 19 beginning

Announce:

• Exam 3 isn’t that far away – Tues 25\textsuperscript{th} unless there are objections

Outline:

Kinetics
rate laws
  - isolation
  - initial rates
zero order
first order
second order
higher order
Reversible rxns
T dependence – Arrhenius
Transition state theory – Eyring

Review

\[ D = \frac{k_B T}{f} \]

Usually, \( D \) is measured, allowing calculation of the friction, \( f_{\text{EXP}} \).

\[ f_{\text{EXP}} = \frac{k_B T}{D} \]

Theoretically,

\[ f_{\text{THEO}} = 6\pi \eta r \]

\[ r = \left( \frac{3M(v_2 + \delta_1 v_1)}{4\pi N_A} \right)^\frac{1}{3} \]

\( v_1 = \) specific volume of the free solvent (cm\(^3\) g\(^{-1}\)) - inverse of density

\( v_2 = \) partial specific volume of the macromolecule (cm\(^3\) g\(^{-1}\)) - dependent on pH, salt concentration, etc. (shape of macromolecule can respond to many parameters).

\( \delta_1 = \) hydration (unitless) - weight of solvent bound per weight of molecule

Now, let’s define the general rxn:

\[ \nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z \]

and its velocity

\[ v(t) = \frac{d\left( \frac{\xi(t)}{V} \right)}{dt} = \frac{1}{\nu_A} \frac{d[A]}{dt} = \frac{1}{\nu_Z} \frac{d[Z]}{dt} \]
For example, nitrogen dioxide formation $2 \text{NO(g)} + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$

has the rate of reaction:

$$v(t) = \frac{-1}{2} \frac{d[\text{NO}]}{dt} = \frac{-d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

**Define rate law**

For most chemical reactions, $v$ is a function of time, or really a function of the species concentrations, which are themselves time dependent. The relationship between the rate of reaction and the species concentrations are given by the rate law. e.g.

$$v(t) = k [\text{NO}]^2 [\text{O}_2]$$

This one happens to, but the rate law generally does **NOT** correspond to the stoichiometry of the balanced reaction, because it depends on the details of the reaction mechanism.

$k$ is constant and is called the **rate constant** for the reaction

In general, rate laws look like:

$$v(t) = k [A]^{m_A} [B]^{m_B} \ldots$$

Each $m_j$ is called the order of the reaction for component $j$. The overall reaction order is simply the sum of all $m_j$.

overall order $= m_A + m_B + \ldots$

Reaction orders are usually integers, but fractions are possible if the mechanism is actually more complex than implied by the rate law. Often (many multistep rxns) a simple rate law cannot be written down and the order is undefined.

**How to determine a rate law**

Knowing the balanced chemical rxn does nothing to elucidate the rate law. The kinetics of the reaction must be measured. Understanding the rate law can then allow the rxn dynamics to be understood.

Back to our general reaction:

$$v_A A + v_B B \rightarrow v_Y Y + v_Z Z$$

Assume it has the rate law:

$$v = k [A]^{m_A} [B]^{m_B}$$

We can attempt to discover the reaction orders through a couple methods
**Method of isolation**

If we put one of the components in huge excess (A for instance), then the concentration of that component is essentially constant throughout the reaction.

Therefore, \( v = k \ [A]^{mA} \ [B]^{mB} \) becomes \( v = k' \ [B]^{mB} \)

So, measuring rate as a function of \([B]\) ([A] always >> [B]) gives \( m_B \)

The process is then repeated with \([B] >> [A]\) to find \( m_A \) from \( v = k'' \ [A]^{mA} \)

This can easily be extended to reactions of many components.

**Method of initial rates**

If we can measure the rate over a very short time interval, i.e. \( \xi \) is only slightly different at the beginning and end of the time interval, then \([A]\) and \([B]\) are both essentially constant. Doing this for two initial B concentrations gives:

\[
v_1 = -\frac{1}{V_A} \left( \frac{\Delta A}{\Delta t} \right) = k \ [A_1]^{mA} \ [B_1]^{mB}
\]

\[
v_2 = -\frac{1}{V_A} \left( \frac{\Delta A}{\Delta t} \right) = k \ [A_2]^{mA} \ [B_2]^{mB}
\]

Dividing these two equations gives:

\[
\frac{v_1}{v_2} = \left( \frac{B_1}{B_2} \right)^{mB} \quad \text{or} \quad m_B = \frac{\ln \left( \frac{v_1}{v_2} \right)}{\ln \left( \frac{B_1}{B_2} \right)}
\]

Note that both methods are limited to reactions that are slower than the time it takes to mix things together – generally milliseconds. Methods exist for faster rxns.

**Zero order reactions**

\( v(t) = k \quad \text{or} \quad \frac{d[A]}{dt} = -v_A k \)
Rearranging and integrating gives:
\[ d[A] = -\nu_A k dt \]

\[
\int_{[A]_b}^{[A]_t} d[A] = -\nu_A \int_0^t k dt'
\]

\[ [A]_t - [A]_b = -\nu_A kt \]

\[ [A]_t = -\nu_A kt + [A]_0 \]

So, plotting \([A]\) versus time gives a line.

Note that the half-life is given by
\[ \frac{1}{2}[A]_0 = -\nu_A k t_{1/2} + [A]_0 \]

\[ t_{1/2} = [A]_0 / 2\nu_A k \]

**First order reactions**

\[ v(t) = k [A] \quad \text{or} \quad \frac{d[A]}{dt} = -\nu_A k [A] \]

Similarly:

\[
\int_{[A]_b}^{[A]_t} \frac{d[A]}{[A]} = -\nu_A \int_0^t k dt'
\]

\[ \ln[A]_t - \ln[A]_b = -\nu_A kt \]

\[ \ln[A]_t = -\nu_A kt + \ln[A]_0 \]

\[ [A]_t = [A]_0 e^{-\nu_A kt} \]

So a plot of \(\ln[A]\) versus time gives a line (\([A]\) vs. \(t\) gives exp)
Note that for first order, the half life is:
\[ t_{\frac{1}{2}} = \frac{\ln 2}{\nu_A k} = 0.693 / \nu_A k \]

and is independent of the initial concentrations (radioactive decay and many simple photochemical reactions are first order)

Second and higher order reactions
(is in the notes – definitely check it out)
\[ v(t) = k [A]^2 \quad \text{or} \quad \frac{d[A]}{dt} = -\nu_A k [A]^2 \]

\[ \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -\nu_A k \int_0^t dt' \]

\[ -\left( \frac{1}{[A]} - \frac{1}{[A]_0} \right) = -\nu_A k t \]

\[ \frac{1}{[A]_t} = \nu_A k t + \frac{1}{[A]_0} \]

So, a plot of \(1/[A]\) versus time gives a line.

Higher order reactions are integrated exactly the same way and give
\[ [A]^{-(n-1)} = (n-1)\nu_A k t + [A]^{-(n-1)}_0 \]

The half-life for a second order reaction is \( t_{\frac{1}{2}} = 1 / \nu_A k [A]_0 \)

You should be able to derive any of these integrated rate law expressions for arbitrary order along with their half-lives.
Reversible Reactions

Of course, reactions are always reversible to some extent. Many times, the back reaction is very slow and we can safely ignore it but not in general. Usually, we write $A \leftrightarrow Z$ with forward rate $k_1$ and backward rate $k_{-1}$

At equilibrium we know 2 things?

The relative amounts of $A$ and $Z$: $K_{eq} = [Z]_{eq} / [A]_{eq}$

and the forward and backward rates must be equal: $k_1[A] = k_{-1}[Z]$ this is dynamic equilibrium and is described by the principle of detailed balance

How do we find $k_1$ and $k_{-1}$?

Let’s assume we have a rate law that is first order in both $A$ and $Z$. Then at any given time the rate of change in $A$ is:

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

If we started with $[A] = [A]_0$ and $[Z]_0 = 0$, then at any time $[Z] = [A]_0 - [A]$ so

$$-\frac{d[A]}{dt} = (k_1 + k_{-1})[A] - k_{-1}[A]_0$$

Integrating similarly to before gives

$$\ln([A] - [A]_{eq}) = -(k_1 + k_{-1})t + \ln([A]_0 - [A]_{eq})$$

so plotting $\ln(A-A_{eq})$ vs. $t$ gives a line with the slope that is the sum of the rates.

But, we also know that at equilibrium $k_1[A]_{eq} = k_{-1}[Z]_{eq}$

so

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

(Detailed Balance!)

Therefore, we can find both the sum and ratio of the rates and know both of them.
Relaxation methods

Many kinds of relaxation methods are used to measure these rates. We don’t have time to explore them, but they involve a fast perturbation of the equilibrium away from the current equilibrium (say a temperature jump with a capacitor or laser or something more subtle) and measuring how quickly the system adjusts itself. We can get into these in more detail during the last two days of the semester if you like.

Temperature dependence of rates

Empirically, we find that most reaction rates depend very strongly on temperature. Much more than you would expect just from the collision rates of molecules. From empirical studies, \( \frac{d \ln k}{dT} = \text{const} \frac{RT^2}{E_a} \) This constant behaves like energy, and we call it? activation energy.

\[
\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad \text{or} \quad \frac{d \ln k}{d\left(\frac{1}{T}\right)} = -\frac{E_a}{R}
\]

This integrates to \[
\int d(\ln k) = \frac{E_a}{R} \int T^{-2} dT
\]

\[
\ln k = -\frac{E_a}{RT} + \text{Const(\ln A)}
\]

\[
k = Ae^{-E_a/RT}
\]

(Arrhenius 1889)

The constant \(A\) is called the pre-exponential factor. \(E_a\) is the (internal energy) difference between reactants and the transition state along a coordinate called the reaction coordinate. For something like \(I_2\) dissociating it is the I-I bond length. For other reactions it is a complex collection of coordinates.