Foundations of Chemical Kinetics

Lecture 1: Review of basic concepts in kinetics

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Rate of change

\[ \frac{dx}{dt} = \lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t} \]
Consider a reaction $aA + bB \rightarrow cC + eE$. 
The rates of change of the concentrations ($d[A]/dt$, $d[B]/dt$, $d[C]/dt$ and $d[E]/dt$) are all related by stoichiometry:

$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{e} \frac{d[E]}{dt}$$

We arbitrarily define the rate of reaction, $\nu$, as the rate of change of the concentration of a product with a unit stoichiometric coefficient. Thus,

$$\nu = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{e} \frac{d[E]}{dt}$$
Rate of reaction examples

1. For the reaction $A + B \to C$,

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

2. For the reaction $2A \to B$,

$$v = -\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt}$$
An elementary reaction occurs in one step, exactly as written.

A complex reaction occurs in multiple steps.

A reaction mechanism is a list of all the steps in a complex reaction.
Order of a reaction

- A rate law is a relationship between the rate of a reaction and the concentrations of the chemical species in the reactive mixture.
- All elementary reactions and some complex reactions have rate laws of the form

\[ v = k[X]^x[Y]^y \ldots \]

where X, Y, \ldots are chemical species (usually reactants, but also possibly products or even substances that do not appear in the overall reaction).
- \( x \) is the (partial) order of the reaction with respect to X.
- \( x + y + \ldots \) is the overall order of the reaction.
- \( k \) is called a rate constant.
Properties of the rate constant

- Rate constants are always positive.
- Elementary rate constants depend on the temperature and solvent, and may depend indirectly on the concentrations of reactants and products through the pH and ionic strength. Elementary rate constants have no direct dependence on the concentrations of reactants and products.
- Rate constants can vary over many orders of magnitude, even within a family of related reactions.
Law of mass-action

The rate of an elementary reaction is proportional to the product of the reactant concentrations.

In other words, the partial orders are equal to the molecularity of the reactants.
Mass-action examples

1. For the reaction \( A + B \rightarrow C \),

\[ v = k[A][B] \]

2. For the reaction \( 2A \rightarrow B \),

\[ v = k[A]^2 \]

Since

\[ v = -\frac{1}{2} \frac{d[A]}{dt}, \]

\[ \frac{d[A]}{dt} = -2v = -2k[A]^2. \]
A hand-waving explanation of the law of mass-action

- An $A + B$ reaction requires that the two reactants come together.
- All other things being equal, we would expect that encounters between $A$ and $B$ molecules, and thus the rate, would increase when we increase either the concentration of $A$ or the concentration of $B$.
- Note that this line or argument does not require the relationship between $v$ and $[A]$ or between $v$ and $[B]$ to be a simple proportionality.
A unimolecular elementary reaction $A \rightarrow$ implies that $A$ spontaneously decays into products without any direct involvement of other molecules.

- Stereotypical example: radioactive decay

- If $A$ really can decay to products without any help, then $k$ represents a reaction probability per unit time.

- Doubling the concentration of $A$ should double the number of reactive events per unit time, i.e. the rate.
Temperature dependence of chemical reactions

Over relatively large temperature ranges, the temperature dependence of almost any elementary rate constant is given by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

- $A$ is the preexponential factor.
- $E_a$ is the activation energy.

In Arrhenius theory, both $A$ and $E_a$ are positive constants. In particular, they are independent of $T$.

What happens at small $T$?

What happens at large $T$?