Foundations of Chemical Kinetics Lecture 1: Review of basic concepts in kinetics

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Elementary and complex reactions

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.

Intermediates are species that are formed and removed in the process of converting reactants to products.

Rate of reaction

- Consider a reaction $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + e\mathrm{E}$.
  The rates of change of the concentrations ($d[\mathrm{A}]/dt$, $d[\mathrm{B}]/dt$, $d[\mathrm{C}]/dt$ and $d[\mathrm{E}]/dt$) are all related by stoichiometry:

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

- We arbitrarily define the rate of reaction, v, as the rate of change of the concentration of a product with a unit stoichiometric coefficient. Thus,

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

Rate of reaction examples

1. For the reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$,

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

2. For the reaction $2\mathrm{A} \rightarrow \mathrm{B}$,

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

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 simple rate laws of the form

  $$v = k[\mathrm{X}]^x[\mathrm{Y}]^y \ldots$$

  where X, Y, … 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.
- 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 stoichiometric coefficients of the reactants.

Mass-action examples

Assume that all of the following reactions are elementary.

1. For the reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$,

$$v = k[\mathrm{A}][\mathrm{B}]$$

2. For the reaction $2\mathrm{A} \rightarrow \mathrm{B}$,

$$v = k[\mathrm{A}]^2$$

Since

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

$$\frac{d[\mathrm{A}]}{dt} = -2v = -2k[\mathrm{A}]^2.$$

Mass-action examples

3. For the reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{P}$,
    - $v = k[\mathrm{A}][B]$
    - $d[\mathrm{A}]/dt = 0$
    - A is a catalyst.

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 hand-waving explanation of the law of mass action

(continued)

- 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.

Rates in complex reactions

- The rate of change of a particular concentration in a complex reaction is obtained by adding the rates of change due to all of the reactions in which a species appears.
- Example:

$$2\,\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_2} \mathrm{A} + \mathrm{P}$$

$$\begin{aligned}
\frac{d[\mathrm{A}]}{dt} &= -2k_1[\mathrm{A}]^2 + 2k_{-1}[\mathrm{C}] + k_2[\mathrm{C}] \\
\frac{d[\mathrm{C}]}{dt} &= k_1[\mathrm{A}]^2 - k_{-1}[\mathrm{C}] - k_2[\mathrm{C}] \\
\frac{d[\mathrm{P}]}{dt} &= k_2[\mathrm{C}]
\end{aligned}$$

The steady-state approximation

- Complex mechanisms are often treated using approximations, typically based on the fact that intermediates are usually highly reactive.
- Consider the mechanism

$$2\,\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_2} \mathrm{A} + \mathrm{P}$$

- When the reaction starts, $[\mathrm{C}] = 0$.
  $[\mathrm{C}]$ will increase initially, but because it is (usually) highly reactive, we soon reach a condition in which C is removed as fast as it can be made.
- The latter phrase implies that the concentration of C becomes steady, i.e. that

$$\frac{d[\mathrm{C}]}{dt} \approx 0$$

The steady-state approximation (continued)

$$2\,\mathrm{A} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{C} \xrightarrow{k_2} \mathrm{A} + \mathrm{P}$$

Get a rate using the following steps:

1. The overall reaction is A → P, so the rate of reaction is $v = d[\mathrm{P}]/dt$.
2. From the mechanism and the law of mass action, $d[\mathrm{P}]/dt = k_2[\mathrm{C}]$.
3. Write down an equation for [C] and apply the SSA to solve for the intermediate:

$$\frac{d[\mathrm{C}]}{dt} = k_1[\mathrm{A}]^2 - k_{-1}[\mathrm{C}] - k_2[\mathrm{C}] \approx 0$$

$$\therefore [\mathrm{C}] \approx \frac{k_1[\mathrm{A}]^2}{k_{-1} + k_2}$$

$$\therefore v = k_2[\mathrm{C}] \approx \frac{k_1 k_2[\mathrm{A}]^2}{k_{-1} + k_2}$$

The equilibrium approximation

$$2\,\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_2} \mathrm{A} + \mathrm{P}$$

- What if 2A $\rightleftharpoons$ C equilibrates much faster than the decay to product?
- Use the equilibrium approximation:

$$k_1[\mathrm{A}]^2 \approx k_{-1}[\mathrm{C}]$$
$$\therefore [\mathrm{C}] \approx k_1[\mathrm{A}]^2/k_{-1}$$
$$\therefore v = k_2[\mathrm{C}] \approx k_1 k_2[\mathrm{A}]^2/k_{-1}$$

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:

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

A	is the preexponential factor.
ϵ_a, E_a	is the activation energy (resp. per molecule or per mole)

- 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?