

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

Marc R. Roussel

September 7, 2021

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 $aA + bB \rightarrow cC + eE$.

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, v , as the rate of change of the concentration of a product with a unit stoichiometric coefficient. Thus,

$$v = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{e} \frac{d[E]}{dt}$$

Rate of reaction examples

1 For the reaction $A + B \rightarrow C$,

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

2 For the reaction $2A \rightarrow B$,

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

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

$$v = k[X]^x[Y]^y \dots$$

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.
- $x + y + \dots$ 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 $A + B \rightarrow C$,

$$v = k[A][B]$$

2 For the reaction $2A \rightarrow B$,

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

Since

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

Mass-action examples

- 3 For the reaction $A + B \rightarrow A + P$,
- $v = k[A][B]$
 - $d[A]/dt = 0$
 - 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 of argument does not require the relationship between v and $[A]$ or between v and $[B]$ to be a simple proportionality.

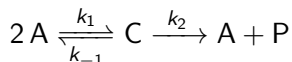
A hand-waving explanation of the law of mass action

(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:



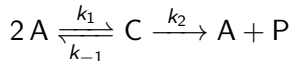
$$\frac{d[A]}{dt} = -2k_1[A]^2 + 2k_{-1}[C] + k_2[C]$$

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

$$\frac{d[P]}{dt} = k_2[C]$$

The steady-state approximation

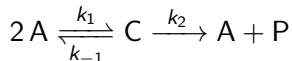
- Complex mechanisms are often treated using approximations, typically based on the fact that intermediates are usually highly reactive.
- Consider the mechanism



- When the reaction starts, $[C] = 0$.
 $[C]$ 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

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

The steady-state approximation (continued)



Get a rate using the following steps:

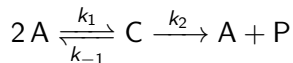
- 1 The overall reaction is $A \rightarrow P$, so the rate of reaction is $v = d[P]/dt$.
- 2 From the mechanism and the law of mass action, $d[P]/dt = k_2[C]$.
- 3 Write down an equation for $[C]$ and apply the SSA to solve for the intermediate:

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

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

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

The equilibrium approximation



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

$$k_1[A]^2 \approx k_{-1}[C]$$

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

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

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 ?