Rate laws
Reaction mechanisms
Reaction mechanisms and rate
Effect of temperature on reaction rates
Catalysis
Chemical Kinetics (I-1)
• Why do some chemical reactions proceed with lightning speed when others require days, months, or even years?
• How do catalysts increase the rates of chemical reactions?
• Why do small changes in temperature often have large effects on the reaction rate?
• How does a study of the rate of a chemical reaction inform us about the way in which molecules combine to form products?

All of these questions is the subject of chemical kinetics.
Rate of chemical reactions

<Measuring reaction rates>

\[ aA + bB \rightarrow cC + dD \]

Average reaction rate = \frac{\text{change in concentration}}{\text{change in time}}

Average rate = \frac{\Delta [P]}{\Delta t}, \ [P] = \text{concentration of a product}

\[
\begin{align*}
\text{rate} &= - \frac{1}{a} \frac{d[A]}{dt} = - \frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \\
\end{align*}
\] [18.1]
The relation between the rate of a reaction and concentration is called a rate law.

Rate law (or empirical rate expression)

\[
\text{rate} = k[A]^n[B]^m
\]

zeroth order in A for \(n = 0\); first order in A for \(n = 1\); second order in A for \(n = 2\); the order of a reaction does not have to be an integer. Overall reaction order is \(n + m\).
<Integrated rate laws>

Integrated rate law expresses the concentration of a species directly as a function of time.

**First-order reactions**

\[ \text{N}_2\text{O}_5(g) \rightarrow 2 \text{NO}_2(g) + \frac{1}{2} \text{O}_2(g) \]

rate \( = -\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5] \)

\( c = c_0 e^{-kt} \) (\( c_0 \): initial concentration) \[18.2\]

\( t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k} \) \[18.3\]
second-order reactions

\[ 2 \text{ NO}_2(g) \rightarrow 2 \text{ NO}(g) + \text{ O}_2(g) \]

rate \(= -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k[\text{NO}_2]^2 \)

\[ \frac{1}{c} = \frac{1}{c_0} + 2kt \quad [18.4] \]

\[ t_{1/2} = \frac{1}{2k[\text{NO}_2]_0} \]
Many reactions do not occur in a single step, but rather proceed through a sequence of steps to arrive at the products. Each step is called an elementary reaction and occurs through the collisions.

**<Elementary reactions>**

A unimolecular elementary reaction involves only a single reactant molecule.

\[
N_2O_5^*(g) \rightarrow NO_2(g) + NO_3(g)
\]

\[
\text{rate} = k[N_2O_5^*]
\]
The most common type of elementary reaction involves the collision of two atoms, ions, or molecules, and is called **bimolecular**.

\[
\text{NO}(g) + O_3(g) \rightarrow \text{NO}_2(g) + O_2(g)
\]
\[\text{rate} = k\left[\text{NO}\right]\left[O_3\right]\]

A **termolecular** reaction step involves the simultaneous collision of three molecules.

\[
\text{I}(g) + \text{I}(g) + \text{Ar}(g) \rightarrow \text{I}_2(g) + \text{Ar}(g)
\]
\[\text{rate} = k[\text{I}]^2[\text{Ar}]\]

Elementary reactions involving collisions of four or more molecules are not observed, and even termolecular collisions are rare if other pathways are possible.
Solvent molecules are present in liquid phase and may affect the reaction, even though they do not appear in the rate expression because the solvent concentration cannot be varied appreciably.
A reaction mechanism is a detailed sequence of elementary reactions.

\[
\begin{align*}
\text{NO}_2(g) + \text{NO}_2(g) & \rightarrow \text{NO}_3(g) + \text{NO}(g) \quad \text{(slow) eq 1} \\
\text{NO}_3(g) + \text{CO}(g) & \rightarrow \text{NO}_2(g) + \text{CO}_2(g) \quad \text{(fast) eq 2}
\end{align*}
\]

\[
\text{eq 1 + eq 2} \rightarrow
\begin{align*}
2 \text{NO}_2(g) + \text{NO}_3(g) + \text{CO}(g) & \rightarrow \text{NO}_3(g) + \text{NO}(g) + \text{NO}_2(g) + \text{CO}_2(g) \\
\text{NO}_2(g) + \text{CO}(g) & \rightarrow \text{NO}(g) + \text{CO}_2(g)
\end{align*}
\]

A reaction intermediate (here, NO\textsubscript{3}) is a chemical species that is formed and consumed in the reaction.
<Kinetics and chemical equilibrium>

\[
\begin{align*}
2 \text{NO}(g) + 2 \text{H}_2(g) & \rightleftharpoons \text{N}_2(g) + 2 \text{H}_2\text{O}(g) \\
\text{NO}(g) + \text{NO}(g) & \rightleftharpoons \text{N}_2\text{O}_2(g) \\
\text{N}_2\text{O}_2(g) + \text{H}_2(g) & \rightleftharpoons \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g) \\
\text{N}_2\text{O}(g) + \text{H}_2(g) & \rightleftharpoons \text{N}_2(g) + \text{H}_2\text{O}(g)
\end{align*}
\]

\[
K = K_1K_2K_3 = \frac{[\text{H}_2\text{O}]_{eq}[\text{N}_2]_{eq}}{[\text{NO}]_{eq}^2[\text{H}_2]_{eq}^2}
\]

\[
= \frac{k_1k_2k_3}{k_{-1}k_{-2}k_{-3}} = \frac{[\text{N}_2\text{O}_2]_{eq}[\text{N}_2\text{O}]_{eq}[\text{H}_2\text{O}]_{eq}[\text{N}_2]_{eq}[\text{H}_2\text{O}]_{eq}}{[\text{NO}]_{eq}^2[\text{N}_2\text{O}_2]_{eq}[\text{H}_2]_{eq}[\text{N}_2\text{O}]_{eq}[\text{H}_2]_{eq}}
\]
Chemical Kinetics (I-2)
In many reactions mechanisms, one step is significantly slower than all the others; this step is called the rate-determining step.

If the rate-determining step is the first one, the analysis is particularly simple.

\[
2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g)
\]

\[
\text{rate} = k_{\text{obs}}[\text{NO}_2][\text{F}_2]
\]

A possible mechanism is

\[
\text{NO}_2(g) + \text{F}_2(g) \xrightarrow{k_1} \text{NO}_2\text{F}(g) + \text{F}(g) \quad \text{(slow)}
\]

\[
\text{NO}_2(g) + \text{F}(g) \xrightarrow{k_2} \text{NO}_2\text{F}(g) \quad \text{(fast)}
\]

The first step is slow and determines the rate \(k_{\text{obs}} = k_1\), and the subsequent fast step does not affect the reaction rate.
Mechanisms in which the rate-determining step occurs after one or more fast steps are often signaled by a reaction order greater than 2, by a non-integral reaction order, or by an inverse concentration dependence on one of the species.

An example is

\[
\begin{align*}
2 \text{ NO}(g) + \text{ O}_2(g) &\rightarrow 2 \text{ NO}_2(g) \\
\text{rate} &= k_{\text{obs}}[\text{NO}]^2[\text{O}_2]
\end{align*}
\]

One possible mechanism would be a single-step termolecular reaction, but termolecular collisions are rare, and if there is an alternative pathway it is usually followed.
One such alternative is the two-step mechanism

\[
\begin{align*}
\text{NO}(g) + \text{NO}(g) & \xrightleftharpoons[k^{-1}_1]{k_1} \text{N}_2\text{O}_2(g) \quad \text{(fast equilibrium)} \\
\text{N}_2\text{O}_2(g) + \text{O}_2(g) & \xrightleftharpoons[k^{-2}_2]{k_2} 2 \text{NO}_2(g) \quad \text{(slow)} \\
\text{rate} &= k_2[\text{N}_2\text{O}_2][\text{O}_2] \\
\frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} &= \frac{k_1}{k^{-1}_1} = K_1 \\
[\text{N}_2\text{O}_2] &= K_1[\text{NO}]^2 \\
\text{rate} &= k_2 K_1[\text{NO}]^2[\text{O}_2]
\end{align*}
\]
In some reaction mechanisms, there is no single step that is much slower than the others. In such cases we use the steady-state approximation.

\[
\begin{align*}
N_2O_5(g) & \rightarrow 2 \ NO_2(g) + \frac{1}{2} \ O_2(g) \\
N_2O_5(g) + M(g) & \xrightleftharpoons{k_1}{k^{-1}} N_2O_5^*(g) + M(g) \\
N_2O_5^*(g) & \rightarrow NO_3(g) + NO_2(g) \\
NO_3(g) + NO_2(g) & \rightarrow NO(g) + NO_2(g) + O_2(g) \quad \text{(fast)} \\
NO_3(g) + NO(g) & \rightarrow 2 \ NO_2(g) \quad \text{(fast)}
\end{align*}
\]
The $\text{N}_2\text{O}_5^*$ is a reactive intermediate. The net rate of change of $[\text{N}_2\text{O}_5^*]$ is then

$$\frac{d[\text{N}_2\text{O}_5^*]}{dt} = k_1[\text{N}_2\text{O}_5][\text{M}] - k_{-1}[\text{N}_2\text{O}_5^*][\text{M}] - k_2[\text{N}_2\text{O}_5^*]$$

The approximation consists of the assumption that after the short time the rate of production and loss of $\text{N}_2\text{O}_5^*$ becomes equal, and setting the rate of change of the $\text{N}_2\text{O}_5^*$ concentration to 0 gives

$$\frac{d[\text{N}_2\text{O}_5^*]}{dt} = 0 = k_1[\text{N}_2\text{O}_5][\text{M}] - k_{-1}[\text{N}_2\text{O}_5^*][\text{M}] - k_2[\text{N}_2\text{O}_5^*]$$

solving for $[\text{N}_2\text{O}_5^*]$ gives

$$[\text{N}_2\text{O}_5^*](k_2 + k_{-1}[\text{M}]) = k_1[\text{N}_2\text{O}_5][\text{M}]$$

$$[\text{N}_2\text{O}_5^*] = \frac{k_1[\text{N}_2\text{O}_5][\text{M}]}{k_2 + k_{-1}[\text{M}]}$$
The rate of the overall reaction \( \text{N}_2\text{O}_5 \rightarrow 2 \text{ NO}_2 + \frac{1}{2} \text{ O}_2 \) is

\[
rate = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_2[\text{N}_2\text{O}_5^*] = \frac{k_1k_2[\text{N}_2\text{O}_5][\text{M}]}{k_2 + k_{-1}[\text{M}]}
\]

The expression has two limiting cases:

1. **Low pressure** When \([\text{M}]\) is small enough, \(k_2 \gg k_{-1}[\text{M}]\) and we can use the approximation.

   \[
   rate = k_1[\text{N}_2\text{O}_5][\text{M}] \quad \text{(second order)}
   \]

2. **High pressure** When \([\text{M}]\) is large enough, \(k_{-1}[\text{M}] \gg k_2\) and we can use the approximation.

   \[
   rate = \left(\frac{k_1}{k_{-1}}\right) k_2[\text{N}_2\text{O}_5] = K_1k_1[\text{N}_2\text{O}_5] \quad \text{(first order)}
   \]
General Chemistry

Chemical Kinetics (II-1)

박준원 교수(포항공과대학교 화학과)
Effect of temperature on reaction rates

<Gas-phase reaction rate constants>

Some reactions do proceed at each collision event; rate constant of $1 \times 10^{10} \text{ Lmol}^{-1}\text{s}^{-1}$.

However, reaction rates that are much lower – by factors of $10^{12}$ or more – are common.

The rate of many chemical reactions increase extremely rapidly at temperature increases, typically a $10^\circ \text{C}$ rise in temperature may double the rate. In 1889 Svante Arrhenius suggested

$$k = Ae^{-E_a/RT} \quad [18.5]$$

Where $E_a$ is a constant with dimensions of energy and $A$ is a constant with the same dimensions as $k$. Taking the natural logarithm of this equation gives

$$\ln k = \ln A - \frac{E_a}{RT} \quad [18.6]$$
$E_a$ is known as the activation energy. The fraction of molecules having more than the critical energy $E_a$ increases exponentially as $\exp(-E_a/RT)$. 

Fraction of molecules 

$\bar{u} = \sqrt{2\varepsilon/m}$

Speed

$T_2 > T_1$
<The reaction coordinate and the activated complex>

\[ A-B + C \rightarrow A + B-C \]

Activated complex or transition state

The activation energy for an elementary reaction is always positive, but some overall reactions manifest “negative activation energies”.

Reactions in solution are much more complicated to describe than their gas-phase counterparts because the transport mechanism in solutions is much different. Collisions between reactants in solution occur much less frequently than for those in the gas phase, but the reactants may be bound together by a “cage” of solvent molecules for sufficiently long periods that they can acquire enough energy through collisions with the solvent to react.

\[ A + B \rightleftharpoons AB \]

\[ AB \rightarrow \text{products} \]

\[ k_1 \ll k_2 \text{, if } k_1 \text{ is limited by the rate at which the reactants encounter one another by diffusion we call the reaction diffusion-controlled.} \]

\[ k_2 \ll k_1 \text{ and } k_2 \text{, reactions are often called activation-energy-controlled.} \]
Chemical Kinetics (Ⅱ-2)
A catalyst is a substrate that takes part in a chemical reaction and speeds up the rate but undergoes no permanent chemical change itself. Catalysts therefore do not appear in the overall balanced chemical equation.
In **homogeneous** catalysis the catalyst is present in the same phase as the reactants.

\[
\text{TI}^+ (aq) + 2 \text{Ce}^{4+} (aq) \xrightarrow{\text{Ag}^+ (aq)} \text{TI}^{3+} (aq) + 2 \text{Ce}^{3+} (aq)
\]

In heterogeneous catalysis the catalyst is present as a phase distinct from the reaction mixture.

\[\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)\] solid oxide of **vanadium** (V$_2$O$_5$) as a catalyst.
<Enzyme catalysis>

The vast majority of chemical reactions in living organisms are catalyzed by enzymes, proteins that have evolved to enhance reaction rates by many orders of magnitude with exquisite selectivity.

The major classes and the reactions they catalyze include (1) oxidoreductase – redox reactions; (2) transferase – functional group transfer reactions; (3) hydrolase – hydrolysis reactions; (4) lyase – addition to carbon-carbon double bonds; (5) isomerase – isomerization reactions; (6) ligase – bond-forming reactions.
<Enzyme kinetics>

The kinetics of enzyme-catalyzed reactions is generally treated using the steady-state approximation in a form that has become known as Michaelis-Menten kinetics.

\[
E + S \xrightleftharpoons[k_1]{k_2} ES \xrightarrow{k_{-1}} E + P
\]

In which \( E \) represents the free enzyme, \( S \) is the substrate, \( ES \) represents the complex formed, and \( P \) is the final product.

The concentration of \([ES]\) reaches a steady state.

\[
\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]
\]
The concentration of the free enzyme ([E]) is \([E_T] – [ES]\), where \([E_T]\) is the total concentration of enzyme present (i.e., the concentration of enzyme initially added \([E_o]\)).

\[
\frac{d[ES]}{dt} = 0 = k_1 [E_T][S] - k_1[ES][S] - k_{-1}[ES] - k_2[ES]
\]

\[
[ES] = \frac{k_1 [E_T][S]}{(k_{-1} + k_2) + k_1[S]}
\]

We define the **Michaelis constant** \(K_m\) (in units of molarity) as

\[
K_m = \frac{k_{-1} + k_2}{k_1}
\]
which allows us to express the steady state concentration of [ES] as

$$[ES] = \frac{[E_T][S]}{K_m + [S]}$$

$$\frac{d[P]}{dt} = k_2[ES] = \frac{k_2[E_T][S]}{K_m + [S]}$$

[18.15] Michaelis-Menten equation
The rate is linear (first-order) with respect to [S] at low substrate concentrations but rolls over to become independent of [S] at higher concentrations, saturating at $[S] \gg K_m$, rate $= V_{max} = k_2[E_T]$ from eq [18.15]

At $[S] \gg K_m$, rate $= V_{max} = k_2[E_T]$ from eq [18.15]

Rate $\approx \frac{k_2}{K_m} [E_T][S]$ at $[S] \ll K_m$
An alternative form of Michaelis-Menten equation is

\[
\frac{d[P]}{dt} = k_2[ES] = \frac{V_{\text{max}}[S]}{K_m+[S]}
\]

\[
K_m = [S]\left[\left(\frac{V_{\text{max}}}{d[P]/dt}\right) - 1\right]
\]

When \(d[P]/dt = V_{\text{max}}/2\), \(K_m = [S]\), so we simply use \([S]\) to find \(K_m\) experimentally.

A small value of \(K_m\) indicates that the formation of ES complex is faster than the dissociation of ES complex to the starting materials and the product.
**Turnover number** is defined as the number of substrate molecules converted into product per enzyme molecule per second, and is easily calculated from $k_{\text{cat}}$.

at saturation,

\[
[S] >> K_m, [ES] = [E_T], \text{rate} = V_{\text{max}} = k_2[E_T], k_{\text{cat}} \equiv k_2 = V_{\text{max}} /[E_T]
\]

The turnover numbers for different enzymes vary over an enormously wide range; each catalase molecule can decompose 40 million molecules of hydrogen peroxide per second, whereas the turnover number of chymotrypsin is about 100 and that of lysozymes is about 0.5.
A linear version of Michaelis-Menten equation is

\[
\frac{1}{d[P]/dt} = \left(\frac{K_m}{V_{max}}\right)\left(\frac{1}{[S]}\right) + \frac{1}{V_{max}}
\]

Plot the inverse of the rate versus 1/[S], the slope is \(K_m/V_{max}\), and the intercept is 1/\(V_{max}\).

From the plot, the key parameters \((k_{cat}, K_m)\) can be obtained from the rates at a few concentrations of the substrate.

\[
K_{cat} = \frac{V_{max}}{[E_T]}
\]

\[
K_m = \frac{k_{-1} + k_2}{k_1}
\]