For elementary reaction steps the rate law can be inferred.

Unimolecular elementary step:

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

Rate: \[ -\frac{d[A]}{dt} = k[A] \]

Bimolecular elementary step:

\[ A + B \rightarrow \text{products} \]

Rate: \[ -\frac{d[A]}{dt} = k[A][B] \]

Molecularity: Number of particles coming together to react in an elementary step.
An overall reaction often consists of consecutive elementary steps

Example: $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$

Elementary steps:

1.) $2\text{NO}(g) \rightarrow \text{N}_2\text{O}_2(g)$

$$\frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}]^2$$

2.) $\text{N}_2\text{O}_2(g) \rightarrow 2\text{NO}(g)$

$$- \frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{N}_2\text{O}_2]$$

3.) $\text{N}_2\text{O}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$

$$- \frac{d[\text{N}_2\text{O}_2]}{dt} = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

and

$$- \frac{d[\text{N}_2\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

$$\Rightarrow \frac{d[\text{NO}_2]}{dt} = 2k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

problem: intermediate
The steady-state approximation

\[
\frac{\mathrm{d}[\text{N}_2\text{O}_2]}{\mathrm{d}t} = k_1[\text{NO}]^2 - \frac{\mathrm{d}[\text{N}_2\text{O}_2]}{\mathrm{d}t} = k_{-1}[\text{N}_2\text{O}_2] - \frac{\mathrm{d}[\text{N}_2\text{O}_2]}{\mathrm{d}t} = k_2[\text{N}_2\text{O}_2][\text{O}_2]
\]

Overall: \( \Sigma = \frac{\mathrm{d}[\text{N}_2\text{O}_2]}{\mathrm{d}t} = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_2[\text{N}_2\text{O}_2][\text{O}_2] \equiv 0 \)

Steady-state approximation = [intermediate] remains small and constant

\[
\Rightarrow [\text{N}_2\text{O}_2] = \frac{k_1[\text{NO}]^2}{k_{-1} + k_2[\text{O}_2]}
\]

and

\[
\frac{\mathrm{d}[\text{NO}_2]}{\mathrm{d}t} = 2k_2[\text{N}_2\text{O}_2][\text{O}_2]
\]

and \( k_{-1} \gg k_2[\text{O}_2] \) 2\textsuperscript{nd} approximation

Indeed observed \( \Rightarrow \) the proposed reaction mechanism is correct!
The rate-determining step (RDS) and reaching equilibrium

The RDS is the slow bottleneck in consecutive elementary steps

Reversible reaction \( A \xrightleftharpoons[k_{-1}]{k_1} B \)

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

At equilibrium:

\[
\frac{d[B]}{dt} = k_1[A]_{eq} - k_{-1}[B]_{eq} = 0
\]

\[
\frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}} = K
\]
Temperature dependence of the reaction rate constant

Maxwell velocity distribution of a gas at temperature $T$

- $N_v$ vs. $|v|$
- Critical velocity for reaction, $v_c$
- $|v| < v_c$: No Reaction
- $|v| > v_c$: Reaction

The minimum energy that must be supplied by a collision as $E_{\text{kin}} = \frac{1}{2}mv^2$ per mole reaction is the activation energy $E_a$ [kJ/mol]

$$k = A_\infty e^{-\frac{E_a}{RT}}$$

Rate constant

Population with $E_a$ sufficient to drive the reaction

Nils Walter: Chem 260
The Arrhenius equation

\[ k = A_\infty e^{-\frac{E_a}{RT}} \]

\( A_\infty \) = maximum possible rate at infinite temperature

\[ \ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A_\infty \]

A plot of \( \ln k \) vs \( \frac{1}{T} \) will be linear!

Activation energies are determined experimentally by measuring the rate over as large a range of \( T \) as possible.
Typical activation energies

An exothermic reaction will occur rapidly if $E_a < RT$ and only slowly if $E_a >> RT$

An endothermic reaction will normally have a large activation energy, $E_a$
What is catalysis?

Consider: \[ 2 \text{H}_2\text{O}_2(\text{l}) \rightarrow 2 \text{H}_2\text{O} (\text{l}) + \text{O}_2(\text{g}) \]

\[ \Delta_r G^\Theta = 2(-237.13) + 0 - 2(-120.35) = -233.56 \text{ kJ} \]

\[ \Delta_r H^\Theta = 2(-285.83) + 0 - 2(-187.78) = -196.10 \text{ kJ} \]

This reaction is exothermic and spontaneous!

In fact the equilibrium constant is huge:

\[ K = \exp \left( \frac{233.56 \times 10^3 \text{ J}}{8.31451 \text{ J K}^{-1} \times 298 \text{ K}} \right) = 1.15 \times 10^{41} \]

BUT: Very high activation energy \( \Rightarrow \) slow
Adding a catalyst

\[ 2 \text{H}_2\text{O}_2(\text{l}) \xrightarrow{\text{MnO}_2} 2 \text{H}_2\text{O (l)} + \text{O}_2(\text{g}) \]

Add MnO₂:
The reaction becomes very fast

**MnO₂ acts as a catalyst** – that is, it provides a mechanism with a much smaller activation energy

Initial and final states are unaffected by catalyst; but the nature of the reaction coordinate is changed, reducing \( E_a \)