
F. Reaction mechanisms and rate laws.

The reaction mechanism is the sequence of steps that define the path from reactants to products. Each step is an elementary reaction, a reaction involving 1 (unimolecular), 2 (bimolecular), or, at most, 3 (termolecular) molecules. The sum of all elementary steps is the overall reaction. Any species which appears in an elementary reaction but not the overall reaction is a reaction intermediate.

Ex. Mechanism for the decomposition of nitrous oxide (laughing gas).

Overall reaction: \( 2N_2O(g) \rightarrow 2N_2(g) + O_2(g) \)

Reaction mechanism:

1. \( N_2O(g) \rightarrow N_2(g) + O(g) \) (unimolecular step)
2. \( N_2O(g) + O(g) \rightarrow N_2(g) + O_2(g) \) (bimolecular step)

O(g) (atomic oxygen) is a reaction intermediate.

The overall rate law can be deduced from the reaction mechanism. The rate law for an elementary reaction follows directly from the equation (see Table 12.5 of M&F):

Rate law for step (1): Rate = \( k_1[N_2O] \)
Rate law for step (2): Rate = \( k_2[N_2O][O] \)

If the reaction mechanism contains a single step, then the overall rate law and the elementary rate law are identical.

Ex. Rearrangement of methyl isonitrile: \( \text{CH}_3\text{-N}=\text{C}(g) \rightarrow \text{CH}_3\text{-C}=\text{N}(g) \)
Rate = \( k[\text{CH}_3\text{-N}=\text{C}] \)

If the reaction mechanism contains two or more steps, one step (the rate-determining step) is often much slower than the other steps. The rate-determining step controls the overall rate of the reaction. The overall rate law will contain only those substances that are involved up to and including the rate-determining step.

Ex. What is the rate law for the following mechanism?

\[
\begin{align*}
(1) & \quad A + B \rightarrow AB \quad \text{(slow)} \\
(2) & \quad AB + A \rightarrow C + D \quad \text{(fast)}
\end{align*}
\]
Overall: \( 2A + B \rightarrow C + D \)
The 1\textsuperscript{st} step is rate-determining. The overall rate law is: rate = \( k[A][B] \)

What is step (2) is rate-determining? Then the rate law includes all reactants: rate = \( k[A]^2[B] \)

Usually the overall rate law is determined experimentally, and a possible reaction mechanism is deduced from the rate law.

Ex. (Nakon, 16-8) Overall reaction is: \( 2A + B \rightarrow C + D \). The rate law is: rate = \( k[A]^2 \).

Write a possible mechanism.

The easiest approach is to let the 1\textsuperscript{st} step be rate-determining.

\[
\begin{align*}
(1) & \quad A + A \rightarrow A_2 \quad \text{(slow)} \\
(2) & \quad A_2 + B \rightarrow C + D \quad \text{(fast)}
\end{align*}
\]

G. The Arrhenius Equation.

Everyday experience shows that reaction rates increase with temperature (Ex. reduced cooking times in a pressure cooker, increased cooking times at high altitudes, due to changes in b.p. of water). Thus, the rate constant \( k \) must depend on temperature.

Arrhenius proposed that all rate constants obey the following general equation:

\[ k = A \exp(-E_a/RT) \]

\( E_a \) is the activation energy, \( A \) is a constant.

This equation is predicted by collision theory. The 3 basic elements of collision theory are:

(a) Molecules must collide to weaken bonds and reach an activated complex (a species between reactants and products).

Ex. \( A + B \rightarrow (A--B)^* \rightarrow A + B \)

(b) The energy required to reach the activated complex is \( E_a \).

(c) The tiny fraction of collisions with sufficient energy to reach the activated complex is given by \( \exp(-E_a/RT) \), which is the major source of temperature dependence.

Elements (a) and (b) are often represented in a potential energy profile (plot of potential energy vs reaction progress); see Fig. 12.13 of M&F.

We can relate \( E_a \) to the temperature-dependence of rate constants and rates using a variation of the Arrhenius equation.

\[
\log(k_2/k_1) = (-E_a/(2.303R)((1/T_2) - (1/T_1))) \quad \text{(temperatures in Kelvin; } R = 8.314 \text{ J/K·mol)}
\]

Ex. Rates for decomposition of \( N_2O_5(g) \) are \( 3.7 \times 10^{-5}/s \) at \( 25^\circ C \) and \( 1.7 \times 10^{-3}/s \) at \( 55^\circ C \). What is \( E_a \)? What is the rate at \( 35^\circ C \)?
IMPORTANT: convert all temperatures to Kelvin: 25°C → 298K; 55°C → 328K; 35°C → 308K

\[
\log(1.7 \times 10^{-3}/3.7 \times 10^{-5}) = \log(46) = 1.66 = \frac{-E_a}{(2.303)(8.314)}((1/328)-(1/298))
\]

\[E_a = 1.66/1.6 \times 10^{-5} = 1.0 \times 10^5 \text{ J/mol} \times 1 \text{ kJ/1000 J} = 100 \text{ kJ/mol} \text{ (2 sig. fig.)}
\]

\[
\log(k_2/3.7 \times 10^{-5}) = (-5.2 \times 10^3/19.15)((1/308)-(1/298)) = (-5.2 \times 10^3)(-1.1 \times 10^{-4}) = +0.57
\]

\[k_2/3.7 \times 10^{-5} = 10^{0.57} = 3.7; \quad k_2 = (3.7)(3.7 \times 10^{-5}) = 1.4 \times 10^{-4}/s
\]

(Note the use of log and antilog base 10, the use of J/mol, NOT kJ/mol, as the units of \(E_a\), and the loss of significant figures on subtraction)

H. Catalysis.

A catalyst increases the rate of the reaction without being consumed in the reaction.

Ex. The decomposition of hydrogen peroxide is catalyzed by many substances, such as \(\text{MnO}_2(s)\):

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

(a very exothermic reaction)

The catalyst changes the mechanism of the reaction. It usually provides a path with a lower \(E_a\) (see Fig. 12.16 of M&F). The catalyst usually appears in the rate law. Homogeneous catalysts exist in the same phase as the reaction. Heterogeneous catalysts exist in a different phase (e.g., \(\text{MnO}_2(s)\) in the liquid phase reaction above). The importance of catalysts in natural and industrial chemistry is too great to describe here; see M&F for examples.