
Topic: Kinetics
   I. Effect of Temperature on Reactions Rates
   II. The Reaction Coordinate and the Activation Complex

I. Effect of Temperature on Reaction Rates

Gas-Phase
A qualitative observation is that reaction rates tend to _______________ with increased temperature. Now we will consider the quantitative effect.

In 1889, Svante Arrhenius plotted ln k versus inverse temperature and got a straight line.

\[ \ln k = -\frac{E_a}{R} + \ln A \]

\[ y = mx + b \]

Rate constants vary _______________ with inverse temperature

A and \( E_a \) depend on the reaction being studied.

Is factor A temperature dependent?

Is \( E_a \) temperature dependent?
Example: Using the activation energy to predict a rate constant

The hydrolysis of sucrose to form a molecule of glucose and a molecule of fructose is part of the digestive process.

\( E_a = 108 \text{ kJ/mol} \)

\( k_{\text{obs}} = 1.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1} \text{ at } 37^\circ\text{C} \) (normal body temperature)

Calculate \( k_{\text{obs}} \) at 35°C.

\[
\ln k_1 = \ln A - \frac{E_a}{RT_1}
\]

\[
\ln k_2 = \ln A - \frac{E_a}{RT_2}
\]

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\[
\ln \left( \frac{k_2}{1.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}} \right) = \frac{-108 \times 10^3 \text{ J mol}^{-1}}{8.315 \text{ JK}^{-1}\text{mol}^{-1}} \left( \frac{1}{308 \text{ K}} - \frac{1}{310 \text{ K}} \right)
\]

\( k_2 = 7.6 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1} \)

Equation to relate change in T to change in k

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

A large activation energy means that the rate constant is ______________ sensitive to changes in temperature.

What do you think happens to the rate of an enzymatic reaction at liquid N\(_2\) temperatures?

What about the rate of a non-enzymatic reaction at liquid N\(_2\) temperatures?
II. The Reaction Coordinate and the Activation Complex

Consider $\text{CH}_3(g) + \text{CH}_3(g) \rightarrow \text{C}_2\text{H}_6(g)$

2 molecules collide to form product (bimolecular) but every two molecules that collide won’t form product. Why?

Only those collisions for which the collision energy exceeds some critical energy ($E_{\text{min}}$) (also known as _________________ energy, $E_a$) result in a reaction.

**Why** is there a critical collision energy, $E_{\text{min}}$ or $E_a$, for the reaction between two molecules?

As two reactant molecules approach each other along a reaction path, their potential energy_______________ as the bonds within them distort.

The encounter results in the formation of an activated complex or _________________, a combination of molecules that can either go on to form products or fall apart again into unchanged reactants.

Only molecules with sufficient energy can overcome the activation energy barrier.

This is where temperature becomes important.

At low temperatures, only a small fraction of molecules will have sufficient energy.

At higher temperatures, a larger fraction will have sufficient energy.
Reaction Coordination Diagrams

Example: \( \text{NO}_2 (g) + \text{CO} (g) \rightarrow \text{NO} (g) + \text{CO}_2 (g) \)

Potential energy (P.E.)

\[ \Delta E = \]

Activated complex or transition state

\[ E_{a, f} = \]

\[ E_{a, r} = \]

\[ \Delta E = E_{a, f} - E_{a, r} \]

Recall \( \Delta H = \Delta E + \Delta (PV) \)

For gases, these quantities differ by 1-2\% and for liquids and solids, there is a negligible difference.

For elementary reactions, the activation energy barrier is always positive (some barrier to overcome).

Therefore, increasing the temperature \______\ the rate of an elementary reaction.

For overall reactions, increasing temperature can decrease or increase the overall rate.

Example: \( 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \) with proposed mechanism:

1st step (Fast, reversible)

\[ \text{NO} + \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \]

\[ \text{k}_1 \]

\[ \text{k}^{-1} \]

2nd step (slow)

\[ \text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2 \]

\[ \text{k}_2 \]

rate of product formation \( = 2\text{k}_2 [\text{N}_2\text{O}_2] [\text{O}_2] \)

intermediate
Since first step is fast and reversible and the second step is slow, we can solve for \([\text{N}_2\text{O}_2]\) by setting up an equilibrium expression:

\[
K_1 = \frac{[\text{N}_2\text{O}_2]}{\text{rate of product formation}}
\]

Substituting:

\[
\text{rate} = 2k_2K_1[\text{NO}]^2[\text{O}_2]
\]

Here the reaction is exothermic, so increasing temperature decreases the equilibrium constant.

\[
k_{\text{obs}} = 2k_2K_1 \quad \text{with increased temperature,}
\]

- \(k\) increases (elementary rate constants always increase with \(T\))
- \(K\) decreases (for exothermic reaction)

Magnitude of change depends on \(E_a\) (for rate constant) and \(\Delta H\) (for equilibrium constant).

For \(2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2\), \(E_a\) is a small number and \(\Delta H\) is a big number

- Since \(E_a\) is a small positive, the rate constant increases only a little
- Since \(\Delta H\) is a big negative, the equilibrium constant decreases a lot with temperature

Thus, increasing the temperature actually decreases \(k_{\text{obs}}\).

A large \(E_a\) means that \(k\) is very sensitive to changes in temperature.

A large \(\Delta H\) means that \(K\) is very sensitive to changes in temperature.
Rate constants always increase with temperature, since $E_a$ is always ____________.

Equilibrium constants can increase or decrease with temperature, since $\Delta H$ can be (-) or (+).

The magnitude of $\Delta H$ indicates the **magnitude** of the change, and the sign of $\Delta H$ indicates the ______________ of the change.

Le Chatelier's Principle - when a stress is applied to a system in equilibrium, the equilibrium tends to adjust to ______________ the effect of the stress.

Increasing the temperature, shifts the reaction in the ______________ direction.

Inc T, easier to overcome $E_{a,f}$
Equilibrium shifts toward products

Inc T, easier to overcome $E_{a,r}$
Equilibrium shifts toward reactants

Most molecules have enough energy to overcome small barriers: increasing temperature allows more molecules to overcome larger barriers

Recall, a large $E_a$ means that the rate constant is very sensitive to changes in temperature.

Big $E_a$ - increasing the temperature makes a _____________ difference
Small $E_a$ - increasing the temperature does not make much of a difference.