**Reaction Rates and Temperature; Arrhenius Theory**

**CHEM 102**
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**Arrhenius Theory**

**The Arrhenius Equation**

\[ k = \text{Ae}^{-\frac{E_a}{RT}} \]

- \( k \) is the rate constant
- \( T \) is the temperature in K
- \( E_a \) is the activation energy
- \( R \) is the ideal-gas constant \((8.314 \text{ J/Kmol})\)

\( \text{A} \) is known as the frequency or pre-exponential factor

In addition to carrying the units of the rate constant, \( \text{A} \) relates to the frequency of collisions and the orientation of a favorable collision probability.

Both \( \text{A} \) and \( E_a \) are specific to a given reaction.

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**Activation Energy**

The progress of a chemical reaction as the reactants transform to products can be described graphically by a Reaction Coordinate.

In order for the reaction to proceed, the reactants must possess enough energy to surmount a reaction barrier.

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**Energy profile for a reaction**

- \( E_a \) (activated complex)
- \( \Delta E_{rxn} \) (thermodynamic quantity)

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**The reverse direction**

- \( E_a \) (reverse)
- \( \Delta E_{rxn} \) (thermodynamic quantity)

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**E\text{a}, The Activation Energy**

- Energy of activation for forward reaction:
  \[ E_{a} = E_{\text{transition state}} - E_{\text{reactants}} \]
- A reaction can’t proceed unless reactants possess enough energy to give \( E_{a} \).
- \( \Delta E \), the thermodynamic quantity, tells us about the net reaction. The activation energy, \( E_{a} \), must be available in the surroundings for the reaction to proceed at a measurable rate.

**Orientation Factors (affects ‘A’)**

The orientation of a molecule during collision can have a profound effect on whether or not a reaction occurs.

The reaction occurs only when the orientation of the molecules is just right...

When the green atom collides with the green atom on the molecule, a reactive or effective collision occurs.

**Orientation Factors (affects ‘A’)**

In some cases, the reactants must have proper orientation for the collision to yield products.

This reduces the number of collisions that are reactive!

When the green atom collides with the red atom on the molecule, a non-reactive or ineffective collision occurs.

**The Arrhenius Equation**

Arhenius discovered that most reaction-rate data obeyed an equation based on three factors:
1. The number of collisions per unit time.
2. The fraction of collisions that occur with the correct orientation.
3. The fraction of the colliding molecules that have an energy greater than or equal to \( E_{a} \).

From these observations Arhenius developed the eponymously-named **Arrhenius equation**

\[
\text{Rate (M s}^{-1} = \xi[A][B]^y \\
{k} = A e^{-\frac{E_{a}}{RT}}
\]

As \( T \) increases, the value of the exponential part of the equation becomes less negative thus increasing the value of \( k \).
Arrhenius Equation

- Arrhenius noted that reaction rates could be understood to depend on $E_a$ and $T$ with the exponential form:
  \[ k = A \exp(-\frac{E_a}{RT}) \]
- Or, in logarithmic form:
  \[ \ln k = \ln A - \frac{E_a}{RT} \]
  using base 10 logs: \[ \log k = \log A - \frac{E_a}{2.303RT} \]

Arrhenius Eqn., Alternative Form

- Taking two measured values of the rate (at two different temperatures) one can write:
  \[ \ln k_1 = \ln A - \frac{E_a}{RT_1} \]
  \[ \ln k_2 = \ln A - \frac{E_a}{RT_2} \]
  \[ \ln k_2 - \ln k_1 = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1}) \]
  \[ \ln(\frac{k_2}{k_1}) = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1}) \]

Arrhenius Eqn., Graphical Form

A “best fit” to many data is better!

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

Arrhenius Equation, Example

- If a reaction has an activation energy of 50 kJ/mol, then how much should the rate of the reaction accelerate if the temperature is raised from 300 K to 310 K?

\[ \ln(\frac{k_{310}}{k_{300}}) = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1}) \]
\[ = -\frac{(50,000 \text{ J/mol})/(8.314 \text{ J/mol K})}{[(1/310K) - (1/300K)]} = 0.647 \]
\[ k_{310} = e^{0.647}k_{300} \]
roughly, rate doubles
\[ = 1.9k_{300} \]
for every 10 °C.
Catalysts - lowering $E_a$. Mechanism may change.

Catalytic Converters, $2\text{NO} \rightarrow \text{O}_2 + \text{N}_2$

Iodine-Catalyzed Isomerization of cis-2-Butene

$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

Iodine-Catalyzed Isomerization of cis-2-Butene

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