Skills to Develop

- Explain activation energy.
- Describe how energy varies during a chemical reaction.
- Plot chemical potential energy of the system as a function of the reaction coordinate.
- Explain the model \( k = \ce{A e}^{\Large{E_{\Large\ce a}/RT}} \) for chemical kinetics.
- Plot \( k \) versus \( 1/T \) when \( k \) is measured at several \( T \).
- Calculate \( E_a \) when a series of \( k \) and \( T \) are given.
- Calculate \( k \) at certain \( T \).

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Energy of a Chemical System as the Reaction Proceeds

A spontaneous reaction usually releases energy. The mixture of reactants has more energy than that of the products. This energy is referred to as the **chemical potential energy**. The difference between the potential energies is called the **enthalpy of reaction**. A simple diagram illustrating this relationship is given below.

**Figure 1**: Chemical potential energies of reactants and products. The difference is the enthalpy of reaction.

This potential energy difference is the driving force for a chemical reaction to take place. After the reaction energy is released, the products are at a more stable energy level than the reactants.

**The Activation Energy, \( E_a \)**

We all know that a mixture of \( \ce{H2} \) and \( \ce{O2} \) will not react until its temperature has reached the ignition point, despite the large amount of energy released in the oxidation reaction. This phenomenon is best described by the requirement of an activation energy, \( E_a \). The relation between \( E_a \) and chemical potential energy in a reaction is given below:
The rate constant \(k\) is affected by the temperature and this dependence may be represented by the Arrhenius equation:

\[
k = A \, e^{-\frac{E_a}{RT}}
\]

where the pre-exponential factor \(A\) is assumed to be independent of temperature, \(R\) is the gas constant, and \(T\) the temperature in K. Taking the natural logarithm of this equation gives:

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

or

\[
\ln k = \frac{-E_a}{RT} + \text{constant}
\]

or

\[
\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \text{constant}
\]

These equations indicate that the plot of \(\ln k\) vs. \(1/T\) is a straight line, with a slope of \(-E_a/R\). These equations provide the basis for the experimental determination of \(E_a\).

**Example 1**

The reaction constants \(k\) determined at 298 K and 350 K are 0.00123 \(/(M \cdot s)\) and 0.0394 \(/(M \cdot s)\) respectively.

a. Calculate \(E_a\).

b. What is the rate constant at 308 K?

**SOLUTION**

Let \(k_1\) and \(k_2\) be the rate constants determined at \(T_1\) and \(T_2\), respectively. Then you have two equations:

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

and

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

Solving for \(E_a\):

\[
E_a = -RT \ln \left(\frac{k_2}{k_1}\right)
\]
\[ \ln k_2 = \ln A - \frac{E_{\text{a}}}{RT_2} \]

From these, you should be able to derive the following relationships,
\[ \ln \frac{k_2}{k_1} = -\frac{E_{\text{a}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

a. Further, you should give

\[
\begin{align*}
E_{\text{a}} &= \frac{T_1 T_2 R}{T_2 - T_1} \ln \frac{k_2}{k_1} \\
&= \frac{(350 \, \text{K})(298 \, \text{K}) \left(8.314 \, \frac{\text{J}}{\text{K} \cdot \text{mol}}\right)}{(350 - 298) \, \text{k}} \ln \frac{0.0394}{0.00123} \\
&= \frac{57811 \, \text{J/mol}}{57.8 \, \text{kJ/mol}}
\end{align*}
\]

It is a good idea to manipulate the formula with symbols until you have obtained the desirable form before you substitute numerical values into it. The necessary units are included here to show you the derivation of units for \( E_{\text{a}} \).

b. To calculate \( k \) at 308 K,

\[
\begin{align*}
\ln k &= \ln (0.00123) - \frac{57811}{8.314} \left( \frac{1}{308} - \frac{1}{298} \right) \\
&= -6.70 + 0.758 \\
k &= 0.00263
\end{align*}
\]

**DISCUSSION**
An increase of 10 \( k \) doubles the rate constant in this case.

If \( E_{\text{a}} \) is positive, increasing temperature always leads to an increase in the rate constant.

**Example 2**
For a particular reaction the rate constant doubles when the temperature is raised by 10 K from 300 K. Calculate the activation energy.

**SOLUTION**
The statement of the problem is equivalent to the condition given:
\[ (k_{310}) = 2 (k_{300}) \]

or
\[ (k_{1}) = 2 (k_{0}) \]

Then, using the same equation as you have used in the previous example, you have
DISCUSSION
This question is intended to show the general magnitude of $E_a$ for the rule of thumb: For every 10 K increase in temperature, the reaction rate doubles.

Professor Frank L. Lambert of Occidental College has given an interesting view of the chemical ideas related to activation energy in his website about second law of thermodynamics.

Arhenius Parameters for Some Reactions:
Not all chemical reactions agree with the Arhenius model in terms of temperature dependence, but the following reactions are known to agree well with the Arhenius equation. Parameters in the Arhenius equation for these reactions have been determined. (Note that $3\times 10^{11}$ means $3\times 10^{11}$)

First order gas phase reactions:

\[
\begin{align*}
\ce{N2O \rightarrow N2 + O}) &; \ (A = 8\times 10^{11}), \ (E_{\Large\ce a} = 251 \text{ kJ/mol}) \\
\ce{N2O5 \rightarrow 2 NO + O2}) &; \ (A = 6\times 10^{14}), \ (E_{\Large\ce a} = 88 \text{ kJ/mol})
\end{align*}
\]

Second order gas phase reactions:

\[
\begin{align*}
\ce{N2 + O \rightarrow N + NO}) &; \ (A = 1\times 10^{11}), \ (E_{\Large\ce a} = 315 \text{ kJ/mol}) \\
\ce{OH + H2 \rightarrow 2 H2O + H}) &; \ (A = 1\times 10^{11}), \ (E_{\Large\ce a} = 42 \text{ kJ/mol})
\end{align*}
\]

Second order reactions in aqueous solution:

\[
\begin{align*}
\ce{CO2 + OH- \rightarrow HCO3}) &; \ (A = 1\times 10^{11}), \ (E_{\Large\ce a} = 315 \text{ kJ/mol})
\end{align*}
\]

Confidence Building Questions

1. **The effect of temperature on chemical reaction is a manifestation of**
   a. the kinetic energies of molecules
   b. the activation energy of the reaction
   c. heat content of reactants and products
   d. the size of molecules

2. **If the activation energy is positive, an increase in temperature will always lead to**
a. an increase in reaction rate
b. a decrease in reaction rate
c. no change in reaction rate

3. For a spontaneous reaction the activation energy for the reverse reaction \( E_{ar} \) is
   a. greater than
   b. the same as
   c. smaller than

   the activation energy \( E_a \) of the forward reaction.

4. For a reaction, \( k_1 = 0.0503 \text{ /} (\text{M s}) \) at 289 K and \( k_2 = 6.71 \text{ /} (\text{M s}) \) at 333 K. Calculate the activation energy of the reaction.

   \((R = 8.314 \text{ J/(mol K)}, \text{ give your answer in kJ/mol})\)

5. For a reaction, \( k_1 = 0.0503 \text{ /} (\text{M s}) \) at 289 K and \( k_2 = 6.71 \text{ /} (\text{M s}) \) at 333 K.
   What is the rate constant at 305 K?

   (Use your results from the previous problem)

6. If the rate for a particular reaction at 373 K is four (4) times faster than it was at 323 K, what is the activation energy? \((R = 8.314 \text{ J/(mol K)})\)
   a. 27.8 kJ/mol
   b. -27.8 kJ/mol
   c. 27.8 J/mol

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**Solutions**

1. a.
   **Discussion -**
   Only a fraction of molecules have sufficient energy to react at a specified temperature. The distribution of kinetic energy amongst molecules and the required energy for molecules to react give rise to the activation energy. The activation energy quantitatively describes the effect of temperature on reaction rates.

2. a.
   **Discussion -**
   A positive \( E_a \) means increased rate at higher temperature.

3. a.
   **Discussion -**
   Usually, \( E_{ar} > E_a \).

4. 89.0 kJ
   **Discussion -**
\( E_{\text{\( \Large \text{a} \)}} = \dfrac{\text{R} \ T_1 \ T_2}{T_2 - T_1} \ln \left( \dfrac{k_2}{k_1} \right) \)

The data were given for the reaction

\( \text{C}_2\text{H}_5\text{I} + \text{OH}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{I}^- \)

5. 0.35 /\text{(M s)}

**Discussion -**

\( \ln k_2 = \ln k_1 - \dfrac{E_{\text{\( \Large \text{a} \)}} (T_1 - T_2)}{\text{R} \ T_1 \ T_2} \)

The experimental value is 0.37 /\text{(M s)}

6. a.

**Discussion -**

\( E_{\text{\( \Large \text{a} \)}} = \dfrac{\text{R} \ T_1 \ T_2}{T_2 - T_1} \ln \left( \dfrac{k_2}{k_1} \right) \)

\( E_{\text{\( \Large \text{a} \)}} \) must be positive if the rate increases at higher temperature. \( E_{\text{\( \Large \text{a} \)}} = \dfrac{\ln(4) \times 8.314 \times 373 \times 323}{50} \)

**Contributors**

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)