Chemistry 132 NT

Education is the ability to listen to anything without losing your temper or your self-confidence.

Robert Frost

- Kinetics of complex chemical systems

Reaction Rates

Module 3

Temperature and Rate
- **Collision and Transition State Theory**
- **The Arrhenius Equation**

The burning of steel wool

Review

- The **concentration-time equations**.
- **Half-lives** of first-order reactions.
- **Graphing** kinetic data to determine rate laws.

Collision Theory

- Rate constants vary with temperature and consequently, the actual rate of a reaction is very temperature dependent.
- Why the rate depends on temperature can by explained by **collision theory**.

Collision Theory

- **Collision theory** assumes that for a reaction to occur, reactant molecules must collide with sufficient energy and the proper orientation.
- The minimum energy of collision required for two molecules to react is called the **activation energy, E_a**.

Transition State Theory

- **Transition-state theory** explains the reaction resulting from the collision of two molecules in terms of an **activated complex**.
  - An **activated complex** (transition state) is an unstable grouping of atoms that can break up to form products.
  - A simple analogy would be the collision of three billiard balls on a billiard table.

Transition State Theory

- **Transition-state theory** explains the reaction resulting from the collision of two molecules in terms of an **activated complex**.
  - Suppose two balls are coated with a slightly stick adhesive and joined together.
  - We’ll take a third ball covered with an extremely sticky adhesive and collide it with our joined pair.

Transition State Theory

- **Transition-state theory** explains the reaction resulting from the collision of two molecules in terms of an **activated complex**.
  - The “incoming” billiard ball would likely stick to one of the joined spheres and provide sufficient energy to dislodge the other, **resulting in a new “pairing”.**
  - At the instant of impact, when all three spheres are joined, we have an unstable **transition-state complex.**

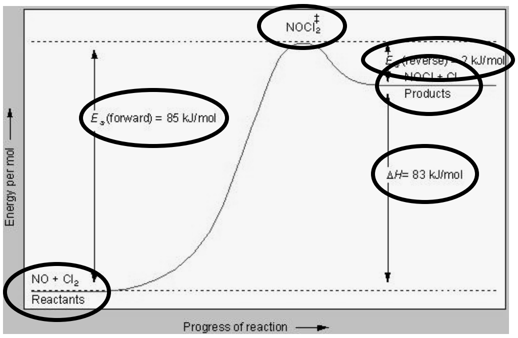
Transition State Theory

- **Transition-state theory** explains the reaction resulting from the collision of two molecules in terms of an **activated complex**.
  - If we repeated this scenario several times, some collisions would be successful and others (because of either insufficient energy or improper orientation) would not be successful.
  - We could compare the energy we provided to the billiard balls as the **activation energy,** E_a.

Potential-Energy Diagrams for Reactions

- To illustrate graphically the formation of a transition state, we can plot the **potential energy** of a reaction vs. **time**.
  - The next slide illustrates the endothermic reaction of nitric oxide and chlorine gas.
  - Note that the **forward activation energy** is the energy necessary to form the activated complex.
  - The D**H** of the reaction is the net change in energy between reactants and products.

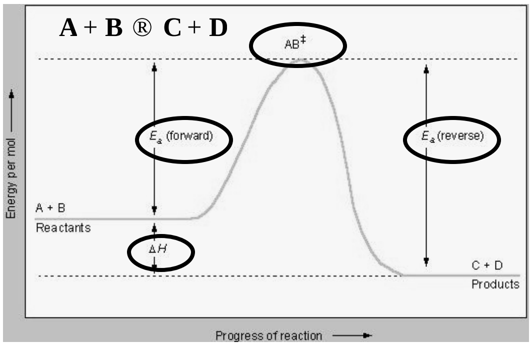
Potential-energy curve for the endothermic reaction of nitric oxide and chlorine.



Potential-Energy Diagrams for Reactions

- The **potential-energy diagram** for an exothermic reaction shows that the products are more stable than the reactants.
  - The next slide illustrates the potential-energy diagram for an exothermic reaction.
  - We see again that the **forward activation energy** is required to form the transition state complex.
  - In both of these graphs, the reverse reaction must still supply enough activation energy to form the activated complex.

Potential-energy curve for an exothermic reaction.


A + B ® C + D

Summary

- Successful collisions require a minimum activation energy, E_a.
- Some collisions are successful, some are not.
- Heating reactants increases the likelihood of a successful collision.
- So **how exactly does temperature affect the rate constant** and consequently the reaction rate?

Collision Theory and the Arrhenius Equation

- Collision theory maintains that the rate constant for a reaction is the product of three factors.

$$\mathbf{k = Zpf}$$

1. **Z**, the collision frequency
2. **f**, the fraction of collisions with sufficient energy to react
3. **p**, the fraction of collisions with the proper orientation to react.

Collision Theory and the Arrhenius Equation

- The factor, **Z**, is only slightly temperature dependent.
  - This is illustrated using the Kinetic Theory of gases which shows the relationship between the velocity of gas molecules and their absolute temperature**.**

$$\text{velocity} = \sqrt{\frac{3RT_{abs}}{M_m}} \quad \textbf{or} \quad \text{velocity}\ \mu\ \sqrt{T_{abs}}$$

Collision Theory and the Arrhenius Equation

- The factor, **Z**, is only slightly temperature dependent.
  - **This alone does not account the observed increases in rates with only small increases in temperature.**
  - **From kinetic theory, it can be shown that a 10 °C rise in temperature will only produce a 2% rise in collision frequency.**

Collision Theory and the Arrhenius Equation

- On the other hand, **f**, the fraction of molecules with sufficient activation energy turns out to be very temperature dependent.
  - It can be shown that **f** is related to $\mathbf{E_a}$ by the following expression.

$$f = e^{\frac{-E_a}{RT}}$$

  - Here e = 2.718… , and R is the ideal gas constant, 8.31 J/(mol·K).

Collision Theory and the Arrhenius Equation

- On the other hand, **f**, the fraction of molecules with sufficient activation energy turns out to be very temperature dependent.
  - From this relationship, **as temperature increases, f increases.**

$$f = e^{\boxed{\frac{-E_a}{RT}}}$$

  - Also, a **decrease in the activation energy, E_a, increases the value of "f".**

Collision Theory and the Arrhenius Equation

- On the other hand, **f**, the fraction of molecules with sufficient activation energy turns out to be very temperature dependent.
  - This is the primary factor relating temperature increases to observed rate increases.

$$\mathbf{f = e^{\frac{-E_a}{RT}}}$$

Collision Theory and the Arrhenius Equation

- The reaction rate also depends on **p**, the fraction of collisions with the proper orientation.
  - This factor is **independent of temperature changes**.
  - So, with changes in temperature, Z and p remain fairly constant.
  - We can use that fact to derive a mathematical relationship between the rate constant, **k**, and the **absolute temperature**.

The Arrhenius Equation

- If we were to combine the relatively constant terms, **Z** and **p**, into one constant…let's call it **A**, we obtain the **Arrhenius equation**.

$$\mathbf{k = A\, e^{\frac{-E_a}{RT}}}$$

  - The Arrhenius equation expresses the dependence of the rate constant on absolute temperature and activation energy.

The Arrhenius Equation

- If we were to combine the relatively constant terms, **Z** and **p**, into one constant…let's call it **A**, we obtain the **Arrhenius equation**.

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

  - The constant, "A", is sometimes referred to as the "frequency factor". (see Problem 13.93 at the end of the chapter in your text)

The Arrhenius Equation

- It is useful to recast the Arrhenius equation in logarithmic form.
  - Taking the natural logarithm of both sides of the equation, we get:

$$\ln k = \ln A - \frac{E_a}{RT}$$

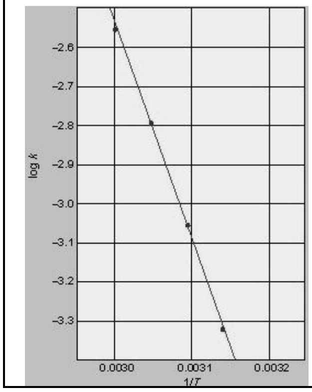
The Arrhenius Equation

- It is useful to recast the Arrhenius equation in logarithmic form.
  - We can relate this equation to the (somewhat rearranged) general formula for a straight line.

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$
$$y \;=\; b \;+ m\,x$$

  - A plot of ln k vs. (1/T) should yield a straight line with a **slope of $(-E_a/R)$** and an **intercept of ln A**.

Plot of log k versus 1/T.



The logarithm for the rate constant for the decomposition of N_2O_5 is plotted versus 1/T(K). A straight line is then fitted to the points: the slope equals $-E_a/2.303R$.

The Arrhenius Equation

- A more useful form of the equation emerges if we look at two points on the line this equation describes, that is **(k_1, ($1/T_1$))** and **(k_2, ($1/T_2$)).**
  - The two equations describing the relationship at each coordinate would be:

$$\ln k_1 = \ln A - \frac{E_a}{R}\left(\frac{1}{T_1}\right)$$

and

$$\ln k_2 = \ln A - \frac{E_a}{R}\left(\frac{1}{T_2}\right)$$

The Arrhenius Equation

- A more useful form of the equation emerges if we look at two points on the line this equation describes, that is **(k_1, ($1/T_1$))** and **(k_2, ($1/T_2$)).**
  - We can eliminate ln A by subtracting the two equations to obtain:

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

The Arrhenius Equation

- A more useful form of the equation emerges if we look at two points on the line this equation describes, that is **$(k_1, (1/T_1))$** and **$(k_2, (1/T_2))$**.
  - With this form of the equation, given the activation energy and the rate constant k_1 at a given temperature T_1, we can find the rate constant k_2 at any other temperature, T_2.

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

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.7×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Substitute the given data into the Arrhenius equation.

$$\ln\frac{3.5 \times 10^{-3}}{2.7 \times 10^{-4}} = \frac{E_a}{8.31\ \text{J/(mol} \cdot \text{K)}}\left(\frac{1}{600\text{K}} - \frac{1}{650\text{K}}\right)$$

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.7×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Simplifying, we get:

$$\ln(1.30 \times 10^{1}) = 1.11 = \frac{E_a}{8.31\ \text{J/(mol)}} \times (1.28 \times 10^{-4})$$

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \text{ ® } 2HI(g)$$

is 2.7 x 10^{-4} L/(mol·s) at 600 K and 3.5 x 10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Solving for E_a:

$$E_a = \frac{1.11 \text{ ´ } 8.31 J/mol}{1.28 \text{ ´ } 10^{-4}} = 1.66 \text{ ´ } 10^5 J$$

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \text{ ® } 2HI(g)$$

is 2.7 x 10^{-4} L/(mol·s) at 600 K and 3.5 x 10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- So, what's k_3 at 750 K ?

$$\ln\frac{\boxed{k_3}}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{\boxed{T_3}}\right)$$

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \text{ ® } 2HI(g)$$

is 2.7 x 10^{-4} L/(mol·s) at 600 K and 3.5 x 10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Substitute the given data into the Arrhenius equation.

$$\ln\frac{k_3}{\boxed{2.7 \text{ ´ } 10^{-4}}} = \frac{\boxed{1.66 \text{ ´ } 10^5 J}}{8.31 J/(mol \text{ x } K)}\left(\frac{1}{\boxed{600K}} - \frac{1}{750K}\right)$$

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.7×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Simplifying the temperature term we get:

$$\ln \frac{k_3}{2.7 \times 10^{-4}} = \frac{1.66 \times 10^5\ \mathrm{J}}{8.31\ \mathrm{J/(mol \cdot K)}}(2.05 \times 10^{-4})$$

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.7×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Reducing the right side of the equation we get:

$$\ln \frac{k_3}{2.7 \times 10^{-4}} = 4.098$$

Take inverse ln of both sides

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.7×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Taking the inverse natural log of both sides we get:

$$\frac{k_3}{2.7 \times 10^{-4}} = e^{4.098}$$

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.7×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Taking the inverse natural log of both sides we get:

$$\frac{k_3}{2.7 \times 10^{-4}} = 60.2$$

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.7×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Solving for k_3 we get:

$$k_3 = 2.7 \times 10^{-4}\ \text{L/(mol} \cdot \text{sec)} \times (60.2)$$

A Problem To Consider

- The rate constant for the formation of hydrogen iodide from its elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.7×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K. Find the activation energy, E_a.

- Solving for k_3 we get:

$$k_3 = 1.6 \times 10^{-2}\ \text{L/(mol} \cdot \text{sec)}$$

At 750 Kelvin

Operational Skills

- **Using the Arrhenius equation**

Time for a few review questions.