



☞ Dear students: - Copy the note and do the given homework on your exercise book!

Subject: **Chemistry**

Grade & section **11 (B-E)**

Unit: **4**

Main topic: **Collision Theory**

Sub topic/s: **The Arrhenius Equation**

Page range from: **195-197**

Monday, April 06, 2020

The Arrhenius Equation

The dependence of the rate constant of a reaction on temperature can be expressed by the following equation, known as the Arrhenius equation:

$$k = Ae^{-E_a/R} \quad \text{.....(1)}$$

Where,

- E_a is the activation energy of the reaction (in kJ/mol),
 - R is the gas constant (8.314 J/K / mol),
 - T is the absolute temperature, and
 - e is the base of the natural logarithm scale.
- ✓ The quantity A represents the collision frequency and is called the frequency factor. It can be treated as a constant for a given reacting system over a fairly wide temperature range.
- ✚ Equation (1) shows that:
- The rate constant is directly proportional to A and, therefore, to the collision frequency.
 - In addition, because of the minus sign associated with the exponent E_a/RT :
 - The rate constant decreases with increasing activation energy
 - Increases with increasing temperature.
- ❖ This equation can be expressed in a more useful form by taking the natural logarithm of both sides:

$$\begin{aligned} &\text{➤ } \ln k = \ln A e^{-E_a/RT} \text{ or} \\ &\text{➤ } \ln k = \ln A - E_a/RT \dots\dots\dots(2) \end{aligned}$$

❖ Equation (2) can be rearranged to a linear equation:

$$\begin{aligned} &\text{➤ } \ln k = (-E_a/R) (1/T) + \ln A \\ &\text{.....(3)} \\ &\text{➤ } Y = m x + b \end{aligned}$$

- ❖ Thus, a plot of $\ln k$ versus $1/T$ gives a straight line whose slope m is equal to $-E_a/R$ and whose intercept b with the y axis is $\ln A$.
- ❖ The following example demonstrates a graphical method for determining the activation energy of a reaction. Go to Tuesday's lesson

Tuesday, 07, 2020

Main point: Collision Theory

Subtopic: Example and practical exercise on Arrhenius Equation

1. The rate constants for the decomposition of acetaldehyde

$\text{CH}_3\text{CHO (g)} \longrightarrow \text{CH}_4(\text{g}) + \text{CO(g)}$, were measured at five different temperatures. The data are shown in the table. Plot $\ln k$ versus $1/T$, and determine the activation energy (in kJ/mol) for the reaction. Note that the reaction is "3/2" order in CH_3CHO , so k has the units of $1/\text{M}^{1/2} \cdot \text{s}$.

k ($1/\text{M}^{1/2} \cdot \text{s}$)	T (K)
0.011	700
0.035	730
0.105	760
0.343	790
0.789	810

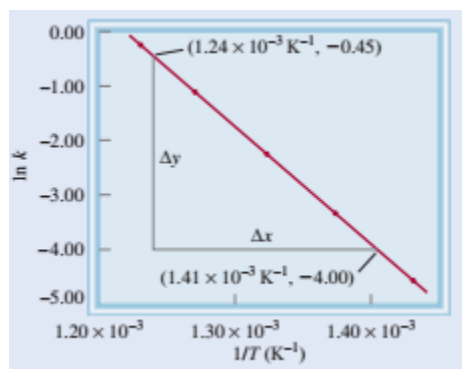
➤ Strategy: Consider the Arrhenius equation written as a linear equation

$$\ln k = (-E/R) (1/T) + \ln A$$

- A plot of $\ln k$ versus $1/T$ (y versus x) will produce a straight line with a slope equal to $-E_a/R$. Thus, the activation energy can be determined from the slope of the plot.
- **Solution:** First we convert the data to the following table.

$\ln k$	$1/T \text{ (K}^{-1}\text{)}$
-4.51	1.43×10^{-3}
-3.35	1.37×10^{-3}
-2.254	1.32×10^{-3}
-1.070	1.27×10^{-3}
0.237	1.23×10^{-3}

- A plot of these data yields the following the graph. The slope of the line is calculated from two pairs of coordinates:



- ✓ Slope = $\frac{-4.00 - (-0.45)}{(1.41 - 1.24) \times 10^{-3} \text{ K}^{-1}} = -2.09 \times 10^4 \text{ K}$
- ✓ From the linear form of Equation (3):
- ✓ Slope = $-E_a/R = -2.09 \times 10^4 \text{ K}$
- ✓ $E_a = (8.314 \text{ J/K} \cdot \text{mol})(2.09 \times 10^4 \text{ K})$

$$= 1.74 \times 10^5 \text{ J/mol} = 1.74 \times 10^2 \text{ kJ/mol}$$

Practice Exercise

1. The second-order rate constant for the decomposition of nitrous oxide (N₂O) into nitrogen molecule and oxygen atom has been measured at different temperatures:

k (1/M.s)	T (°C)
0.00187	600
0.0113	650
0.0569	700
0.244	750

Determine graphically the activation energy for the reaction.

2. Exercise 4.7 question #3

Wednesday, 08, 2020

Main point: Collision Theory

Subtopic: Arrhenius Equation with 3 various temperatures

- ❖ An equation relating the rate constants k_1 and k_2 at temperatures T_1 and T_2 can be used to calculate the activation energy or to find the rate constant at another temperature if the activation energy is known.
- ❖ To derive such an equation we start with Equation (2) from Monday's lesson:

$$\ln k_1 = \ln A - E_a / RT_1$$

$$\ln k_2 = \ln A - E_a / RT_2$$

- Subtracting $\ln k_2$ from $\ln k_1$ gives

$$\ln k_1 - \ln k_2 = E_a / K (1/T_2 - 1/T_1)$$

$$\ln(k_1/k_2) = E_a / K (1/T_2 - 1/T_1) \quad (4)$$

Example

1. The rate constant of a first-order reaction is $3.46 \times 10^{-2} \text{ s}^{-1}$ at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol

➤ Strategy: A modified form of the Arrhenius equation relates two rate constants at two different temperatures [see Equation (4)]. Make sure the units of R and E_a are consistent.

➤ **Solution:** The data are

$$k_1 = 3.46 \times 10^{-2} \text{ s}^{-1}$$

$$k_2 = ?$$

$$T_1 = 298 \text{ K}$$

$$T_2 = 350 \text{ K}$$

$$\text{Using equation (4)} \quad k_2 = 0.702 \text{ s}^{-1}$$

Practice Exercise

1. The first-order rate constant for the reaction of methyl chloride (CH_3Cl) with water to produce methanol (CH_3OH) and hydrochloric acid (HCl) is $3.32 \times 10^{-10} \text{ s}^{-1}$ at 25°C . Calculate the rate constant at 40°C if the activation energy is 116 kJ/mol.
2. Exercise 4.7 # 1, 2

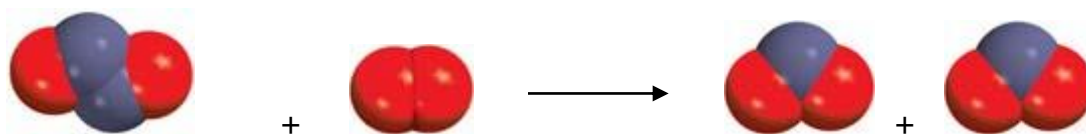
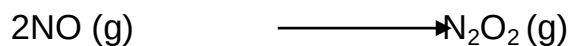
Thursday, April 09, 2020

Main point: Rate Law

Subtopic: Reaction Mechanism

- As we mentioned earlier, an overall balanced chemical equation does not tell us much about how a reaction actually takes place.
- In many cases, it merely represents the sum of several elementary steps, or elementary reactions, a series of simple reactions that represent the progress of the overall reaction at the molecular level.
- The term for the sequence of elementary steps that leads to product formation is reaction mechanism. The reaction mechanism is comparable to the route of travel followed during a trip; the overall chemical equation specifies only the origin and destination.

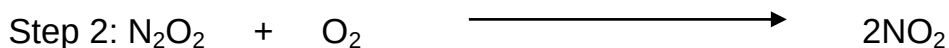
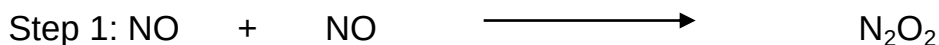
- As an example of a reaction mechanism, let us consider the reaction between nitric oxide and oxygen:



In the first elementary step, two NO molecules collide to form a N_2O_2 molecule.

This event is followed by the reaction between N_2O_2 and O_2 to give two molecules of NO_2 .

The net chemical equation, which represents the overall change, is given by the sum of the elementary steps:



Species such as N_2O_2 are called intermediates because they appear in the mechanism of the reaction (that is, the elementary steps) but not in the overall balanced equation.

Keep in mind that an intermediate is always formed in an early elementary step and consumed in a later elementary step.

- The molecularity of a reaction is the number of molecules reacting in an elementary step. These molecules may be of the same or different types.

- Each of the elementary steps discussed above is called a bimolecular reaction, an elementary step that involves two molecules.
- An example of a uni-molecular reaction, an elementary step in which only one reacting molecule participates, is the conversion of cyclopropane to propene discussed in Tuesday's lesson example. Very few termolecular reactions, reactions that involve the participation of three molecules in one elementary step, are known, because the simultaneous encounter of three molecules is a far less likely event than a bimolecular collision.

Home Work

✓ Exercise 4.9

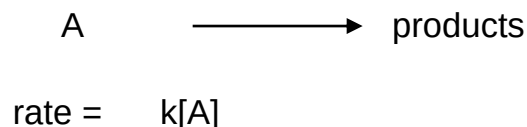
Friday, April 10, 2020

Main point: Chemical Kinetic

Subtopic: Rate Laws and Elementary Steps

Rate Laws and Elementary Steps

Knowing the elementary steps of a reaction enables us to deduce the rate law. Suppose we have the following elementary reaction:

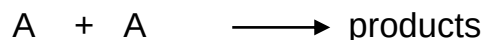


For a bimolecular elementary reaction involving A and B molecules

$\text{A} + \text{B} \longrightarrow \text{product}$, the rate of product formation depends on how frequently A and B collide, which in turn depends on the concentrations of A and B. Thus, we can express the rate as

$$\text{Rate} = k[\text{A}][\text{B}]$$

Similarly, for a bimolecular elementary reaction of the type



or $2A \longrightarrow \text{products}$, the rate becomes

$$\text{rate} = k[A]^2$$

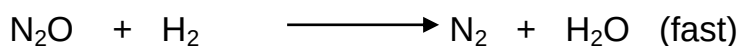
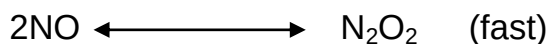
The preceding examples show that the reaction order for each reactant in an elementary reaction is equal to its stoichiometric coefficient in the chemical equation for that step. In general, we cannot tell by merely looking at the overall balanced equation whether the reaction occurs as shown or in a series of steps. This determination is made in the laboratory.

When we study a reaction that has more than one elementary step, the rate law for the overall process is given by the rate-determining step, which is the slowest step in the sequence of steps leading to product formation.

An analogy for the rate-determining step is the flow of traffic along a narrow road. Assuming the cars cannot pass one another on the road, the rate at which the cars travel is governed by the slowest-moving car.

The sum of the elementary steps must give the overall balanced equation for the reaction. The rate-determining step should predict the same rate law as is determined experimentally

Example



Homework`

✓ **Review Questions of unit 4 part II**