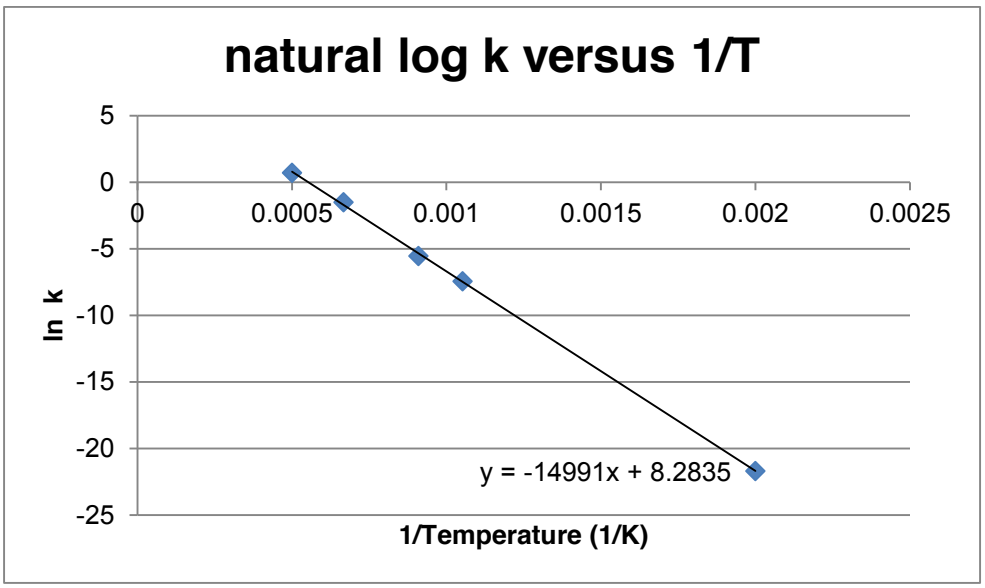
Kinetics: The Arrhenius Equation

1. Question: The rate constants for the decomposition of a certain substance were measured at five different temperatures. The data is given in the table below. Graphically determine the activation energy of the reaction in kJ/mol.

k ($M^{-1}s^{-1}$)	T (K)
3.81×10^{-10}	500
5.90×10^{-4}	950
3.90×10^{-3}	1100
0.221	1500
2.05	2000

Answer: A plot of ln *k* vs 1/T (in Kelvin) will yield a straight line with slope, $m = -\frac{E_a}{R}$



We can plug the value of the slope into the equation given above:

$$-14991\,\frac{1}{K} = -\frac{E_a}{8.314\,\frac{J}{mol\cdot K}}$$

$$-14991\,\frac{1}{K} \times \left(-8.314\,\frac{J}{mol\cdot K}\right) = E_a$$

$$1.25\times10^{5}\,\frac{J}{mol} = 125\ kJ/mol$$

2. Question: A reaction has an activation energy of 205 kJ/mol. At 250.°C, the rate constant is 4.45×10^{-3} s^{-1}. Calculate the rate constant at 350.°C.

   Answer: To determine the value of the rate constant at 350 °C, use the two point Arrhenius equation:

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

   The temperature must be in Kelvins.

   $T_1 = 250.°C + 273 = 523\ K$ $\quad k_1 = 4.45 \times 10^{-3}\ s^{-1}$

   $T_2 = 350.°C + 273 = 623\ K$ $\quad k_2 = ?$

   Need to match the energy units of the activation energy with the energy units or R.

$$\ln\left(\frac{k_2}{4.45\times10^{-3}\ s^{-1}}\right) = -\frac{205{,}000\ J/mol}{8.314\ J/(mol\cdot K)}\left(\frac{1}{623\ K} - \frac{1}{523\ K}\right)$$

$$\ln\left(\frac{k_2}{4.45\times10^{-3}\ s^{-1}}\right) = 7.57$$

$$\frac{k_2}{4.45\times10^{-3}\ s^{-1}} = e^{7.56}$$

$$\frac{k_2}{4.45\times10^{-3}\ s^{-1}} = 1.93\times10^{3}$$

$$k_2 = 8.61\,s^{-1}$$

Kinetics: Reaction Mechanisms

1. Question: Consider the following two step mechanism for decomposition of hydrogen peroxide.

   Step 1: $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)

   Step 2: $H_2O_2 + IO^- \rightarrow H_2O + + O_2 + I^-$ (fast)

   Answer each of the following questions.

   a. Which substance or substances are intermediates?
   b. Which substance (if any) is a catalyst?
   c. What is the overall reaction?
   d. What is the rate law?

   Answer:

   a. Intermediates are formed (a product) in an early step of the mechanism and is consumed (reactant) in a later step. It will not show up in the overall reaction. IO^- is the only intermediate in the mechanism.

   b. A catalyst is consumed (reactant) in an early step of the mechanism and is produced (product) in a later step. It too, will not show up in the overall reaction. I^- is the catalyst for this reaction.
   c. Cancel out intermediates and catalysts. The reaction overall equation is:

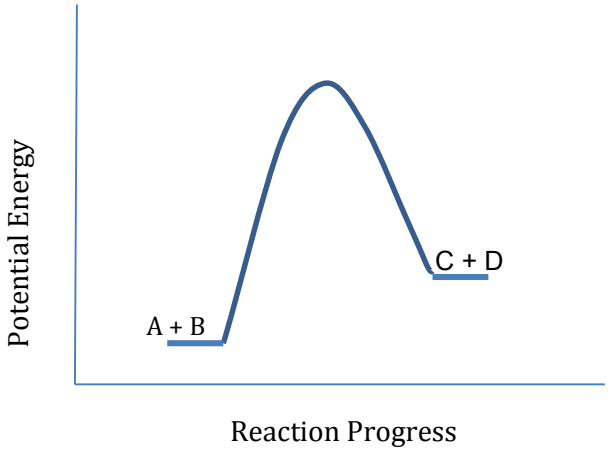
      $$2H_2O_2 \rightarrow 2H_2O + O_2$$

   d. When given a mechanism, find the slow step (rate determining step) and use the coefficients of the elementary step to determine the order.

      $$\text{Rate} = k[H_2O_2][I^-]$$

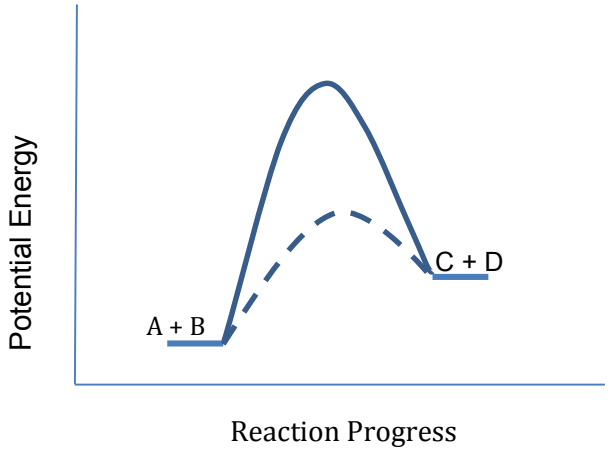
Kinetics: Catalysts

1. Question: Examine the following diagram depicting the potential energy diagram for the reaction: $A + B \rightarrow C + D$.



Draw (within the same diagram above) the potential energy curve if an effective catalyst is used in the reaction.

Answer: A catalyst works by lowering the activation energy of the reaction.



2. Question: Describe the similarities and differences between the following.

    a. A homogeneous catalyst.
    b. A heterogeneous catalyst.
    c. An enzyme.

    Answer: All catalysts work by lowering the activation energy and are not consumed in the course of the reaction. Below are the differences of each.

    a. Homogeneous catalysts are catalysts which are in the same phase as the reactants. For example, if the reactants are aqueous, the catalyst is also aqueous.
    b. A heterogeneous catalyst is in a different phase than the reactants. For example, if the reactants are gases, a heterogeneous gas might be a solid.
    c. An enzyme is a biological catalyst produced in a living organism.