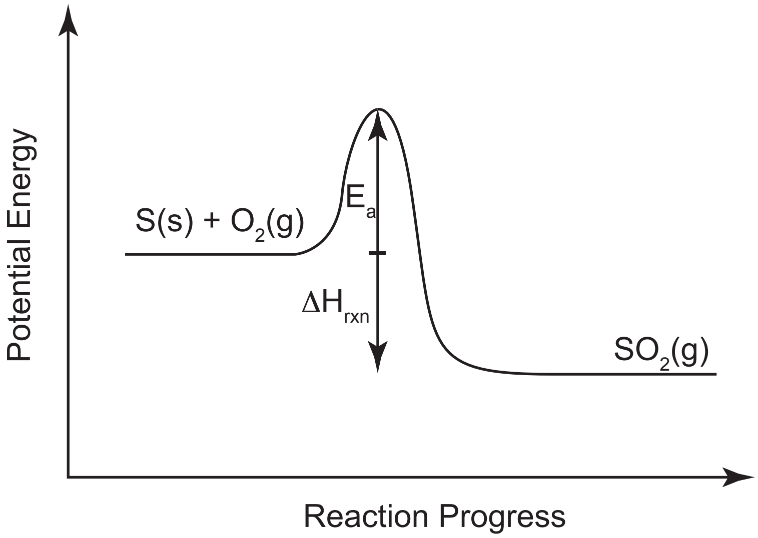
1. Sketch a potential energy versus reaction progress plot for the following reaction:

   $S(s) + O_2(g) \longrightarrow SO_2(g),\ \Delta H_{rxn} = -296\ kJ/mol$

   Label the axes, write the reactants and products in the correct location, label the activation energy (E_a), and label the enthalpy of reaction (ΔH_{rxn}).



2. Given an activation energy of 56.8 kJ/mol and a frequency factor of $1.5 \times 10^{11}\ s^{-1}$, calculate the rate constant of the reaction at 25°C and 50°C.

   Must use J and K for the units to work correctly. $R = 8.314\ \frac{J}{mol \cdot K}$. Also, note that you can get the units of k from the units of the frequency factor. In this case, the reaction order is first order.

   $k = Ae^{\frac{-E_a}{RT}}$

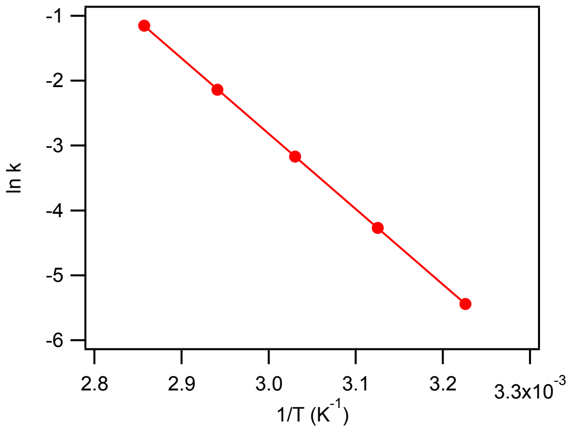
   At 25°C, $T = 298.15\ K$, $E_a = 5.68 \times 10^4\ J/mol$.

   $k = 17\ s^{-1}$.

   At 50°C. $T = 323.15\ K$, $E_a = 5.68 \times 10^4\ J/mol$.

   $k = 99\ s^{-1}$

3. The rate constant for a reaction was measured at several temperatures and an Arrhenius plot was made, shown below. A straight line fit through the data had the following equation: $y = -1.162 \times 10^5 x + 32.06$. Calculate the activation energy and the frequency factor for the reaction.



$lnk = \frac{-E_a}{R}\left(\frac{1}{T}\right) + lnA$

slope = $\frac{-E_a}{R} = -1.162 \times 10^5\ K$

$E_a = 966086.8\ J/mol$ or $966.1\ kJ/mol$

Intercept = $lnA = 32.06$

$e^{lnA} = e^{32.06}$

$A = 8.4 \times 10^{13}$

4. Consider this two-step mechanism for a reaction:

$NO_2(g) + Cl_2(g) \xrightarrow{k_1} ClNO_2(g) + Cl(g)$ slow

$NO_2(g) + Cl(g) \xrightarrow{k_2} ClNO_2(g)$ fast

(a) What is the overall reaction?
(b) Identify any intermediates in the mechanism.
(c) What is the predicted rate law?

Overall Reaction:
$2\,NO_2 + Cl_2 \longrightarrow 2\,ClNO_2$

Cl(g) is an intermediate.

Slow step will determine the overall rate. In this case, $Rate = k_1[NO_2][Cl_2]$

5. Consider the following mechanism:

step 1: $A + B \underset{k_{reverse}}{\overset{k_{forward}}{\rightleftharpoons}} C$ (equilibrium)
step 2: $C + A \xrightarrow{k} D$ (slow)
overall: $2A + B \xrightarrow{k'} D$

Determine the rate law for the overall reaction (where the overall rate constant is represented as k).

Note: An intermediate should not appear in the rate law.

We know the slow step determines the overall rate, so $Rate = k[C][A]$. But we cannot have an intermediate (C) in the rate law (it does not appear in the overall reaction).

So we need to solve for $[C]$ in terms of values that appear in the overall reaction.

For step 1, $Rate_{forward} = k_{forward}[A][B]$

and, $Rate_{reverse} = k_{reverse}[C]$.

At equilibrium, the forward and reverse rates are equal.

$k_{forward}[A][B] = k_{reverse}[C]$

so: $[C] = \left(\frac{k_{forward}}{k_{reverse}}\right)[A][B]$

Now plug into the overall rate law:

$Rate = k[C][A] \Rightarrow k\left(\frac{k_{forward}}{k_{reverse}}\right)[A][B][A]$

All of the k values can be incorporated into one rate constant, so $Rate = k'[A]^2[B]$