Week 5 Worksheet

Chem 11300-2: Section 33

April 26, 2022

***Problem* 1:** The reaction

$$2\,\mathrm{NO\,(g)} + 2\,\mathrm{H_2\,(g)} \longrightarrow \mathrm{N_2\,(g)} + 2\,\mathrm{H_2O\,(g)}$$

has beeen proposed to follow a 3 step mechanism, partially shown below

Step 1: $\mathrm{NO\,(g)} + \mathrm{NO\,(g)} \rightleftharpoons \mathrm{N_2O_2\,(g)}$ (fastest)

Step 2: $\mathrm{N_2O_2\,(g)} + \mathrm{H_2\,(g)} \longrightarrow \mathrm{N_2O\,(g)} + \mathrm{H_2O\,(g)}$ (slow)

Step 3: ... (fast)

a) Determine the reaction that occurs in step 3 to complete the mechanism.

b) Determine the rate law for the overall reaction based on the mechanism given above.

c) Kinetic data was collected for this reaction, as seen in the table below. Do these data give us any sense of whether or not the mechanism proposed above is possible or not? Explain.

Trial	Inital [NO] (M)	Initial [H_2] (M)	Initial Rate (M/s)
1	0.360	0.200	0.051
2	0.360	0.600	0.460
3	1.080	0.600	1.380

***Problem* 2:** 10.22 g of water vapor is placed into an empty, 200 mL fixed-volume container at 25° C, at which point it is decomposed according to the following reaction

$$\mathrm{H_2O\,(g)} \longrightarrow \mathrm{H_2\,(g)}\,\frac{1}{2}\,\mathrm{O_2\,(g)}$$

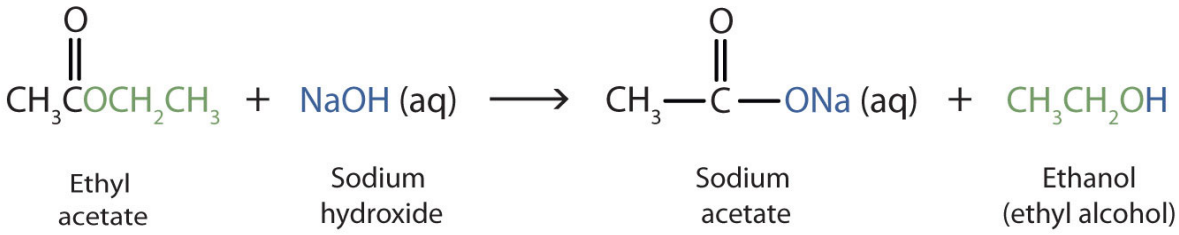
Time (min)	[H_2O (g)] (M)
0	?
10	2.20
15	1.93
20	1.70
25	1.50

a) What is the initial concentration of water vapor in the container?

b) Given the data below, calculate the value of the rate constant for this one-step process.

c) Calculate the total pressure in the container after 30 minutes of decomposition.

***Problem* 3** (Hard)**:** Esters can be hydrolyzed via the well-known saponification reaction which is present in the production of natural soap from animal fats. Consider the following acetate ester saponification



It is hypothesized that this reaction proceeds via a second order rate law given by

$$\frac{dC_A}{dt}(t) = kC_{OH}(t)C_E(t) \tag{1}$$

where C_A is the concentration of sodium acetate, C_{OH} is the concentration of hydroxide ions, and C_E is the concentration of ethyl acetate (all of which are functions of time).

1. You first want to determine k for this reaction. Suppose in lab, you were able to determine $C_A(t)$ and you also knew the initial concentrations of hydroxide (C^0_{OH}) and ethyl acetate (C^0_E) for each reaction you performed.

   a) Argue, physically that you can write $C_{OH}(t) = C^0_{OH} - C_A(t)$. Come up with a similar expression for C_E.

   b) Substitute your expressions for $C_{OH}(t)$ and $C_E(t)$ into Eq. 1. Consider only the case where $C^0_E = C^0_{OH}$ and show that (integrate and apply the initial value condition!)

   $$\frac{C_A(t)}{C^0_E - C_A(t)} = C^0_E kt \tag{2}$$

   c) A little harder, but in the case $C^0_E \neq C^0_{OH}$, show that

   $$\ln\left[\frac{C^0_{OH}(C^0_E - C_A(t))}{C^0_E(C^0_{OH} - C_A(t))}\right] = k(C^0_E - C^0_{OH})t \tag{3}$$

   Hint: Use the partial fraction expansion before integrating.

   d) Using Eq. 2 and 3, and given the initial concentrations of OH^- and ethyl acetate as well as $C_A(t)$, explain how you would determine k. Your graphs would look like those in Figure 1 for an appropriately chosen $\Gamma(t)$ function (you should know what the $\Gamma(t)$ function is for each graph).

2. We are now interested in determining the energy of activation (E_a) for this reaction.

   (a) Write the Arrhenius relationship between k and E_a.

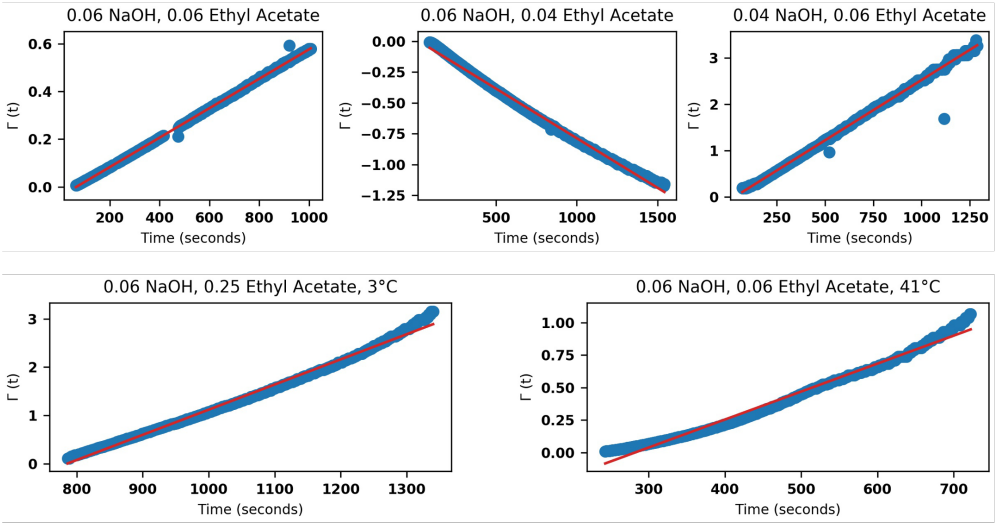


Figure 1: Plots of $\Gamma(t)$ versus time (blue curve) with the red line being the linear regression (best fit line for the data) for various initial concentrations of NaOH and ethyl acetate and reaction temperatures. If no temperature is specified, assume $T = 23°\text{C}$.

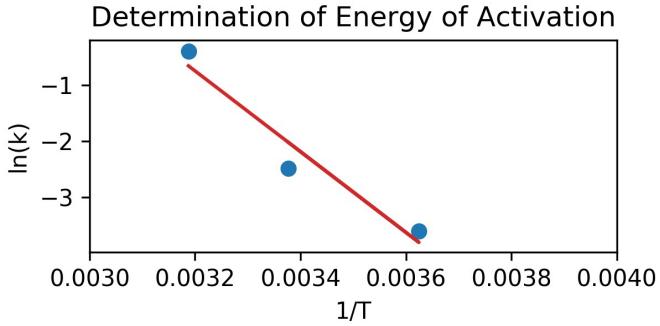


Figure 2: Plot of k versus $1/T$ from those value given from Figure 1.

(b) Using the data provided in Figure 1, you make the plot in Figure 2. Explain how you can determine E_a from this plot.

(c) From the Figure 2, the best fit line can be approximated by just the 2 end-points. Given the following data, determine the activation energy. Compare this to E_a given by the red line, 14.30 ± 3.66 kcal/mole, as well as the literature accepted value 11.56 kcal/mol.

k [M^{-1} s^{-1}]	T [°C]
0.0272	3
0.6729	41

The following problems are written by Professor Mcleod or Head TA Miah Turke. They may mimic homework problems closely, but will be highly beneficial for the midterms and final.

***Problem* 4:** Lets use the integrated rate law and the definition of a half-life to derive equations

for $t_{1/2}$.

a) First, what is the definition of a half-life?

b) Derive the equation for half-life ($t_{1/2}$) for a reaction with a rate given by

$$rate = k$$

using the definition from (a) and the integrated rate law that corresponds to a reaction of this type.

c) Derive the equation for half-life ($t_{1/2}$) for a reaction with a rate given by

$$rate = k[A]$$

using the definition from (a) and the integrated rate law that corresponds to a reaction of this type.

d) Derive the equation for half-life ($t_{1/2}$) for a reaction with a rate given by

$$rate = k[A]^2$$

using the definition from (a) and the integrated rate law that corresponds to a reaction of this type.

***Problem* 5:** Let us explore the rate of the decomposition of oxygen to ozone with an overall balanced reaction given by

$$2\,O_3\,(g) \longrightarrow 3\,O_2(g)$$

and elementary steps given by

$$O_3\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2\,(g) + O\,(g)$$

$$O\,(g) + O_3\,(g) \xrightarrow{k_2} 2\,O_2\,(g)$$

a) First, assuming that the second step is rate-determining, what is the rate expression that you would predict consistent with the given reaction mechanism.

b) Now, use the steady-state approximation to predict a rate expression consistent with the given reaction mechanism.

c) According to the experimental data given in the table below, determine the rate expression and rate constant for the overall reaction if the form of the rate expression is given by the following

$$rate = k[O_3]^M[O_2]^n$$

$[O_3](M)$	$[O_2]$ (M)	Initial Rate ($M^{-1}s^{-1}$)
0.100	0.100	2.8×10^{-6}
0.050	0.100	7.0×10^{-7}
0.200	0.050	2.24×10^{-5}

d) Is the experimental data consistent with the reaction rates you predict for the reaction mechanism? Are the two reaction rates consistent with each other?