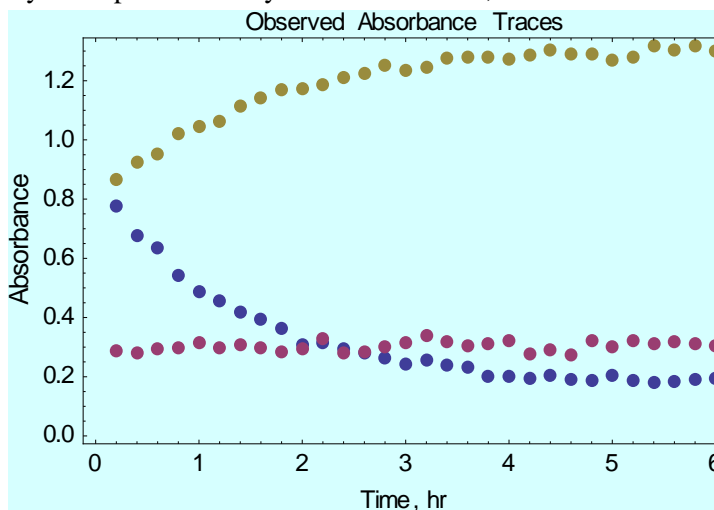


Chemical Kinetics HW1

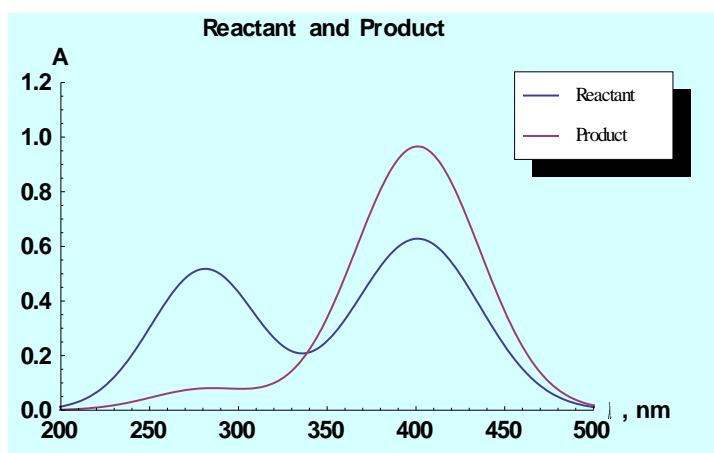
(Kahn, 2013)

Question 1. (8 pts)

Three students monitored the kinetics of a unimolecular irreversible reaction by UV-Vis spectrophotometry. To make things more interesting, they decided to see if the wavelength at which the absorbance is measured affects the reaction rate. Thus, the first student chose 280 nm, the second student observed the reaction at 400 nm, and the third student tuned her spectrophotometer to 338 nm. When they met up the next day to discuss results, the first student declared “When I monitored the reaction at 280 nm, I observed a rapid decrease in absorbance”. The second student stated “When I observed the reaction at 400 nm, I observed a slow increase in absorbance”. The third student was first quiet but then admitted “At 338 nm, I could not see any change; I guess my reaction just did not work”. They plotted their measurements (shown on the right) and tried to calculate rate constants from their own data but could not agree with each other.



Confused, the students headed up to the library and looked up the spectra of the reactant and the product (shown on the right) from their favorite kinetics textbooks. First student found that from one book that molar absorptivities of the reactant are $5911 \text{ M}^{-1} \text{ cm}^{-1}$, $2100 \text{ M}^{-1} \text{ cm}^{-1}$, and $5714 \text{ M}^{-1} \text{ cm}^{-1}$ at 280, 338, and 400 nm, respectively. The second student found from another book that molar absorptivities of the product are $1185 \text{ M}^{-1} \text{ cm}^{-1}$, $2100 \text{ M}^{-1} \text{ cm}^{-1}$, and $9366 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The third student looked through the third book and said “This is all very confusing; the only thing I found was a statement that the total absorbance of a mixture is a sum of absorbance contributions of individual components.” Suspecting that they may have made some mistakes, our three students repeated the measurements (total of 31 times), but got more or less the same results each time.



Help our three students to figure out what is going on by analyzing their data. Could you confirm that the reaction follows first-order kinetics, as anticipated for a unimolecular irreversible reaction? Could you calculate the rate constant for their reaction?

Each of you will analyze one of the 31 replicas (a slightly different datasets). You will find your file in a directory http://web.chem.ucsb.edu/~kalju/chem111/public/HW1_Q1/ with name such as **HW1_Q1_data_PERM.dat** where *PERM* stands for the last four digits of your PERM number. Each file contains four columns. The first one is time (in hours), and the next three correspond to observed absorbance values at 280, 338, and 400 nm, respectively.

Provide graphs and appropriate formulas that illustrate your work. If you think that it is possible to calculate the rate constant from this data, give your best estimate for the rate constant.

Question 2. (4 pts)

One of the first scientists to carefully measure the kinetics of decomposition of azomethane was Herman Ramsperger, who used the manometric method to determine the order of reaction. His original data are shown

<u>Time, min</u>	<u>[Azomethane]</u>
0	21.23
3	16.77
6	13.03
9	10.20
12	8.06
17	5.55
25	3.15

Perform fitting of this data to integrated rate law for the first order reaction in order to check if his data really supports the first order rate law. Use both the linear regression in logarithmic coordinates, and nonlinear regression. Check if fit residuals look random when plotted against time. Provide relevant graphs, and give estimates of rate constants from these two methods.

Question 3. (8 pts)

Background: Esters undergo slow hydrolysis in aqueous solutions. This hydrolysis is usually catalyzed by both acids and bases, and the observed rate is a sum of uncatalyzed, acid-catalyzed, and base-catalyzed reactions:

$$v = (k_n[\text{H}_2\text{O}] + k_a[\text{H}^+] + k_b[\text{OH}^-]) \cdot [\text{Ester}]$$

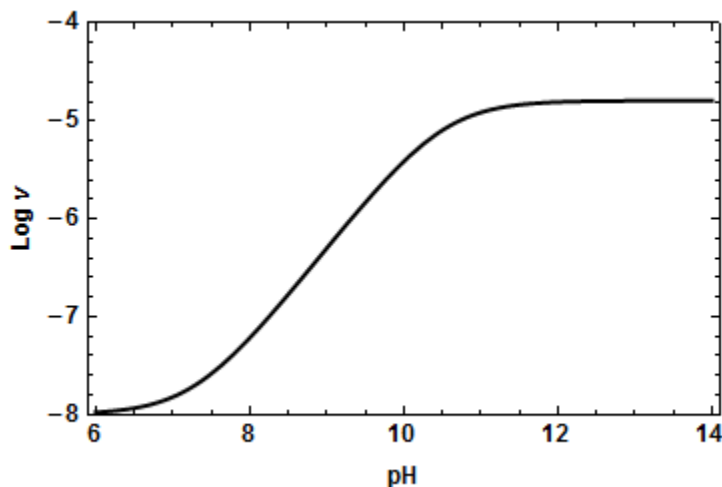
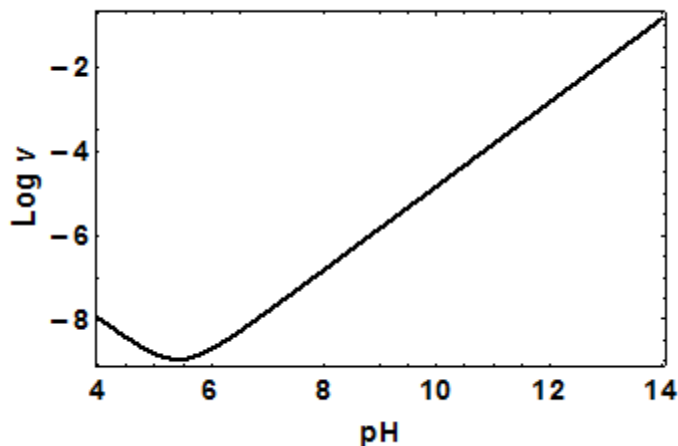
When analyzing the pH-dependence of reaction rates, it is convenient to represent reaction rates in 10-base logarithmic units. The pH-dependence of the rate of hydrolysis of methyl acetate, based on the above equation, is shown on the right.

In the alkaline region, the acid-catalyzed hydrolysis and uncatalyzed reaction are insignificant. Here, the rate of the base-promoted reaction dominates, and the reaction follows a second order rate law:

$$v = k_2[\text{OH}^-][\text{Ester}]$$

This rate law predicts that the logarithm of the rate will increase linearly with the increase in pH in the alkaline region. This is indeed seen in the case of alkaline hydrolysis of most esters.

Hydrolysis of methyl salicylate also appears to be base-catalyzed as evident from a significant increase in reaction rate between pH 6 and pH 10.5. However, beyond pH 10.5, the reaction rate does not change much. (Figure below)



Question. Hydrolysis of methyl salicylate was studied by mixing the sodium salt of methyl salicylate with sodium hydroxide such that the final concentration of the ester and sodium hydroxide were both 0.04 M. After set amounts of time, the reaction was stopped with excess of HCl, and the amount of hydroxide that had reacted was determined by titration. The following data was obtained:

Time, min	Fraction Reacted
20.000	0.086
40.000	0.147
60.000	0.209
80.000	0.269
100.000	0.346
120.000	0.382
140.000	0.435
160.000	0.492
180.000	0.525
200.000	0.577
220.000	0.601
240.000	0.623
260.000	0.668
280.000	0.705
300.000	0.716
320.000	0.721
340.000	0.764
360.000	0.786
380.000	0.794
400.000	0.825

- 1) Determine the order of the reaction from this single time curve using the *differential method*.
- 2) Discuss reasons why alkaline hydrolysis of methyl salicylate shows unusual behavior in comparison with other esters. Your answer could be either intuitive (e.g. you outline your chemical rationale for the observed behavior) or mathematical (e.g. you derive a rate expression based on your proposed chemical mechanism of hydrolysis). If you use literature sources, make sure to cite your sources.