Jeremy · Hook

Homework 4 – Due 10/30/20 @ 12:00pm (Noon)

1) You are living in a tropical paradise. Food is plentiful. The sun is shining. People no longer feel ashamed about their Nickelback CD collections. Humanity has evolved. You are now free to engineer whatever you desire. Your next experiment is on determining the reaction order of a reaction for the synthesis of chemical X, which can be used to catalyze the formation of artificial chocolate (cacao). You take a container labeled "reagents" off the shelf and pour it into an isothermal, isobaric batch reactor and monitor the concentration over time. You suspect the reaction has the chemical equation $A \rightarrow X$ and is irreversible.

time (min)	0	1	2	3	4	5	6	7	8	9	10
C_A (mol/L)	1.337	0.813	0.571	0.438	0.363	0.304	0.267	0.229	0.207	0.191	0.173

a. Using the Integral Method, find the order of the reaction. Create a plot in Python with the kinetic data and your fitted line with the appropriate axes for the order of the reaction. Be sure to label the axes (with units, if applicable) and give it a legend.

b. From your fit in part a, what is the reaction rate constant for this process?

c. After reading the container of "reagents" more carefully, you realize that the chemical equation for the reaction was actually $2A + B \rightarrow X$ all along and the reaction follows an elementary rate law. It also says that the reaction rate constant is 0.02 $L^2\ mol^{-2}\ min^{-1}$. Given this new information, what was the concentration of B if it was held constant when the tabulated data was gathered.

2) Kinetic rate data (which can be found on Canvas) is given for a chemical reaction $A \rightarrow B$, but the order of the reaction is not known. The reaction occurred in an isothermal, isobaric batch reactor. The units of the concentration data are in mol/L and time is in minutes.

a. Use the Differential Method to determine the order of the reaction given the kinetic rate data. You may round to the nearest integer. It would be best to perform these calculations in Python (`np.diff()` is very helpful here).

b. Calculate the rate constant of the reaction as well with the proper units.

c. Include the plot of your fitted line and of the provided data with appropriately labeled axes.

3) Consider a set of three reactions which occur in parallel and produce a desired product D and two undesired products U_1 and U_2 (you are given the experimental rate law of each reaction):

$$A + B \rightarrow D \qquad r_D = k_1 C_A^2 C_B$$
$$A + B \rightarrow U_1 \qquad r_{U_1} = k_2 C_A C_B$$
$$A + B \rightarrow U_2 \qquad r_{U_2} = k_3 C_A^3 C_B$$

a. Write the equation for the instantaneous selectivity of D with respect to U_1, with respect to U_2, and with respect to both U_1 and U_2.

b. Sketch a plot of the instantaneous selectivity with respect to the concentration of A for each case of part a. Explain the shape of your curves and the difference between curves.

c. Which value of C_A results in the largest instantaneous selectivity of D with respect to both U_1 and U_2?

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In [162]:
```
import numpy as np
import matplotlib.pyplot as plt
from scipy.stats import linregress
import numpy as np                      # for scientific functions - mostly nume
rical
from matplotlib import pyplot as plt   # for plotting
from scipy.optimize import leastsq     # the function to carry out leastsquare
 optimization
```

PROBLEM # 1

1)You are living in a tropical paradise. Food is plentiful. The sun is shining. People no longer feel ashamed about their Nickelback CD collections. Humanity has evolved. You are now free to engineerwhatever you desire. Your next experimentis on determining the reaction order of a reaction for the synthesis of chemical X, which can be used to catalyze the formation of artificial chocolate(cacao). You take a container labeled “reagents”off the shelf and pour it into an isothermal, isobaric batch reactor and monitor the concentration over time. You suspect the reaction has the chemical equation A --> X and is irreversible.

time(min)012345678910

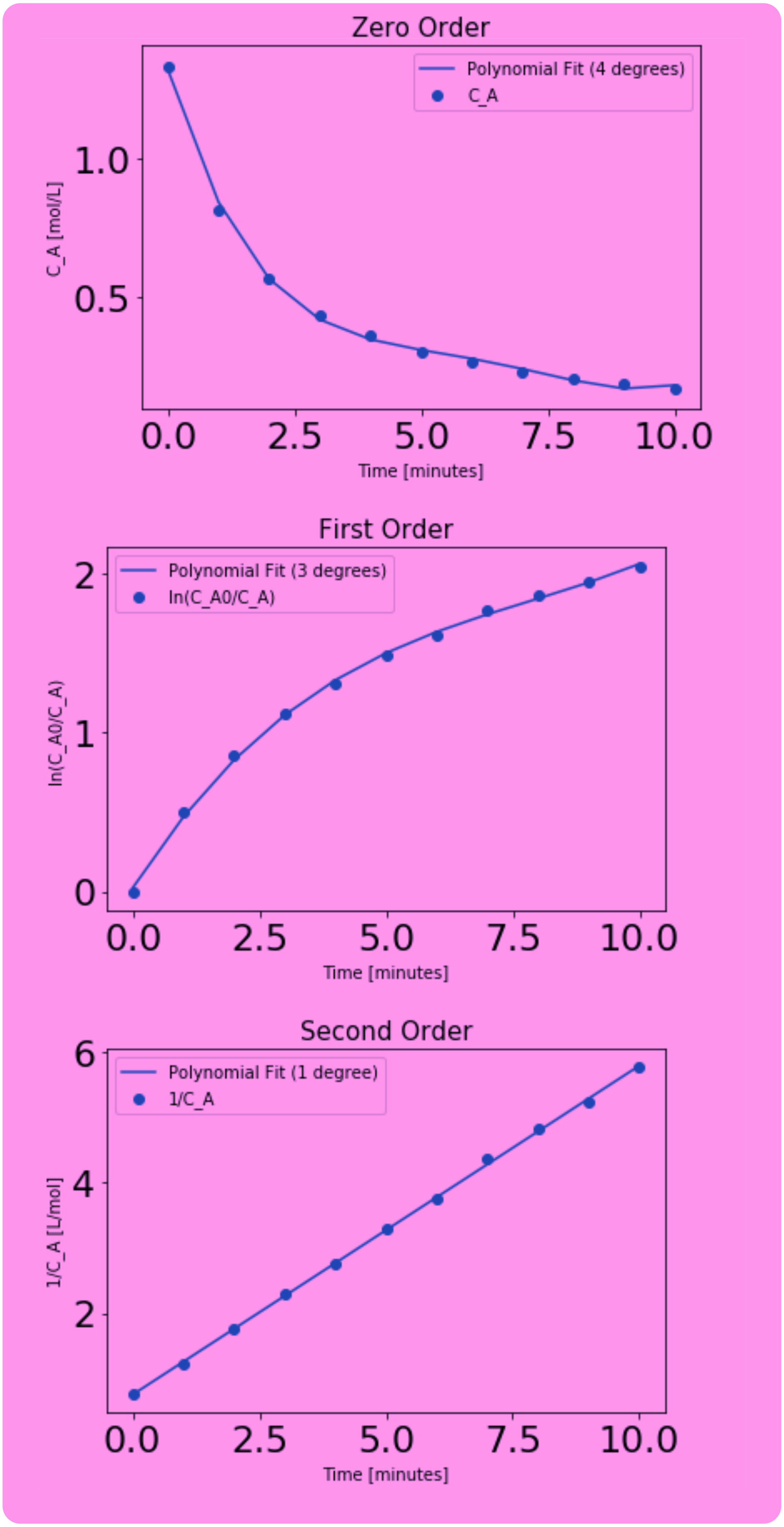
CA(mol/L)1.3370.8130.5710.4380.3630.3040.2670.2290.2070.1910.173

In [163]:
```
time = np.array([0,1,2,3,4,5,6,7,8,9,10]) #Minutes
C_A = np.array([1.337,0.813,0.571,0.438,0.363,0.304,0.267,0.229,0.207,0.191,0.
173]) #mol/L
```

a.Using the Integral Method, find the order of the reaction. Create a plotin Python with the kinetic data and your fitted line with the appropriate axes for the order of the reaction. Be sure to label the axes (with units, if applicable) and give it a legend.

In [164]:
```
fig = plt.figure()
#Guess 1: zero order

plt.scatter(time, C_A, label ="C_A")
m0, b0, c0, d0, e0 = np.polyfit(time, C_A, 4) #Best-fitted line
plt.plot(time, m0*time**4+b0*time**3+c0*time**2+d0*time+e0 ,label ="Polynomial Fit (4 degrees)")
plt.title("Zero Order",size = '15')
plt.xlabel("Time [minutes]",size = '10')
plt.ylabel("C_A [mol/L]",size = '10')

plt.legend(prop={"size":10})

#Guess 2: first order
plt.figure()
ln = np.log(C_A[0]/C_A)
plt.scatter(time, ln, label ="ln(C_A0/C_A)")
m1, b1, c1, d1 = np.polyfit(time, ln, 3) #Best-fitted line
plt.plot(time, m1*time**3+b1*time**2+c1*time+d1, label ="Polynomial Fit (3 degrees)")
plt.title("First Order",size = '15')
plt.xlabel("Time [minutes]",size = '10')
plt.ylabel("ln(C_A0/C_A)",size = '10')
plt.legend(prop={"size":10})

#Guess 3: second order
plt.figure()
inv = (1/C_A)
plt.scatter(time, inv, label ="1/C_A")
m2, b2 = np.polyfit(time, inv, 1) #Best-fitted line
plt.plot(time, m2*time+b2, label ="Polynomial Fit (1 degree)")
plt.title("Second Order",size = '15')
plt.xlabel("Time [minutes]",size = '10')
plt.ylabel("1/C_A [L/mol]",size = '10')
plt.legend(prop={"size":10})
```

```
Out[164]: <matplotlib.legend.Legend at 0x19dc6244a88>
```



Due to the linear fit of the data to our "Second Order" plot we can see that the order of the reaction is 2

b.From your fit in part a, what is the reaction rate constant for this process?

In [165]:
```
#We can see from part a that this is a second order process, because it has a
 linear fit which is 1/C_A = 1/C_A0 + kt
k = m2 # The slope of this linear fit will be out k value
print('Reaction rate constant (k)= {:.5f} [L /(mol)(min)]'.format(k))
```

```
Reaction rate constant (k)= 0.50528 [L /(mol)(min)]
```

c.After reading the container of “reagents”more carefully,you realize that the chemical equation for the reaction was actually 2A + B --> X all alongand the reaction follows an elementary rate law. It also says that the reaction rate constant is 0.02 L2mol-2min-1. Given this new information, what was the concentration of B if it was held constant when the tabulated data was gathered.

In [166]:
```
#Reaction: 2A + B --> X, k = .02 [L^2/(mol^2*min)]
#The reaction follows an  elementary  rate  law = -r_A = -dC_A/dt = k*C_A^2*C_
B
k = 0.02  # [L^2/(mol^2*min)]

C_B = ((-1/C_A[10])-(-1/C_A[0]))/(-k*(time[10]-time[0])) #To find concentratio
n of C_B rearrange equation above and solve the differential to to solve for C
_B
print('If C_B was held constant C_B = {:.5f} [mol/L]'.format(C_B))
```

```
If C_B was held constant C_B = 25.16202 [mol/L]
```

PROBLEM # 2

2)Kinetic rate data (which can be found on Canvas) is given for a chemical reaction A --> B, but the order of the reaction is not known. The reaction occurred in an isothermal, isobaric batch reactor. The units of the concentration data are in mol/L and time is in minutes.

In [172]:
```
cA = np.array([9.871507338462981451e+00,7.043182012988722818e+00,5.74692461466
7721087e+00,4.971537585096347023e+00,4.457849128909017189e+00,4.06496028633292
1946e+00,3.772592721342783229e+00,3.514160649290875238e+00,3.31984500814574801
1e+00,3.160456588877444517e+00,3.009833424250920597e+00,2.879221218135621374e+
00,2.772167910991736317e+00,2.663273581787786171e+00,2.578182658197410326e+00,
2.493854311651262368e+00,2.419711253693596298e+00,2.354660875889686533e+00,2.2
91649331325676275e+00,2.232809013822000477e+00,2.178239995714944754e+00,2.1310
97725638296136e+00]) #mol/L
```

In [173]:
```
t = np.array([0.000000000000000000e+00,5.000000000000000000e-01,1.000000000000000000e+00,1.500000000000000000e+00,2.000000000000000000e+00,2.500000000000000000e+00,3.000000000000000000e+00,3.500000000000000000e+00,4.000000000000000000e+00,4.500000000000000000e+00,5.000000000000000000e+00,5.500000000000000000e+00,6.000000000000000000e+00,6.500000000000000000e+00,7.000000000000000000e+00,7.500000000000000000e+00,8.000000000000000000e+00,8.500000000000000000e+00,9.000000000000000000e+00,9.500000000000000000e+00,1.000000000000000000e+01,1.050000000000000000e+01]) #Minutes
```

a.Use the Differential Method to determine the order of the reaction given the kinetic rate data. You may round to the nearest integer. It would be best to perform these calculations in Python (np.diff()is very helpful here).

In [174]:
```
#Differential Method ln(-dCA/dt) = ln(kA) + alpha * ln(CA)
#plot ln(-dCA/dt) vs ln(CA)

ln_CA = np.log(cA)
diff_CA = np.diff(cA)
diff_time = np.diff(t)

delta_time = diff_time[0]
natlog_derivative = np.double(np.arange(0,22))
natlog_derivative[0] = np.double(np.log(-((-3)*cA[0] +4*cA[1] - cA[2])/(2*delta_time)))
natlog_derivative[21] = np.double(np.log(-((3)*cA[21] -4*cA[20] + cA[19])/(2*delta_time)))

for i in range(1,21):
    natlog_derivative[i] = np.double(np.log(-(cA[i+1]-cA[i-1])))

#From the data we have created we could fit a polynomial line to the data, and whatever the slope of this polynomial line is will be our alpha value which will be the Order of the reaction
m, b = np.polyfit(ln_CA, natlog_derivative, 1) #Polynomial fit line
alpha = m #The slope of our polynomial fit line

print('The Order of Reaction (alpha) = {:.0f}'.format(alpha))
```

```
The Order of Reaction (alpha) = 3
```

b.Calculate the rate constant of the reaction as well with the proper units.

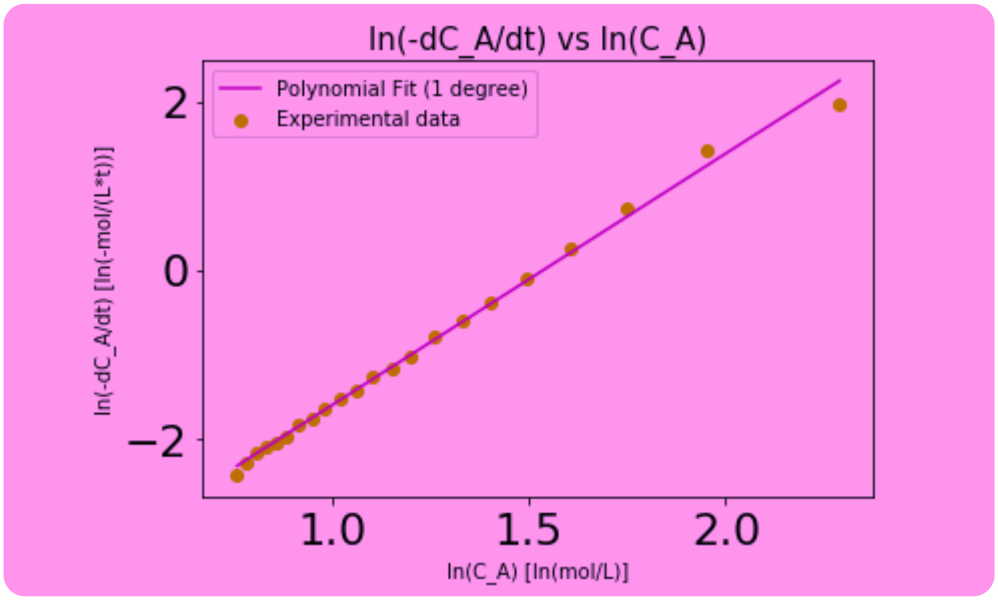
In [175]:
```
#Equation 7-11 from FOLDGER BOOK
#because k is a constant rate change we only need to choose a point from the concentration A and then find the derivative

k = np.exp((m*ln_CA[10]+b)/(alpha*ln_CA[10]))
print('Rate constant (k) =  {:.5f} [L^2/(mol^2)(min)]'.format(k))
```

```
Rate constant (k) =  0.67378 [L^2/(mol^2)(min)]
```

c.Include the plot of your fitted line and of the provided data with appropriately labeled axes.

In [176]:
```
#Plot Differential Method Using the information that we got in part A of this
 problem

plt.scatter(ln_CA, natlog_derivative, label ='Experimental data', color = 'y')
plt.plot(ln_CA, m*ln_CA+b,color = 'm', label ="Polynomial Fit (1 degree)")
plt.title("ln(-dC_A/dt) vs ln(C_A)",size = 15)
plt.xlabel("ln(C_A) [ln(mol/L)]",size = 10)
plt.ylabel("ln(-dC_A/dt) [ln(-mol/(L*t))]",size = 10)
plt.legend(prop={"size":10})
```

Out[176]: <matplotlib.legend.Legend at 0x19dc6303688>



In [ ]:

In [ ]:

3) Consider a set of three reactions which occur in parallel and produce a desired product D and two undesired products U_1 and U_2 (you are given the experimental rate law of each reaction):

$$A + B \rightarrow D \qquad r_D = k_1 C_A^2 C_B$$
$$A + B \rightarrow U_1 \qquad r_{U_1} = k_2 C_A C_B$$
$$A + B \rightarrow U_2 \qquad r_{U_2} = k_3 C_A^3 C_B$$

a. Write the equation for the instantaneous selectivity of D with respect to U_1, with respect to U_2, and with respect to both U_1 and U_2.

b. Sketch a plot of the instantaneous selectivity with respect to the concentration of A for each case of part a. Explain the shape of your curves and the difference between curves.

c. Which value of C_A results in the largest instantaneous selectivity of D with respect to both U_1 and U_2?

$$A + B \rightarrow D \qquad r_D = k_1 C_A^2 C_B$$
$$A + B \rightarrow U_1 \qquad r_{U_1} = k_2 C_A C_B$$
$$A + B \rightarrow U_2 \qquad r_{U_2} = k_3 C_A^3 C_B$$

Selectivity = S

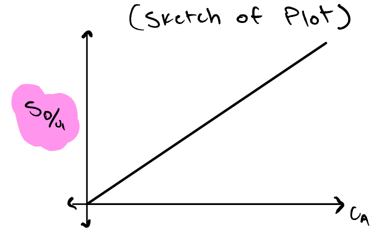
b. Sketch a plot of the instantaneous selectivity with respect to the concentration of A for each case of part a. Explain the shape of your curves and the difference between curves.

a. Write the equation for the instantaneous selectivity of D with respect to U_1, with respect to U_2, and with respect to both U_1 and U_2.

instantaneous selectivity of D with respect to U_1.

$$S_{D/U_1} = \frac{r_D}{r_{U_1}} = \frac{k_1 C_A^2 C_B}{k_2 C_A C_B} = \frac{k_1 C_A}{k_2}$$

(Sketch of Plot)

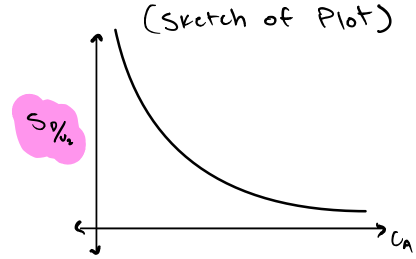


S_{D/U_1} vs. C_A has a linear relationship meaning the more amount of C_A added the greater D will be for this reaction

respect to U_2

$$S_{D/U_2} = \frac{r_D}{r_{U_2}} = \frac{k_1 C_A^2 C_B}{k_3 C_A^3 C_B} = \frac{k_1}{k_3 C_A}$$

(Sketch of Plot)

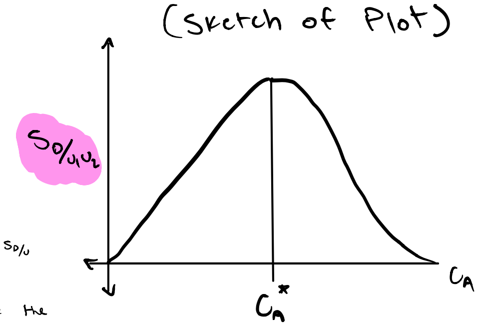


For S_{D/U_2} we have a $1/C_A$ relationship suggesting that the increase in C_A will decrease our D value for this reaction (opposite of S_{D/U_1})

with respect to both U_1 and U_2.

$$S_{D/U_1U_2} = \frac{r_D}{r_{U_1} + r_{U_2}} = \frac{k_1 C_A^2 C_B}{k_2 C_A C_B + k_3 C_A^3 C_B} = \frac{k_1 C_A}{k_2 + k_3 C_A^2}$$

(Sketch of Plot)



For S_{D/U_1U_2} we have an interesting relationship that demonstrate how the individual $S_{D/U}$ reactions when combined retain aspects of both graphs

The S_{D/U_1} reaction dominating initially at low values of C_A than after our C_A^* value the S_{D/U_2} reaction begins to dictate our D conversion rates

c. Which value of C_A results in the largest instantaneous selectivity of D with respect to both U_1 and U_2?

(Use Quotient Rule)

$$\frac{dS}{dC_A} = 0 = k_1\left(k_2 + k_3 C_A^{*2}\right) - k_1 C_A^*\left(2k_3 C_A^*\right)$$

(Solve for C_A^* using Wolfram Alpha)

exiting Concentration

$$C_{A^*} = \left(\frac{k_2}{k_3}\right)^{\frac{1}{2}} = \sqrt{\frac{k_2}{k_3}}$$