Homework 1 – Due 10/9/20

1) Complete the following two items before continuing the assignment:

- **a.** Carefully read the syllabus and homework formatting instructions.
- **b.** Sign up for Piazza on their website directly or through Canvas and post the favorite thing you did this past Summer (not anonymously).

2) List at least three important chemicals that are synthesized industrially. For each, write out the overall chemical equation for the process and describe the type of reactor that is typically used in those processes. Cite your sources properly!

3) Write the rate law with respect to species A for the irreversible reaction

$$A + B \rightarrow 2C$$

if the reaction

- **a.** is second order in A and overall third order
- **b.** is zero order in A and first order in B
- **c.** is zero order in both A and B
- **d.** follows an elementary rate law and is reversible

4) As a side-project to your studies at UW, you are in the business of synthesizing ethylene. Serendipitously, you cover rate laws in your ChemE 465 class and you begin to wonder what your original plan was to synthesize ethylene without knowing what you learned in lecture. Nevertheless, you had already prepared your home-made, industrial-sized reactor. It was made to contain an initial concentration of ethane of 100 mol L^{-1} and you know that the kinetic rate constant for your reaction

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

is 4.34×10^{-4} s^{-1} at 773 K. You also know that the process is first order and irreversible.

- **a.** Write out the rate law with respect to the reactant for this process.
- **b.** You want to know how long you need to watch your reactor before 20 mol L^{-1} of ethylene are produced to see if you can run this reaction in between classes or if you have to wait until the weekend to run it. Derive and calculate how long it would take to produce your required 20 mol L^{-1} of ethylene.

5) You get an email from the Princess of Nigeria telling you that she needs your help in determining the energy barrier for an elementary chemical reaction, but she doesn't know Python well enough to fit a line to his experimental kinetic data. She tells you she uploaded all of her data to the UW Canvas page for ChemE 465 (somehow) and that if you help her solve this problem, she will transfer $1 million to your bank account. Nothing about this arrangement seems odd, so you believe her.

- **a.** Download the kinetic data from Canvas and make a linear Arrhenius plot showing: 1) the provided data and 2) your fitted line. Be sure to label the axes appropriately (don't forget units!), give it a title, and include a legend.
- **b.** Calculate what the activation energy (E_a, in kcal/mol) and pre-exponential factor (A, in s^{-1}) would be from your fitted line.
- **c.** Take your previously fitted E_a and A values and plug them into the Arrhenius equation to create a plot (k vs. T) and overlay the provided data to show agreement.

d. Describe how the rate constant changes as a function of temperature in a Markup cell and explain why you believe this makes sense.

e. Submit the Jupyter notebook that you used to create your plots and calculate your kinetic parameters (both the ipynb file and PDF of the notebook).

<u>Note:</u> the Princess was kind enough to tell you that her temperatures were recorded in K and her kinetic rate constants were in s^{-1}.

Jeremy - Hook

HW #1

1) Complete the following two items before continuing the assignment:

a. Carefully read the syllabus and homework formatting instructions.

b. Sign up for Piazza on their website directly or through Canvas and post the favorite thing you did this past Summer (not anonymously).

(☆ Read Syllabus and made Post ☆)

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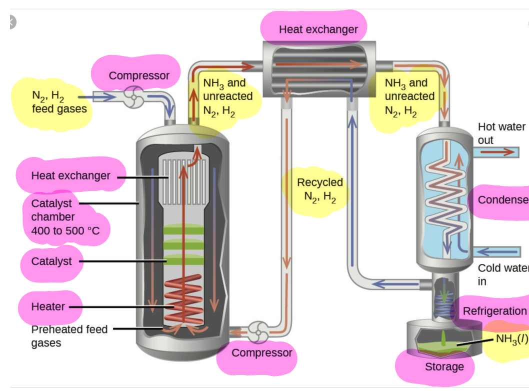
2) List at least three important chemicals that are synthesized industrially. For each, write out the overall chemical equation for the process and describe the type of reactor that is typically used in those processes. Cite your sources properly!

Ammonia Synthesis (NH_3)

$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$



1) $N_2(g) + H_2(g)$

(Nitrogen and hydrogen gas are fed into a heater, Catalyst, heat exchanger)

2)
$N_2 + 2^* \longleftrightarrow 2N^*$
$H_2 + 2^* \longleftrightarrow 2H^*$
$N^* + H^* \longleftrightarrow NH^* + *$
$NH^* + H^* \longleftrightarrow NH_2^* + *$
$NH_2 + H^* \longleftrightarrow NH_3 + 2^*$

(Ammonia takes Place on Iron Catalyst and thought to undergo this change)

3) $NH_3^{(g)} + H_2^{(g)} + N_2^{(g)} \longrightarrow NH_3(l) + H_2(g) + N_2(g)$

(Ammonia and unreacted hydrogen and nitrogen gas are fed into a heat exchanger then a Condenser where the liquid Ammonia is Separated)

Sulfuric Acid Synthesis (H_2SO_4)

The Process of synthesizing Sulfuric Acid first starts with Sulfur, oxygen and water.

1) $S(s) + O_2(g) \rightarrow SO_2(g)$

(Sulfur is burned making Sulfur dioxide)

2) $2SO_2 + O_2(g) \xrightarrow{*} 2SO_3(g)$

* In the presence of V_2O_5

(Sulfur Dioxide is then oxidized to Create Sulfur Trioxide, using Oxygen in presence of Catalyst (Vanadium Oxide))

3) $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

(Sulfur Trioxide is treated with water to produce Sulfuric Acid)

(Directly dissolving Sulfur Trioxide in water is not realistic due to the reaction being highly exothermic, So mists are formed instead of liquids)

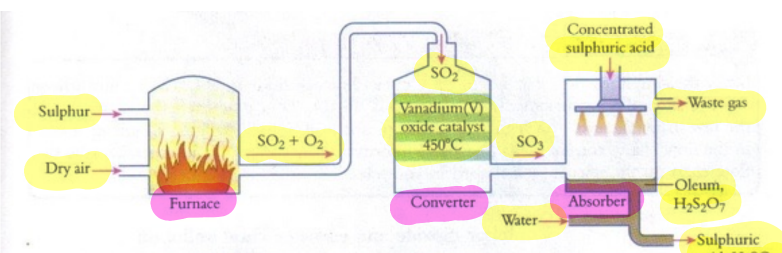


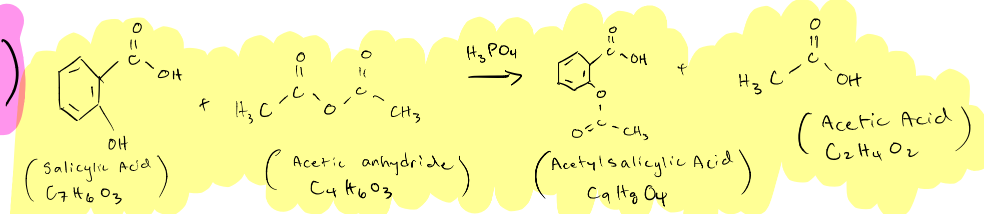
Figure 9.1 The manufacture of sulphuric acid, H_2SO_4 through the Contact Process

(This was a great figure I came across Showing Some of the reactors involved in Synthesizing Sulfuric Acid; Furnace, Catalyst Converter, and absorber)

Acetylsalicylic Acid Synthesis

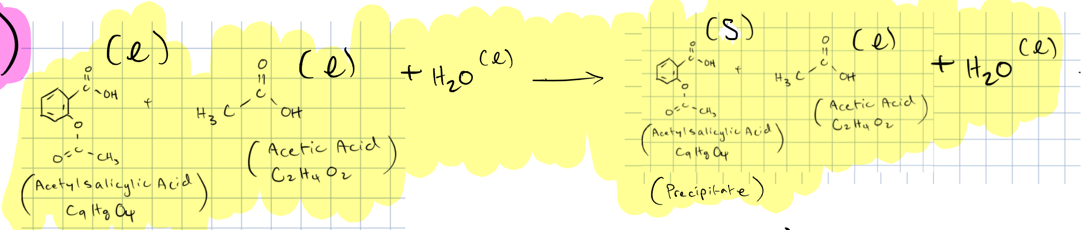
(Aspirin) ($C_9H_8O_4$)

1)



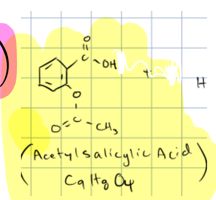
(Salicylic Acid is combined with excess Acetic Anhydride than phosphoric Acid H_3PO_4 is used as a catalyst to make the Process go faster.)

2)



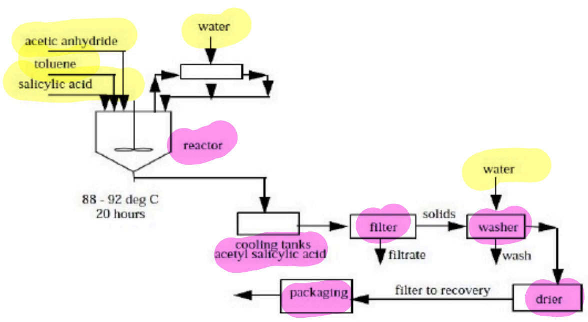
(Acetylsalicylic Acid precipitates out when water is added, acetic acid and water are miscible)

3)



(The Acetylsalicylic Acid is then able to be collected and further refined with filtering and water treatment.)

INDUSTRIAL SCALE SYNTHESIS



(Synthesis in industry often utilizes mixing reactors as well as a series of filter and water treatments to ensure high purity)

(further refinement can take place using ethanol and recrystallization techniques)

Citations

Citations:

Fogler, H. Scott. *Essentials of Chemical Reaction Engineering*. Prentice Hall, 2017.

(Ammonia Synthesis)

"17.7 Catalysis - Chemistry: Atoms First 2e." *OpenStax*, openstax.org/books/chemistry-atoms-first-2e/pages/17-7-catalysis.

"Ammonia Synthesis." *Ammonia Synthesis - an Overview | ScienceDirect Topics*, www.sciencedirect.com/topics/chemical-engineering/ammonia-synthesis.

Marnellos, George, and Michael Stoukides. "Ammonia Synthesis at Atmospheric Pressure." *Science*, American Association for the Advancement of Science, 2 Oct. 1998, science.sciencemag.org/content/282/5386/98.

(Sulfuric Acid Synthesis)

"The Contact Process in the Manufacture of Sulfuric Acid." *Current Technology*, mogckchem.weebly.com/the-contact-process-in-the-manufacture-of-sulfuric-acid.html.

Sulfuric Acid, www.cs.mcgill.ca/~rwest/wikispeedia/wpcd/wp/s/Sulfuric_acid.htm.

Sulfuric Acid, www.essentialchemicalindustry.org/chemicals/sulfuric-acid.html.

"Sulfuric Acid." *Sulfuric Acid - an Overview | ScienceDirect Topics*, www.sciencedirect.com/topics/biochemistry-genetics-and-molecular-biology/sulfuric-acid.

(Aspirin Synthesis)

parva1993 Follow. "Preparation of Aspirin." *SlideShare*, 21 Nov. 2014, www.slideshare.net/parva1993/preparation-of-aspirin.

"Salicylic Acid." *Salicylic Acid 2003 – Chemical Production and Investment Cost*, ihsmarkit.com/products/chemical-technology-pep-reviews-salicylic-acid-2003.html.

Wang, Yang, and Vladimir Gevorgyan. "General Method for the Synthesis of Salicylic Acids from Phenols through Palladium-Catalyzed Silanol-Directed C-H Carboxylation." *Angewandte Chemie (International Ed. in English)*, U.S. National Library of Medicine, 9 Feb. 2015, www.ncbi.nlm.nih.gov/pmc/articles/PMC4565602/.

Chemistry 211 Experiment 3, home.miracosta.edu/dlr/211exp3.htm.

3) Write the rate law with respect to species A for the irreversible reaction

$$A + B \rightarrow 2C$$

if the reaction

a. is second order in A and overall third order
b. is zero order in A and first order in B
c. is zero order in both A and B
d. follows an elementary rate law and is reversible

One of the most common general forms of this dependence is the *power law model*. Here the rate law is the product of concentrations of the individual reacting species, each of which is raised to a power, for example,

$$\boxed{-r_A = k_A C_A^{\alpha} C_B^{\beta}} \tag{3-3}$$

The exponents of the concentrations in Equation (3-3) lead to the concept of *reaction order*. The **order of a reaction** refers to the powers to which the concentrations are raised in the kinetic rate law.[1] In Equation (3-3), the reaction is α *order with respect to reactant* A, *and* β *order with respect to reactant* B. The overall order of the reaction, ***n***, is

$$n = \alpha + \beta$$

A) **a.** is second order in A and overall third order β $A + B \rightarrow 2C$

$n = \alpha + \beta \rightarrow n = 2 + 1$ $\quad -r_A = K_A C_A^2 C_B$

B) **b.** is zero order in A and first order in B $\quad A + B \rightarrow 2C$

$n = \alpha + \beta = n = 0 + 1 = 1$ $\quad -r_A = K_A C_B$

C) **c.** is zero order in both A and B $\quad A + B \rightarrow 2C$

$n = \alpha + \beta \longrightarrow n = 0 + 0$ $\quad -r_A = K_A$

D) **d.** follows an elementary rate law and is reversible $\quad A + B \rightarrow 2C$

$-r_{A\,\text{Forward}} = K_A C_A C_B \longrightarrow r_{A,\text{Forward}} = -K_A C_A C_B$

$-r_{A,\text{Reverse}} = K_{-A} C_C^2$

$r_{A,\text{Total}} = r_{A,\text{forward}} + r_{A,\text{reverse}}$

$r_{A,\text{Total}} = -K_A C_A C_B + K_{-A} C_C^2 \rightarrow -r_A = K_A C_A C_B - K_{-A} C_C^2$

$-r_{A,\text{Total}} = K_A \left[C_A C_B - \frac{K_{-A}}{K_A} \left(C_C^2 \right) \right]$

$-r_A = K_A \left[C_A C_B - \left[\frac{K_{-A}}{K_A} \right] C_C^2 \right]$

4) As a side-project to your studies at UW, you are in the business of synthesizing ethylene. Serendipitously, you cover rate laws in your ChemE 465 class and you begin to wonder what your original plan was to synthesize ethylene without knowing what you learned in lecture. Nevertheless, you had already prepared your home-made, industrial-sized reactor. It was made to contain an initial concentration of ethane of 100 mol L^{-1} and you know that the kinetic rate constant for your reaction

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a. Write out the rate law with respect to the reactant for this process.

b. You want to know how long you need to watch your reactor before 20 mol L^{-1} of ethylene are produced to see if you can run this reaction in between classes or if you have to wait until the weekend to run it. Derive and calculate how long it would take to produce your required 20 mol L^{-1} of ethylene.

$C_2H_6 \rightarrow$ ethane of 100 mol L^{-1} $\qquad$ $C_2H_6 \rightarrow C_2H_4 + H_2$

$K_{C_2H_6} =$ 4.34×10^{-4} s^{-1} at 773 K

the process is first order and irreversible. $\qquad = \left[\frac{\text{mol}}{\text{volume} \cdot \text{Time}}\right]$

$$\boxed{\text{A)}\ -r_{C_2H_6} = k_{C_2H_6} C_{C_2H_6}}$$

B) b. You want to know how long you need to watch your reactor before 20 mol L^{-1} of ethylene are produced to see if you can run this reaction in between classes or if you have to wait until the weekend to run it. Derive and calculate how long it would take to produce your required 20 mol L^{-1} of ethylene.

$\boxed{\text{Assume Tempeature} = 773\,K}$

time $= t$, $t_o =$ initial time, $t_f =$ Final Time ; Let $C_2H_6 = A$

Boundary Conditions

ethylene	ethane
$t_o \rightarrow C_{C_2H_4} = \emptyset$ mol/L	; $C_{C_2H_6} = 100$ mol/L
$t_f \rightarrow C_{C_2H_4} = 20\,\frac{\text{mol}}{L}$	; $C_{C_2H_6} = 80\,\frac{\text{mol}}{L}$

$$-r_A = k_A C_A \ ; \ -r_A = C_A\left(\frac{d}{dt}\right) = \frac{d\,C_A}{dt}$$

$$r_A = C_A\left(d/dt\right) = -k_A C_A \qquad \frac{d(C_A)}{dt} = -k_A C_A$$

(Evaluate C_A from $\underset{\text{initial}}{100}$ to $\underset{\text{final}}{80}$)
(and t from t_o to t_f)

$$\rightarrow \left(\frac{1}{C_A}\right) dC_A = -k\,dt \rightarrow \int_{100}^{80} \frac{1}{C_A}\,dC_A = \int_{t_o}^{t_f} -k\,dt \longrightarrow$$

$K_A =$ 4.34×10^{-4} s^{-1} at 773 K

$$\rightarrow \ln(C_A)\Big]_{100}^{80} = -K_A(t)\Big]_{t_o}^{t_f} \rightarrow \ln\left(\frac{80}{100}\right) = -k\left(t_f - 0\right) \longrightarrow$$

$$\rightarrow -0.22314355 = -(4.34\times10^{-4})(t_f - 0) \longrightarrow 514.16\,s = t_f \approx 514 \text{ seconds}$$

$$\boxed{t_f = 514\,s\left(\frac{1\,\text{min}}{60\,s}\right) = 8.57\,\text{minutes}}$$

5) You get an email from the Princess of Nigeria telling you that she needs your help in determining the energy barrier for an elementary chemical reaction, but she doesn't know Python well enough to fit a line to his experimental kinetic data. She tells you she uploaded all of her data to the UW Canvas page for ChemE 465 (somehow) and that if you help her solve this problem, she will transfer $1 million to your bank account. Nothing about this arrangement seems odd, so you believe her.

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b. Calculate what the activation energy (E_a, in kcal/mol) and pre-exponential factor (A, in s^{-1}) would be from your fitted line.

c. Take your previously fitted E_a and A values and plug them into the Arrhenius equation to create a plot (k vs. T) and overlay the provided data to show agreement.

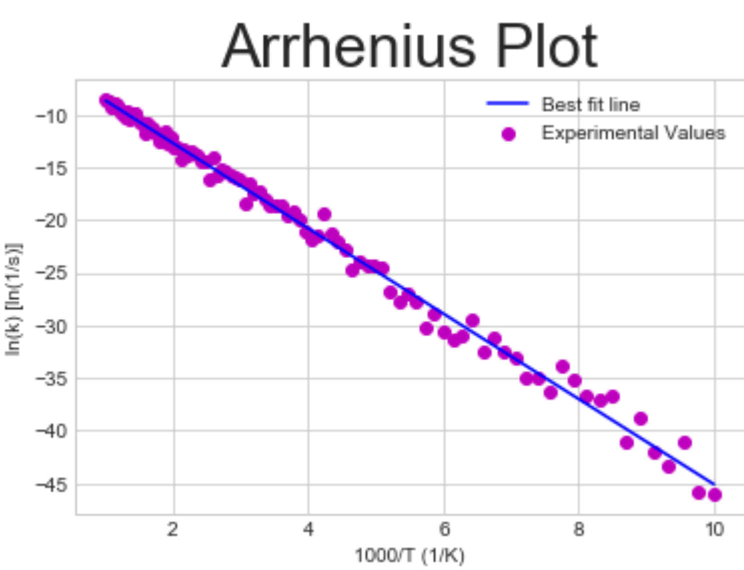
d. Describe how the rate constant changes as a function of temperature in a Markup cell and explain why you believe this makes sense.

e. Submit the Jupyter notebook that you used to create your plots and calculate your kinetic parameters (both the ipynb file and PDF of the notebook).

<u>Note:</u> the Princess was kind enough to tell you that her temperatures were recorded in K and her kinetic rate constants were in s^{-1}.

In [138]:
```
# HW1
import matplotlib.pyplot as plt
import numpy as np
from scipy.stats import linregress

# 5A) Download thekinetic data fromCanvasand make a linear Arrhenius plot show
ing:
#1) the provided data and 2) your fitted line.
#Be sure to label the axes appropriately (don’t forget units!),
#give it a title, and include a legend.

kinetic_data = np.loadtxt('kinetic_data.txt')
Temperature_data = np.loadtxt('temperature_data.txt')

x = 1000/Temperature_data # From python handout Must use 1000 tested other val
ues, 1000 is the only one that lines up with our data
y = np.log(kinetic_data)

slope, intercept, r_value, p_value, std_err = linregress(x, y) # This is used
 to Perform the linear regression:
log_k_fitted = slope * (x) + intercept
#  y      =   m    *    x    + b      you can see this is the slope intercept form
ula
# You can plot (x, m*x + b... or you can use y)
plt.scatter(x, y, color = 'm', label = 'Experimental Values') # Experimental v
alues from Kinetic Data, Temperature data
plt.plot(x, log_k_fitted, color = 'b', label = 'Best fit line') # how to plot
 a fitted line

plt.title('Arrhenius Plot', fontsize = 30)
plt.ylabel('ln(k) [ln(1/s)]')
plt.xlabel("1000/T (1/K)")
plt.legend(loc='best')
```

Out[138]:
```
<matplotlib.legend.Legend at 0x17e5330df08>
```

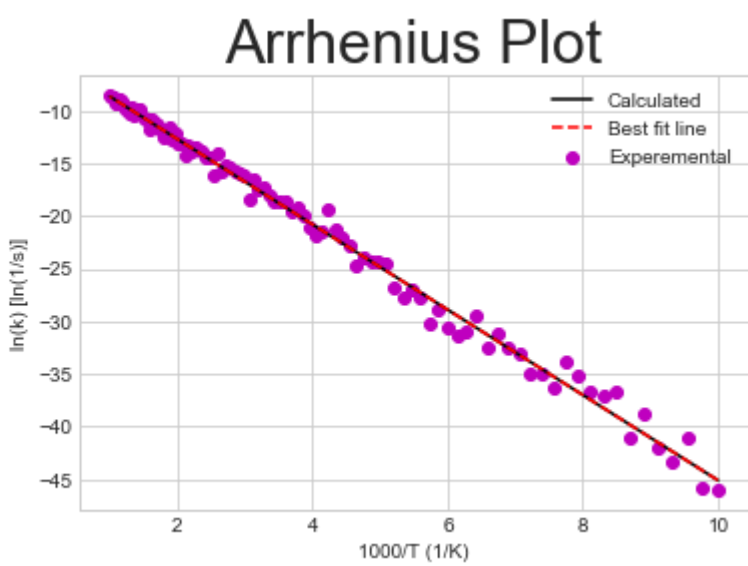


In [139]:
```
#5b) Calculate what the activation energy (Ea, in kcal/mol)and
#pre-exponential factor (A, in s-1) would be from your fitted line.

# Arrhenius equation: ln(k) = ln(A) - E_a/RT
# R gas constant in Kcal/mol*K

R = 0.0019858775 # Kcal/mol*K

# pre-exponential factor A in 1/s
ln_A = intercept # create the intercept
A = np.exp(ln_A)
print("The Pre-Exponential Factor A = " , str(A) , " 1/s")

# Activation energy, E_a in Kcal/mol
# slope = -E_a/R
E_a = -slope*R*1000
print("The Activation Energy = " , str(E_a) , " Kcal/mol")
```

```
The Pre-Exponential Factor A =  0.010148532474906578  1/s
The Activation Energy =  8.043209654261727  Kcal/mol
```

In [140]:
```
# 5c)Take your previously fitted Ea and A values and
#plug them into the Arrhenius equationto
#create a plot(k vs. T)and overlay the provided data to show agreement.
k = A*np.exp(-E_a/(R*T_data)) # Create the k value


plt.scatter(1000/ Temperature_data, y, color = 'm', label = 'Experemental') #F
rom table
plt.plot(1000 / Temperature_data, np.log(k), color = 'k', label = 'Calculated'
) #Calculated using Ea, k
plt.plot(1000 / Temperature_data, log_k_fitted, '--', color = 'r', label = 'Be
st fit line')# Best Fit line

plt.title('Arrhenius Plot', fontsize = 30)
plt.ylabel('ln(k) [ln(1/s)]')
plt.xlabel("1000/T (1/K)")

plt.legend()

#plt.savefig('arrhenius_plot.png')  # allows you to save the figure
```

Out[140]: <matplotlib.legend.Legend at 0x17e53383ec8>



In [141]:
```
### 5d) Describe how the rate constant changes as a
#function of temperature in a Markup cell and explain
#why you believe this makes sense.

#How rate constant changes as a function of Temperature
k_low_T = A*np.exp(-E_a/(R*200)) # Low Temperature
k_high_T = A*np.exp(-E_a/(R*2000)) # High Temperature
print('How rate constant changes as a function of Temperature')
print(k_low_T,'Low Temperature')
print(k_high_T, ' High Temperature')
```

```
How rate constant changes as a function of Temperature
1.6274073942482447e-11 Low Temperature
0.0013394069549207694  High Temperature
```

In [142]:

```
# explain why you believe this makes sense.

print('As we can see from the Arrehenius plot from above for 5:C, as the tempe
rature increases this also increases the value of the Natural Log of the K val
ue. We can see that a higher T Value gives us a higher K value, We can also se
e this is true by looking at the above equation where we see "how rate constan
t changes as a function of temperature" You can see that the High temperature
 has a MUCH larger k value than the Low temp k value. This is all in line with
the reading and lectures, because at higher temperatures we have more collisio
ns between the particles, This means the particles have higher energy, which w
ill mean that the activation energy is lower for the particles to react and fo
rm products.')
```

```
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eading and lectures, because at higher temperatures we have more collisions b
etween the particles, This means the particles have higher energy, which will
mean that the activation energy is lower for the particles to react and form
products.
```
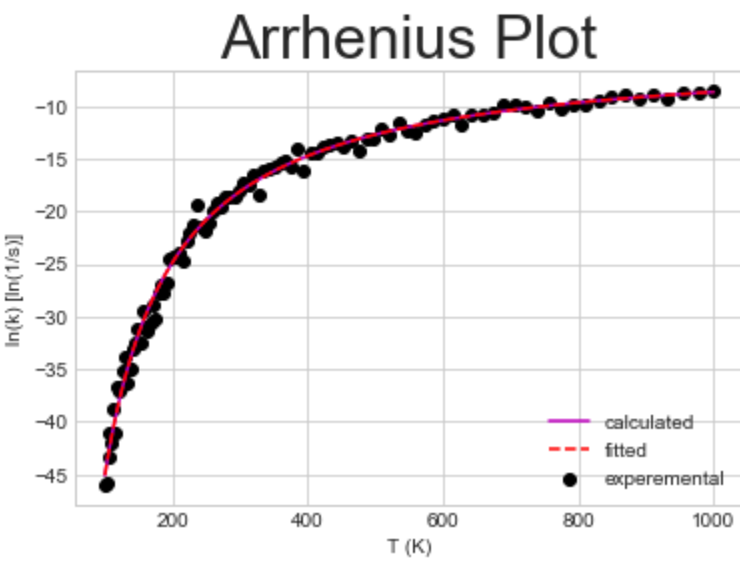

In [143]:

```
# 5) Submit the Jupyter notebook that you used to
#create your plots and calculate your
#kinetic parameters(both the ipynb file and PDF of the notebook).
```

In [144]:
```
##### Extra side note 'A better repsentation of the natural log of k and how i
t behaves as temperature increases.
plt.scatter(Temperature_data, np.log(kinetic_data), color = 'k', label = 'expe
remental')
plt.plot(Temperature_data, np.log(k), color = 'm', label = 'calculated')
plt.plot(Temperature_data, log_k_fitted, '--', color = 'r', label = 'fitted')
plt.title('Arrhenius Plot', fontsize = 30)
plt.ylabel('ln(k) [ln(1/s)]')
plt.xlabel("T (K)")
plt.legend()
```

Out[144]: <matplotlib.legend.Legend at 0x17e53403808>



In [ ]:

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