Experiment 5: Enthalpy of Reaction

Procedure

CHE 347 TA: Alec Beaton

Introduction

In this experiment, we will measure the enthalpy change for three different reactions and use these values to determine the enthalpies of protonation and deprotonation of glycine.

Pre-Lab:

1. Read documents in Reading Folder.

    – Engel + Reid Excerpt (general background)
    – Ramette 1984 (literature values as well as background)
2. Answer Quiz Questions and submit before Monday 9/21 at 2:00 pm.

3. Draft your procedures into your notebook.

Equipment:

*   Parr 6772 Calorimetric Thermometer
*   Parr 6755 Solution Calorimeter
    – Bucket (Dewer)
    – Lid
    – Belt
    – Pulley
    – Sample Cell (130C)
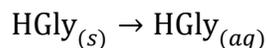   – Bottom Dish (126C)
    – Glass stir rod
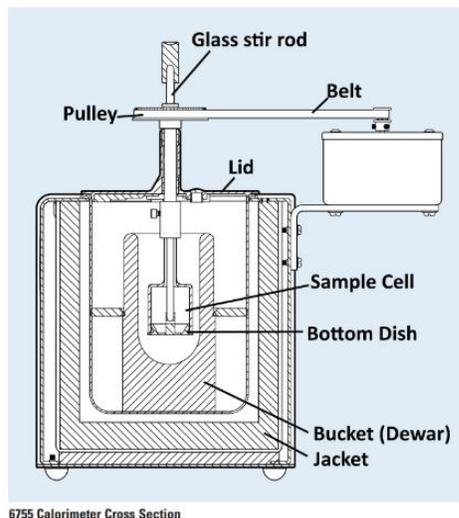
Materials

*   Glycine
*   0.3 M Sodium Chloride (NaCl *(aq)*)
*   0.3 M Hydrochloric Acid (HCl *(aq)*)
*   0.3 M Sodium Hydroxide (NaOH *(aq)*)

Procedure:

Reaction I: Dissolution of glycine in NaCl solution

$$\text{HGly}_{(s)} \rightarrow \text{HGly}_{(aq)}$$

Fill dewar with 100 mL of 0.3 M NaCl solution. Place dewar inside jacket of calorimeter. Measure out 1.5 g of glycine onto rubber bottom of solution cell (place weigh paper between rubber and tray of balance to avoid contamination). Record exact mass in lab notebook.

Move rubber bottom of sample cell to a flat surface and carefully press glass reaction vessel onto rubber bottom. Attach sample cell to pulley/stirrer of calorimeter.

Carefully place glass reaction vessel into Dewar. Attach rubber belt to motor and pulley. Set stir to low. Once system has reached equilibrium, record initial temperature in lab notebook.

Push the stir rod down completely to punch out the rubber bottom and initiate the dissolution reaction. Once system has reached equilibrium, record final temperature in lab notebook.
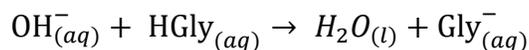
Stop stirring. Empty waste into designated containers. Thoroughly rinse all components with deionized water and dry with paper towels.

Reaction II. HCl and glycine

$$H_3O^+_{(aq)} + \ HGly_{(aq)} \rightarrow H_2O_{(l)} + \ H_2Gly^+_{(aq)}$$
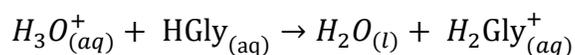
Repeat procedure above with 0.3 M HCl solution.

Reaction III. NaOH and glycine

$$OH^-_{(aq)} + \ HGly_{(aq)} \rightarrow \ H_2O_{(l)} + Gly^-_{(aq)}$$

Repeat procedure above with 0.3 M NaOH solution.

SETTING UP PYTHON

Python is a popular programming language widely used in data science. It has some similarities to Matlab in that regard but is free to use. Python requires a package manager. I recommend downloading Anaconda as your package manager. Using this link, be sure to download the Python 3.7 version. Once installed, you should be able to open a jupyter notebook by opening a terminal and typing **jupyter notebook**.

To open a terminal:

> (A) On Mac, go to Launchpad >> Other >> Terminal, or use Finder to find Terminal. This should open a square window, called the Command Prompt, into which you should type **jupyter notebook**.
> (B) On Windows, type Anaconda Prompt in the start menu search bar (go to the bottom left corner and type in the search bar 'Anaconda Prompt'). This should open a square window, called the Anaconda Prompt, into which you should type **jupyter notebook**.

This should in turn open a webpage using your default browser. On this webpage, create a new notebook using New >> Python 3 notebook.

The basics of a jupyter notebook are that you enter code inside a cell. You then press **Shift + Enter** and this 'runs' the cell – i.e., runs the code inside the cell. It will generate an output of the code (if there is any) directly beneath the cell. The output of a code might be a "print" statement (which is basically exactly as it sounds – the code prints out a string of characters) or a plot of some sort.

In the first cell, try typing:

```
Print("Hello world!")
```

Then run the cell by clicking on it and hitting **Shift+Enter**. Beneath the cell, you should see the words Hello world! appear. It should look like the following:
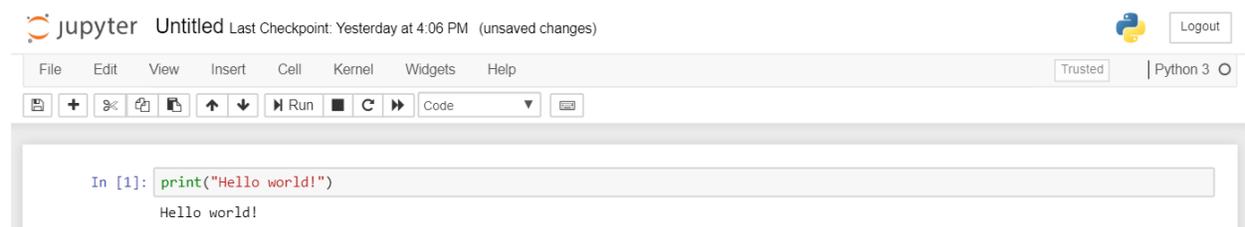
If you have any issues with this, do not hesitate to email me and we can figure out a solution!

USING THE DATA ANALYSIS WORKBOOK

We have written a script which we present to you as a jupyter notebook (.ipynb) file. This file will read the data saved from the calorimeter and plot it accordingly. Some notes on using this jupyter notebook:

- To open this notebook, open a terminal as described above, then type ***jupyter notebook***.

- This should open a browser window. You can then navigate, as though you were using Finder (Mac) or File Explorer (Windows), to the location where you have saved the data from the Google Drive (which contains this notebook file) and open it from there.
- You will need the packages pandas and matplotlib. The former is usually provided with Anaconda distributions of python, but pandas may need to be installed. Run the following in a new terminal: ***conda install pandas***
- You will need to tell the jupyter notebook where you have stored the data from this lab. This is given by a full directory path. You can easily find this by typing ***pwd*** and running the cell. For example, mine looks like this:

```
here, simply run the command pwd (print working directory) to find the directory location of this file

In [2]: pwd
Out[2]: 'C:\\Users\\alecb\\Desktop'
```
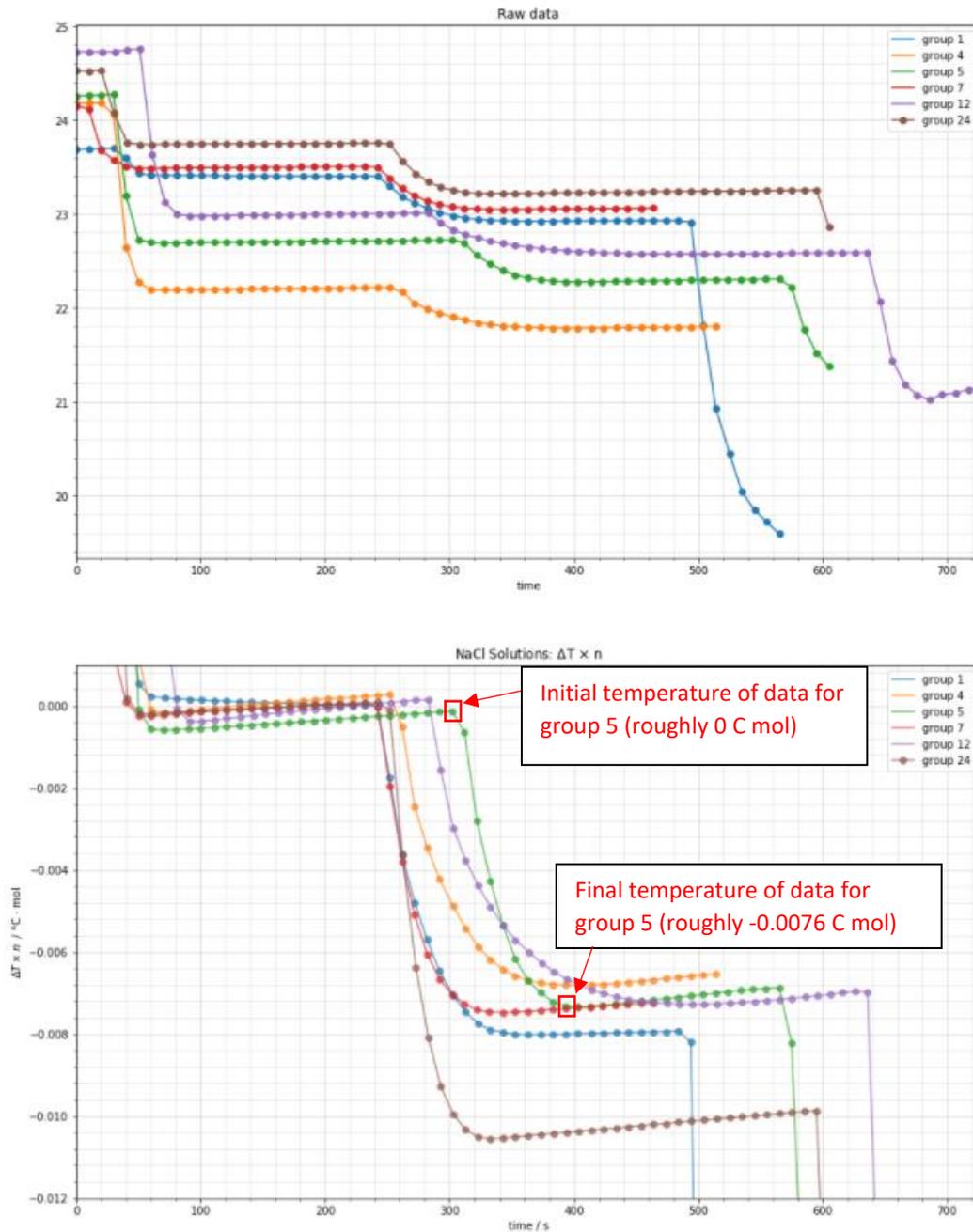
  - o Note that the output here shows I saved the file to my Desktop. Your example will look different.
- In the next cell of your notebook, there is a variable called data_directory next to which is a comment telling you to copy and paste the output here.

```
In [ ]: data_directory = #copy and paste output from pwd here
```

- After you have done this, your cell should look like the following:
  - o **IMPORTANT**: for Windows users, change all double backward slashes (\\) to forward slashes (/) as I show in the example below! (Mac users will not need to make any alterations to the pwd output.)

```
In [ ]: data_directory = 'C:/Users/alecb/Desktop'
```

- Once you run this cell, you will have the path to your data specified. You should now be able to run the cells containing the nice_format function and the cell under the **NaCl solutions** heading. (The cells under both **NaOH solutions** and **HCl solutions** headings require a little bit of work from you before they will run – more on that below).
- The code in the NaCl solutions cell should provide two plots: one displays just the raw data and the others shows the data multiplied by the moles of glycine and shifted to have an initial temperature of 0. They should look like the following:

Raw data

NaCl Solutions: ΔT × n

Initial temperature of data for group 5 (roughly 0 C mol)

Final temperature of data for group 5 (roughly -0.0076 C mol)

- You are now able to read the initial and final temperatures for each NaCl run that was conducted this week. I show an example of how to read from this chart in red – find the highest data point and the lowest data point within the region of interest (where we know we released glycine into the solution), and then carefully find the value by reading off the graph. You should then be able to use these numbers in your further calculations as outlined in the post lab
  - Note that to report Q, which is independent of moles, you will need to divide your number by the appropriate number of moles of glycine).

- o Our goal is to average the data across all the groups that collected data for each reaction. So you should find the initial temperature and final temperatures for each line to get values of ΔT x n for each group for each reaction – then for your calculations of Q and ΔH, take the average across these quantities for each group for a given reaction.
- You should follow the same procedure for the other code blocks that deal with the two other solutions (NaOH and HCl solutions), except you will need to carefully enter in the corresponding mass of glycine for each dataset, based off of the Excel file '**enthalpy_of_reaction_glycine_mass**' also in this Google Drive. Put those numbers in place of where it says ***#mass_here***.
  - o Note that you must be mindful of your commas! There should be a comma before the mass, and after the mass, since it is in the middle of a three-element-long tuple.
- Include screen shots of the second plot from each set (the plots titled NaCl solutions: ΔT x n, NaOH solutions: ΔT x n, and HCl solutions: ΔT x n, respectively)

Experiment 8: Proton Exchange of Pyruvic Acid *via* NMR

Procedure

CHE 347 TA: Alec Beaton

Introduction

In this experiment, we will use NMR spectroscopy to investigate the effect of H^+ concentration on the hydrolysis of pyruvic acid. We will use the linewidths of the proton resonances corresponding to pyruvic acid and to 2,2-dihydroxypropanoic acid to calculate the forward rate constant and the reverse rate constant, respectively. We will then combine this information to determine the overall rate constant for hydrolysis.

Pre-Lab:

1. Read documents in Reading Folder.
   - Griffiths and Socrates (*Faraday Trans.*) → the original result
   - Sime Chapter X Chemical Kinetics (a more modern presentation that explicitly spells out the calculations)
2. Answer Quiz Questions and submit before Monday 10/12 at 2:00 pm.
3. In lieu of writing out a prelab in your notebook, you should complete the PlayPosit posted on blackboard. (Note this video will not be posted on 10/5 as we are waiting for additional instrument time – when the video is posted, we will announce on blackboard.)

Equipment
- 300 MHz NMR Spectrometer
- 400 MHz NMR Spectrometer

Materials
- Pyruvic Acid
- D_2O
- HCl

Experiments

For these experiments, nine samples will be prepared of pyruvic acid in D_2O with varying amounts of H^+ concentration.

Sample No.	Vol. Pyruvic Acid (µL)	Vol. D2O (µL)	Vol. HCl (µL)
1	10	600	0
2	10	575	25
3	10	550	50
4	10	525	75
5	10	500	100
6	10	475	125
7	10	450	150
8	10	425	175
9	10	400	200

The TA has previously acquired ^{1}H NMR spectra on both the 300 MHz and the 400 MHz for these experiments.

The TA has prepared an introductory video explaining how an NMR spectrometer works, and how to operate it. In lieu of writing out a prelab in your notebook, you should complete the PlayPosit of this video.

During the lab period, your TA will provide you with an introduction on loading the raw data and determining the linewidth.

Items to keep in mind for post-lab

1. Introduction discussing basic NMR theory related to this experiment
   – Why D_2O instead of H_2O? What is T_1 relaxation, and how is it different from T_2 relaxation? Which relaxation time is related to linewidth and why? What happens during the course of an NMR experiment – what does ATM, lock, shimming, and acquisition mean, in this context?
2. Introduction discussing kinetics and how they are determined in this experiment.
3. **Plot of linewidth vs. [H⁺]** for pyruvic acid proton resonance at both 300 and 400 MHz, with **linear fits.**
4. **Plot of linewidth vs. [H⁺]** for 2,2-dihydroxypropanoic acid proton resonance at both 300 and 400 MHz, with **linear fits.**
5. Table listing the **forward rate constant** (k_f), **reverse rate constant** (k_r), and **equilibrium constant** determined at both fields. Compare the equilibrium constant to a literature value.
6. **Discussion of your results** – was the equilibrium constant found to be different at one field vs. another? Is this expected and why/why not?
7. **Discuss reasons for deviations** in the values you report compared to the literature values.

For the literature value of the equilibrium constant for pyruvic acid hydrolysis, please see the reference posted on blackboard by Griffiths and Socrates, 1966.

For a detailed discussion of the kinetics, see the **theory** and **methods** sections of the handout **NMR Study of a Reversible Hydrolysis Reaction.**