

**Lecture Notes on Thermochemistry A: Heats of Chemical Processes**  
**Chemistry 141 Laboratory**  
**September 19, 2011**  
**Professor Abrash**

**Q: What is this experiment about?**

It's an introduction to concepts, experimental techniques, and techniques of data analysis used in the subject of thermochemistry.

**Q: What is thermochemistry?**

The study of the heat released or absorbed by a chemical reaction when it is carried out under conditions of constant pressure.

**Q: Why heat? Why constant pressure?**

Many chemical reactions either are initiated by heating under conditions of constant pressure, or release heat under constant pressure conditions. Because the amount of heat released under these conditions is so important we give it a special name, the Enthalpy,  $\Delta H$  (or more archaically, heat of reaction). Since this quantity is involved in so many reactions it is of interest to chemists to know how much heat a reaction requires or how much heat it releases. Today's experiment demonstrates the measurement of  $\Delta H$  for two reactions.

**Q: Does the measurement of the heat absorbed or released by a reaction have a special name?**

Yes. It's called calorimetry.

**Q: How do you do a calorimetry experiment?**

To do a calorimetry experiment, you carry out a reaction in a vessel that doesn't allow the heat to escape (or at least doesn't allow MUCH heat to escape.) Therefore all the heat released by the reaction is trapped in the vessel, and if heat is absorbed by the reaction, all the heat has to come from the contents of the vessel. Then you measure the change in temperature.

**Q: Temperature? Why temperature? I thought we were measuring heat?**

It turns out that the heat of a reaction is related to the temperature change by the equation

$$q = -C\Delta T$$

where  $\Delta T$  is the temperature change you measure in your calorimeter,  $q$  is the symbol for heat, and  $C$  is a quantity called the heat capacity.

**Q: Heat capacity? What is heat capacity?**

The heat capacity just tells how much heat it takes to increase the temperature of some system by 1K or equivalently 1°C. The heat capacity has two parts, the amount of heat it takes to increase the temperature of the calorimeter itself by 1K, called the calorimeter constant,  $C_{cal}$ , and the amount of heat it takes to increase the contents of the calorimeter by 1K. In today's experiment, the contents of the calorimeter will be 20 mL of water in part A or 20 mL of a dilute aqueous solution in parts B and C. Therefore we will treat this amount as being the same in all cases.

If we consider both contributions to the heat capacity, it means we can write:

$$C = C_{cal} + C_{contents}$$

**Q: How do we calculate the heat capacity of the contents,  $C_{contents}$ ?**

Since the contents of the calorimeter are dominated by water, the heat capacity of the contents can be very closely approximated by the heat capacity of the water. The heat capacity of the contents of the calorimeter is given by a very simple equation:

$$C_{contents} \approx C_{water} = C_{sp(H_2O)} * m_{H_2O}$$

where  $C_{sp(H_2O)}$ , the specific heat of the water, is the amount of heat necessary to increase the temperature of one gram of water by 1K, and is equal to 4.184 J/gK, and  $m_{H_2O}$  is the mass of the water in grams.

**Q: But that's based on the mass of the water, and we only know the volume of the water or of our solutions.**

It is convenient that the mass of one mL of water at our temperature is 1.000 g. The solutions in parts B and C are so dilute, that their densities are practically 1, as well, which means that 1 mL of these solutions will be extremely close to 1.000 g as well.

**Q: I see how we determine the heat capacity of the contents of the calorimeter. How do we determine the calorimeter constant,  $C_{cal}$ ?**

In general we determine C by doing an experiment in which we already know q, and then measuring  $\Delta T$ . In our case, we're going to mix hot water of a known temperature with cold water of a known temperature, determine the temperature change, and use this to determine C total. From C total, we'll use our knowledge of the heat capacity of the water to figure out  $C_{cal}$ , since

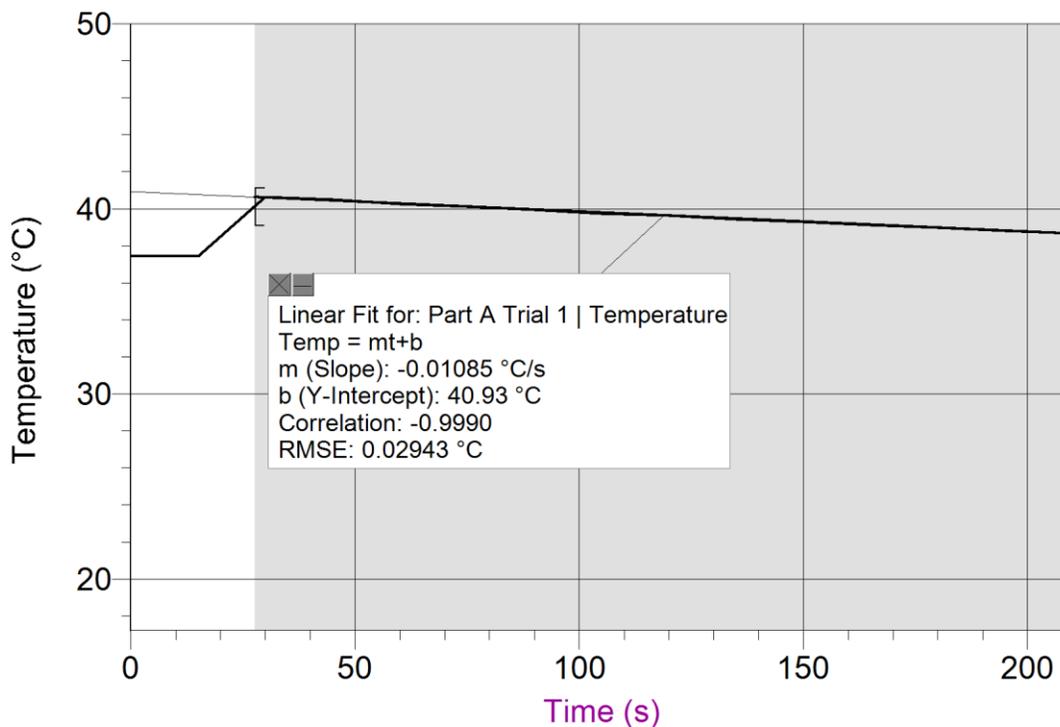
$$C_{cal} = C - C_{water}$$

**Q: In order to know  $\Delta T$  we need to know the initial and final temperatures. How do we measure the final temperature? Just stick the thermometer in the mixture and just wait for the temperature to settle down?**

It's a bit more complicated than that. While your coffee cup calorimeter is a decent approximation of one in which all the heat is trapped (called an adiabatic calorimeter), some heat does leak out, so the temperature will drop slowly and steadily. This means that unless you make a correction, the heat you calculate will be too low for an exothermic reaction, and too high for an endothermic reaction (where heat will leak INTO a system).

**Q: How do we deal with this loss of heat?**

After mixing our hot and cold water, we use the temperature probe to measure the temperature every fifteen seconds for a total of 210 seconds. You'll get a graph like this, with temperature on the y axis and time on the X-axis.



The graph will drop steadily. Because heat is constantly (but slowly) leaking out of your system it is necessary to extrapolate the linear part of your graph back to time zero in order to get an accurate temperature change from mixing. The nice thing is that Logger Lite, the program you'll be using for data collection, does this for you. This "zero time" temperature is simply the y intercept, and is the temperature you'll use as the final temperature in your calculations.

**Q: So now we know the temperature change. How do we determine  $C_{cal}$ ?**

The basic principle behind the calculation is that energy is conserved. Therefore, the amount of heat lost by the hot water has to be the same as the amount of heat gained by the calorimeter and cold water.

The amount of heat lost by the hot water is given by

$$-q_{hot} = -(C_{sp(H_2O)} * m_{H_2O}(hot) * (T_{mix} - T_{hot}))$$

where  $C_{sp}$  is the specific heat capacity of water, and is equal to 4.184 J/g\*K.

The amount of heat gained by the calorimeter and the cold water is given by

$$q_{cold} = (C_{cal} + C_{H_2O}) * (T_{mix} - T_{cold}) = (C_{cal} + (C_{sp(H_2O)} * m_{H_2O})) * (T_{mix} - T_{cold}).$$

Since in order to conserve energy,

$$q_{cold} = -q_{hot},$$

we can conclude that for this experiment,

$$-(C_{sp(H_2O)} * m_{H_2O}) * (T_{mix} - T_{hot}) = (C_{cal} + (C_{sp(H_2O)} * m_{H_2O})) * (T_{mix} - T_{cold}).$$

Since  $C_{sp}$ , the masses of the cold and hot water, and the temperatures are all known,  $C_{cal}$  is easily solved for. Note that this calculation is somewhat simplified because the mass of the cold water and the mass of the hot water are the same. Note also that the mass of the cold water and the mass of the hot water are each 20g.

**Q: Once we know  $C_{cal}$  how do we determine  $\Delta H_{rxn}$  ?**

The experimental procedure will be almost identical to that of the determination of the calorimeter constant. In both cases you add something to water or to an aqueous solution whose temperature you've measured, and then immediately measure temperature for the time stated in your lab manual.

**Q: Once we know the final temperature, how do we calculate  $\Delta H_{rxn}$**

Your calculations will be in two parts, determination of heat of reaction,  $q_{rxn}$ , and calculation of the molar heat of reaction,  $\Delta H_{rxn}$ .

**Q: How do we calculate  $q$ ?**

To calculate  $q_{rxn}$ , you use

$$q_{rxn} = -C * (T_{final} - T_{initial}) = -(C_{cal} + (C_{sp(H_2O)} * m_{H_2O})) * (T_{final} - T_{initial})$$

**Q: Once we know q, how do we calculate  $\Delta H_{rxn}$ ?**

To calculate the molar heat of reaction,  $\Delta H_{rxn}$ , you simply divide the heat of reaction, by the number of moles of reactant, either Mg, NaNO<sub>3</sub>, or NH<sub>4</sub>NO<sub>3</sub>, i.e.,

$$\Delta H_{rxn} = \frac{q_{rxn}}{n_{rxn}},$$

where  $n_{rxn}$  is the number of moles of your limiting reagent. Note that you do not use the mass of the solution, but the mass of the magnesium or sodium nitrate or ammonium nitrate itself.

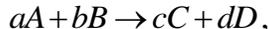
**Q: Is there a way to tell how accurate our results are?**

A way to test your measurements is to compare the results with literature or standard values. To calculate standard values of  $\Delta H_{rxn}$ , we use the equation

$$\Delta H_{rxn} = \text{total of } \Delta H_{\text{formation}} \text{ of products} - \text{total of } \Delta H_{\text{formation}} \text{ of reactants}$$

**Q: What is enthalpy of formation?**

The enthalpy of formation of a compound is an enthalpy that shows the relative stability of compounds compared to the elements they are formed from. For a “reaction”



we would calculate  $\Delta H_{rxn}$  using

$$\Delta H_{rxn} = (c\Delta H_f(C) + d\Delta H_f(D)) - (a\Delta H_f(A) + b\Delta H_f(B))$$

where a, b, c and d are the stoichiometric coefficients for substances A, B, C and D. When you look up enthalpies of formation in tables, be careful! Enthalpies of formation will be different for a substance depending on whether it's a solid, liquid, gas, or aqueous solution. Make sure that you use the correct value!

**Q: Once we know the theoretical value, how do we use it to estimate the accuracy of our result?**

We calculate a % error, using

$$\% \text{ error} = \left| \frac{\text{Experimental } \Delta H - \text{Standard } \Delta H}{\text{Standard } \Delta H} \right| \times 100\%$$

**Q: Are there any things to watch out for in this experiment?**

Sure!

- For all measurements of temperatures before mixing, make sure that you wait for the temperature to stabilize before you record it. It may take up to a minute.
- In parts B and C, make sure you begin your temperature measurements as soon as you add your Mg, or  $\text{KNO}_3$  or  $\text{NH}_4\text{NO}_3$  to the calorimeter.
- Please, please, please don't throw your syringes out. We need them!
- Take the usual safety precautions, including use of hoods, safety glasses, and limiting contact between your skin and the reagents.

**Q: What do we need to include in our lab reports?**

The reports need to be done exactly as described on page 47-48 of your lab manuals.

**Q: What are we allowed to work together on, and what needs to be done individually?**

- You may collaborate on all calculations and graphs required.
- The discussion section in part VI, section v, on page 48, must be done individually by each person.

**Q: Is there anything else we need to know about?**

Next week you and your lab partner will be designing a hot or cold pack. It is important that you make an initial design before you come in to lab next week. The exact prelab work you need to do, in addition to the usual prelab assignment, is listed on page 56 of your manual.