

**Physical Chemistry Laboratory I**  
**CHEM 445**  
**HOC**  
**Heat of Combustion and Heat of Formation**  
(Revised, 1/26/18)

Thermochemistry and the first law of thermodynamics are discussed in high school chemistry, in general chemistry, and in upper level chemistry and chemical engineering courses.

It would be tedious {and impossible} to measure the heat of every reaction of interest. Consequently, one almost always calculates the heat of a reaction from the heats of formation of the components:

$$\Delta H_{\text{Rxn}} = \sum_i v_i \overline{\Delta H_{\text{For},i}} \quad \Delta U_{\text{Rxn}} = \sum_i v_i \overline{\Delta U_{\text{For},i}} \quad (1)$$

In Eq. 1,  $\Delta H$  refers to the change in enthalpy of the reaction or the heat or energy change at constant pressure,  $\Delta U$  refers to the energy change at constant volume,  $v_i$  is the stoichiometric coefficient of each species in the balanced reaction (positive for products, negative for reactants). The  $\overline{\Delta X_{\text{For},i}}$  quantities refer to reactions forming the species from the elements in the standard states.  $\overline{X}_i$  is the molar property of species  $i$ .

Using Eq (1) is easy; measuring reliable values to use in Eq (1) is not easy. In fact, finding reliable literature values to use in Eq (1) is not always easy. Reactions forming compounds from the elements in standard states are generally slow and not quantitative; consequently, heats of formation of most compounds are not obtained directly. Organic compounds containing C, H, and O burn rapidly and quantitatively in excess oxygen to give  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Compounds with heteroatoms other than oxygen have additional problems.

From the heats of combustion of the compounds and auxiliary data for the heats of formation of water and carbon dioxide one can determine the desired heats of formation of a hydrocarbon or oxygenated organic compound. If one burns a nitrogen- or sulfur-containing compound, then additional experiments and calculations must be made to account for the nitric acid or sulfuric acid produced in the reaction.

In this experiment you will

measure the **energy of combustion of solid succinic acid,  $\Delta E_{\text{Comb}}$ {Succinic acid, s};**

calculate the **heat of combustion of succinic acid,  $\Delta H_{\text{Comb}}$ {Succinic acid, s}** from these data;

calculate the **heat of formation of the solid compound** from your combustion data and reference data,  $\Delta H_{\text{For}}$ {Succinic acid, s};

calculate the **heat of formation of the gaseous compound,  $\Delta H_{\text{For}}$ {Succinic acid, g}**, from your experimental data and reference data;

and calculate the **heat of formation of the gaseous compound,  $\Delta H_{\text{For}}$ {Succinic acid, g}**, using Gaussian.

The combustion reactions occur in a {nearly} adiabatic calorimeter (*i. e.*, one with no heat loss from the calorimeter to its surroundings). The calorimeter used in this experiment is an **isoperibol calorimeter**: one in which there is a small transfer of heat between the calorimeter and the surroundings. Appropriate corrections are applied to account for heat transfer and to calculate the temperature rise as if the calorimeter were adiabatic.

The sum of the heat change for combustion of the sample and heating the system in an adiabatic system,  $Q$ {Comb, adiabatic} is zero.  $\Delta H$  and  $\Delta U$  are state variables and are independent of the path by which the reaction occurs. One may choose any convenient path to analyze the

process. A convenient way is to separate the overall process into two steps: 1<sup>st</sup>, the combustion reaction occurs at the initial temperature,  $T_1$ , and 2<sup>nd</sup>, the products are heated to the observed final temperature,  $T_2$ .

$$Q\{\text{Comb, adiabatic}\} = 0 = Q_1\{\text{Rxn}, T_1\} + Q_2\{\text{Heat}, T_1 \rightarrow T_2\} \quad (2)$$

The process occurs at constant volume; therefore,

$$Q_1\{\text{Rxn}\} = \Delta U_{\text{Rxn}} \quad Q_2\{\text{Heat}\} = \int_{T_1}^{T_2} C_V\{\text{System}\} dT \quad (3)$$

and, consequently,

$$\Delta U_{\text{Rxn}} = - \int_{T_1}^{T_2} C_V\{\text{System}\} dT = -C_V\{\text{System}\}(T_2 - T_1) \quad (4)$$

Because the temperature change is not large, 1 - 2 °C, we make the usual assumption in Eq (4) that the heat capacity of the system is independent of temperature.

Determining  $Q_1\{\text{Rxn}\}$  or  $\Delta U_{\text{Rxn}}$  of a compound requires the heat capacity of the system,  $C_V\{\text{System}\}$ : the heat capacity of the calorimeter and all its parts, the water it contains, and the products of the reaction.

One can determine the heat capacity of the system by adding a known amount of electrical energy and measuring the temperature increase. Alternatively, one can burn a measured amount of a compound whose heat of combustion is known (a standard) and determine the heat capacity of the system from the observed increase in temperature. In conventional bomb calorimetry, the heat capacities of reactants and products are small compared with the heat capacities of water and metal in the calorimeter, itself. In this experiment, for example, less than 1 g of compound is burned and approximately 2 L (~ 2 kg) of water plus the metal calorimeter are heated. Consequently, we may legitimately neglect the heat capacities of the small amounts of sample and products in our analysis.

One can determine the heat capacity of the system from the rearrangement of Eq (4):

$$C_V\{\text{System}\} = - \left( \frac{\Delta U_{\text{Comb}}\{\text{Standard}\}}{\Delta T} \right) \quad (5)$$

$C_V\{\text{System}\}$  is always positive,  $\Delta U_{\text{Comb}}\{\text{standard}\}$  is negative, and the temperature of the system rises.

One may then determine the heat of combustion of the compound of interest from the temperature rise on combustion of a known weight sample and the measured heat capacity of the system.

Most reactions are done at constant pressure (on a bench top), rather than at constant volume, as is the case of these combustion reactions in a calorimeter. Consequently, data are more commonly tabulated as  $\Delta H_{\text{Rxn}}$ , rather than  $\Delta U_{\text{Rxn}}$ . The conversion between  $\Delta H$  and  $\Delta U$  is well known.

$$\Delta H = \Delta U + \Delta\{PV\} \quad (6)$$

The correction term should not be neglected for reactions involving gases. If one treats the gases as ideal, then the following relationship holds for an isothermal process, in which  $n_{\text{gas}}$  refers to the number of moles of gaseous species.

$$\Delta\{PV\} = RT\Delta n_{\text{gas}} \quad \text{and} \quad \Delta H = \Delta U + RT\Delta n_{\text{gas}} \quad (7)$$

The usual convention applies for differences in thermochemistry: final state minus initial state. In these combustion experiments at essentially room temperature, water is present as a liquid. The correction may be either positive or negative, depending on the reaction, and will generally be small.

In principle, measuring heats of combustion is simple because one needs only the temperature rise, the heat capacity of the system, and the weight of material being burned. In practice, making accurate measurements may be another matter.

### **Experimental Procedure:**

You will use a Parr Instruments 1341 Oxygen Bomb Calorimeter with an 1108 Oxygen Combustion Bomb and 1672 Calorimetric Thermometer. Pictures of the calorimeter assembly are available at the end of this experiment. Operating instructions from Parr Instruments {www.parrinst.com} are available in the laboratory. There is an interesting and useful animation of a heat of combustion experiment available on the Web by Dr. Gary Bertrand (University of Missouri, Rolla, MO): <http://www.mst.edu/~gbert/cal/cal.html>.

#### **A. Determination of the heat capacity of the system (calorimeter + water)**

A short video about this experiment is available on Canvas and on the computer used for this experiment in the PCHEM Laboratory. Watch this video before you perform the experiment.

1. Pellets of reagent grade benzoic acid, C<sub>6</sub>H<sub>5</sub>COOH, are available. Place a pellet in the aluminum two-piece holder provided and make a hole in the pellet by passing a hot wire (big paper clip) through its center. Handle the pellet as little as possible. Use gloves if you wish.

2. Measure, cut, and **weigh ~ 10 – 12 cm of iron fuse wire, to ± 0.1 mg** {analytical balance, not top loader}. Pass this wire through the hole in the pellet and wrap the wire around the pellet to ensure good contact and subsequent ignition. **Weigh the pellet and wire together** to ± 0.1 mg. Use the analytical balance for both weights. If you lose benzoic acid after weighing, either re-weigh or make a new pellet. Use a small Petri dish. Never put any solid directly on the balance pan.

**Do not reposition the balance. Move you. Handle the balance as you did (or should have done) in QUANT.**

3. Attach the ends of the wire to the electrodes of the bomb head. Place the pellet over the center of the catch pan. Have the pellet close to, but not touching, the catch pan.

Good electrical contact between wire ends and electrodes is critical to successful ignition: use abrasive paper to clean the electrode leads when you begin the set up.

4. To insure safe assembly, bomb components must be put together in EXACTLY the following order.

a. Add 1.00 mL of water to the bomb – to ensure that the water formed will be in the liquid state.

b. Place the bomb head assembly (with your pellet) carefully into the bomb casing, working it downward evenly as far as it will go.

c. Carefully seat the rubber gasket seal, working it evenly downward around the inserted bomb head assembly.

d. Carefully seat the stainless steel ring downward onto the rubber gasket, making sure it is both centered and evenly downward.

e. Add the top, screwing it on to a firm, hand-tight condition.

5. The bomb is a double valve type: an inlet valve and an exhaust valve. The exhaust valve is a screw type that may be opened and closed by loosening and tightening the knob. Fill the bomb with oxygen from the tank. **Consult your Laboratory Instructor before pressurizing the bomb.** Close the black screw valve and open the tank of oxygen. The small gauge reads in both atmospheres and psi (pounds per square inch). You will flush the bomb with oxygen to replace the air with oxygen {to eliminate formation of nitrogen oxides and nitric acid}.

Screw the plastic hose to the inlet of the bomb head. Open the exhaust valve. Open the needle valve. **Slowly** open the black screw valve on the regulator **to a small extent** to allow gas to

flow. You should hear hissing as the gas flows through the tubing, the bomb, and the exhaust valve. Let the gas flow through the cell **slowly** for about a minute. Then **slowly** close the exhaust valve and watch the pressure rise on the large gauge. When the pressure reaches **25 atm**, close the black needle valve. Release pressure in this line and disconnect the hose from the bomb inlet port. **Do not fill the bomb to pressures higher than 25 atm.**

**6.** Place the bomb in the **dry** polished can. The bomb sits on the circular mound in the bottom of the can. Place the can and bomb into the insulating jacket of the calorimeter with the bomb towards the front. Attach electrical leads – either lead to either terminal.

**7.** CAREFULLY (avoid splashing) add water (tap water at room temperature) from a 2 L volumetric flask to the polished can of the calorimeter. Fill the volumetric flask to the mark each time. The volume transferred will not be exactly 2.000 L because some water will remain in the flask, but if you are careful, the same amount of water will be used in each experiment.

Bubbles may appear after the bomb has been submersed in water. However, unless the bomb is leaking, bubbling should cease after a few minutes. **If bubbles continue, consult your Laboratory Instructor:** some seal is leaking and you probably need to start over. **Never ignite a leaking bomb.**

**8.** Place the cover on the insulating jacket with the stirrer propeller towards the rear. Spin the propeller pulley by hand to make sure it is not hitting anything (you can hear the sound if the propeller is hitting anything) and then attach the stirrer drive belt (large O-ring) to the stirrer motor.

**9.** Allow 2 – 3 minutes for the temperature to equilibrate after completing the procedures above.

**10.** Press \*15 and then press **Enter** to begin the combustion experiment.

**11.** Press **Enter** to OK the sample ID. You know what the sample is and a number is not essential.

**12.** Enter pellet weight, in g, (already recorded in your notebook) and press **Enter**.

**13.** The experiment will begin with a short “pre-equilibrium” period (about 6 minutes) as the thermometer records temperature as a function of time. When sufficient data have been obtained for the temperature vs. time curve, the system will “beep” at you.

**14.** When the system “beeps” at you, record the temperature in your notebook. Then ignite the pellet by pushing the ignition button {Hold for a count of **five.**} and press **Enter** to begin the run.

If you do not see a rapid rise in temperature within a minute or so after ignition, the sample did not ignite and the experiment failed. The temperature rise is not instantaneous because you are heating a massive amount of water as well as the bucket. If failure occurs, disassemble the bomb {16} and begin another run. Consult your Lab Instructor about the failure to ignite. Poor electrical connections have been the most common cause of ignition failure.

**15.** The thermometer will take data every few seconds until a plateau is reached in the temperature vs. time plot (about 5 – 10 minutes). The system will “beep” at you when the experiment is finished. **Record T Rise from the thermometer.** This is the essential value for each experiment.

**16.** Stop the stirrer, remove the belt, and remove the cover from the calorimeter.

Disconnect the electrical leads, remove the bomb from the calorimeter, and dry the bomb. Also remove the can, and empty and dry it.

Vent the bomb in the sink in the other lab so that the hissing doesn’t startle others working in the lab. **Slowly** open the exhaust valve on the bomb to reduce pressure to atmospheric pressure before removing the top: reduce pressure until you no longer hear “hissing” from escaping gas.

Bring the bomb back to your station to complete the disassembly. Unscrew the top. Remove the stainless steel ring. Then CAREFULLY remove BOTH the rubber gasket seal AND bomb head assembly TOGETHER. NEVER try to pry out the gasket by itself as damage to the gasket may

occur causing future leakage. Generally, the two will come out together by gently rocking the head assembly while also pulling upwards. Once removed from the bomb casing, you may remove the rubber gasket seal safely and place the head assembly into its stand. If you find you CANNOT do any particular disassembly step, **STOP and consult with your Laboratory Instructor.** Do NOT try to force disassembly: damage may occur, and/or your safety may be at risk!

Find and weigh any iron fuse wire fragments (some may appear as wire, but some may also appear as small ball-shaped particles created through melting). Occasionally the wire has small carbon deposits, as indicated by a heavier weight than the original wire. Wipe these off. **Your correction is based on the weight of the wire that has burned.**

THOROUGHLY dry ALL wetted calorimeter components to avoid carrying unknown amounts of water into the next experiment.

**17.** Dispose of any remaining benzoic acid in the solid organic waste disposal container. {Pellets sometime shatter.} **Do NOT put benzoic acid into the trash.**

**18.** Record the initial temperature and the temperature rise {taken directly from the computer as X.XXXX°} for this and each subsequent experiment. The last decimal is not reliable, but keep it anyway.

**19. Repeat this experiment once to obtain two values for the heat capacity of the calorimeter.** This value is essential to obtain reliable data for the heat of combustion of a compound. Your value for the heat capacity of the calorimeter,  $C_v$ , should be of the order of 10 kJ/<sup>o</sup>, although it must be given as XX.XX kJ/<sup>o</sup>. If your values are not consistent (your decision), repeat. Use the average value for  $C_v$  in all of the subsequent calculations.

## B. Determination of the heat of combustion of a gelatin capsule

Most compounds to be analyzed are not available in pellet form. Some compounds can be compressed to give pellets that are strong enough to survive the pre-combustion handling, but most cannot be.

**Small gelatin capsules** have been used successfully in combustion calorimetry to contain samples. The capsules burn and contribute to the overall energy change in the combustion reaction, as does the wire (correction applied above). Consequently the heat of combustion of the capsule must be determined and an appropriate correction applied to obtain the heat of combustion of the compound.

Although generally uniform in composition, the gelatin capsules do not approach the iron wire in uniformity and purity. The weight of the capsule and heat of combustion may vary from batch to batch.

Take a gelatin capsule and wrap it with iron wire. If you are dexterous, a 10.0 cm wire may work well. However, a 12.0 cm wire may be easier to wrap around the capsule. **Weigh the wire and weigh the wire plus the capsule.** The capsules are somewhat hygroscopic; work quickly. The capsules should be horizontal between the leads so that they don't fall.

The gelatin capsules are not sufficiently uniform in weight that you can neglect differences among capsules. Calculate the value for the **heat of combustion per gram of capsule**. Remember to include the correction for the weight of wire that was **burned**.

Follow the same procedure as above for the combustion process.

Burn a second capsule and use the average value for the **heat of combustion per gram** of the capsule as a correction in subsequent analyses. This value should be -12 to - 16 kJ/g.

## C. Determination of the heat of combustion of succinic acid

**1.** Repeat the entire procedure above with succinic acid. Use gelatin capsules to contain the sample.

Take a small amount of succinic acid (about 2 g) and grind the crystals in the mortal and pestle. The exact weight is not critical, but don't waste the compound. The degree of fineness is not critical, but reduction in particle size is needed.

Weigh a gelatin capsule { $\pm 0.0001$  g}. Carefully fill with 0.5 – 1.0 g of succinic acid and re-weigh. Weigh the wire, 10 – 12 cm, as in part B.

Wrap the wire around the capsule and attach the wire to the posts as before.

Burn the sample in the gelatin capsule as you did the capsule.

### **Do a second combustion analysis of succinic acid.**

## **D. Data Analysis**

The calorimeter produces a temperature rise for each combustion reaction from an analysis of temperature vs. time plots. The procedure (which we did in the past) is tedious. The computer records the temperature every few seconds from initial equilibration through the rapid rise during combustion to the final equilibration. These data are not saved for you to plot.

Figure 1 shows a plot of temperature vs. time from an experiment in 08S, when we were manually determining the corrected temperature rise.

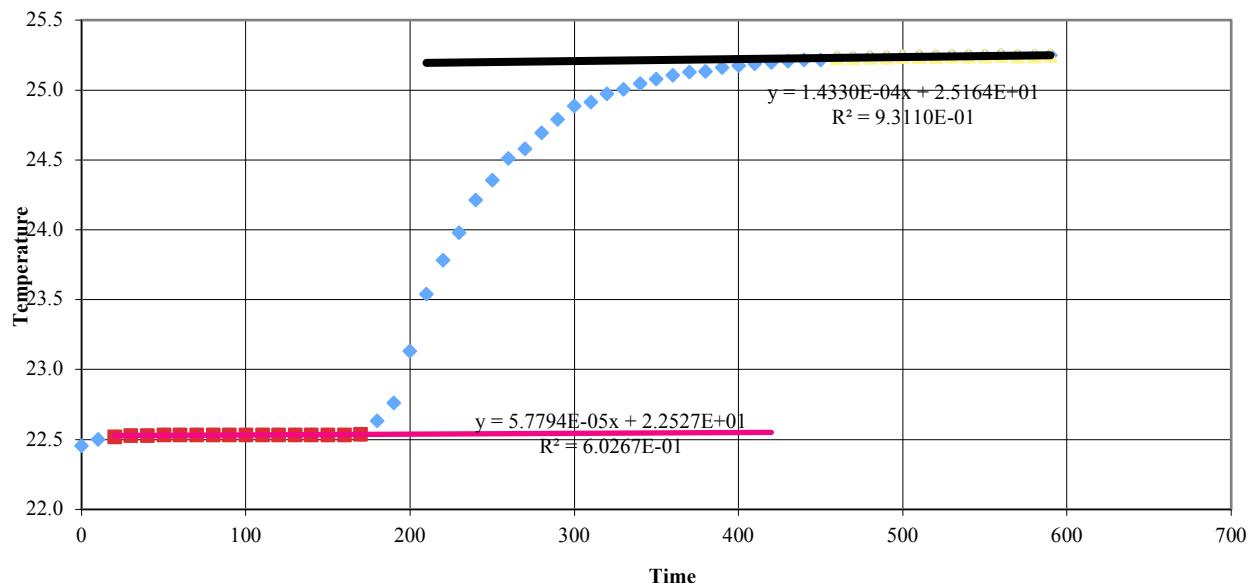


Figure 1. Temperature vs. Time; Trial 1, Combustion of Benzoic Acid.

The red points show the equilibration period prior to reaction, fitted to the equation given in the figure. Ignition occurred at 170 s. The temperature rises rapidly from the combustion reaction. The upper, black, line represents the temperature after the reaction is complete.

The corrected temperature rise from a combustion reaction in an isoperibol calorimeter is the temperature rise at the time at which area I is equal to area II in Figure 1. The calorimeter thermometer makes these plots and calculates the corrected temperature rise. You do not need to make plots – and can't, because data are not available.

The calorimeter output at the completion of the experiment includes the **temperature rise**. Record the temperature rise as X.XXXX°. The last digit isn't really warranted, but keep it anyway. Temperature differences can actually be recorded more accurately than absolute values of temperature. Record the final temperature, xx.xx°.

### 1. Calculating $C_v$ (system).

Calculate  $C_v$ (system) from Eq.(5) with the value of  $\Delta T$ , the temperature rise, from the combustion of benzoic acid. Some of the ignition wire will have burned as well as the benzoic acid and that value must included as part of the total heat of reaction.

$$\Delta U(\text{Total}) = \Delta U(\text{Comb, Benzoic acid}) + \Delta U(\text{Comb, wire}) \quad (8)$$

$\Delta U\{\text{Comb, Benzoic acid}\} = -26.433 \text{ kJ/g}$  and  $\Delta U\{\text{Comb, Fe}\} = -5.86 \text{ kJ/g}$  (Parr). This value for the heat of combustion for the wire should be applied to the weight of wire that burned, because much of the wire did not burn. If the weight of the wire after reaction is greater than the initial weight, the wire probably has a carbon deposit. Remove the carbon deposit. If you cannot, a reasonable assumption for these conditions is that the wire did not burn.

Calculate the value for  $C_v$ (system) from your experiment. The primary data for this part of the experiment should be given in **Table 1** in your report. As noted above, your value for  $C_v$ {system} should be  $\sim 10 \text{ kJ}^\circ$ . Check your calculations if you get a significantly different answer or repeat the measurements.

### 2. Calculating $\Delta U$ (Combustion) of the gelatin capsules

You need the energy of combustion of the gelatin capsules to determine the energy of combustion of the compounds. These data should be presented in **Table 2** in a manner similar to **Table 1**. Because the capsules do not have identical weight, **report your data as  $\Delta U\{\text{Comb/g}\}$** . The heat of combustion of the gelatin capsule should be in the range of  $-12$  to  $-16 \text{ kJ/g}$ , but given as **XX.XX kJ/g**. Check your calculations if you get significantly different values or repeat the measurements.

$$-C_v\{\text{calorimeter}\} * \Delta T = \Delta U\{\text{Comb, Tot}\} = \Delta U\{\text{Comb, wire}\} + \Delta U\{\text{Comb, gel}\} \quad (9)$$

Use your average value of  $C_v\{\text{calorimeter}\}$  to calculate  $\Delta U\{\text{Comb, per gram of gel}\}$ .

### 3. Calculating the heat of combustion of compound

The energy of combustion of the sample,  $\Delta U\{\text{Comb}\}$ , is obtained from the temperature rise, the average value for the heat capacity of the calorimeter, and appropriate corrections for the combustion of the wire and the gelatin capsule.

$$-C_v\{\text{cal}\} * \Delta T = \Delta U\{\text{Comb, Tot}\} = \Delta U\{\text{Comb, sample}\} + \Delta U\{\text{Comb, wire}\} + \Delta U\{\text{Comb, gel}\} \quad (10)$$

Consequently, the total energy of combustion must be corrected for the combustion of the wire that burned and for the combustion of the gelatin capsule to give the energy of combustion of the sample. The correction for combustion of the gelatin capsule is based on the weight of the capsule, because all of it burned and the capsules have slightly different weights.

For these experiments, use your average value for the heat of combustion per gram of the gelatin capsule, in kJ/g, to calculate  $\Delta U\{\text{Comb, gel}\}$  for each capsule. The gel capsules are not identical in weight. Use your average value for  $C_v\{\text{calorimeter}\}$  to calculate  $\Delta U\{\text{Comb, solid succinic acid}\}$  for each combustion experiment using Eq (10).

Because you will use a different amount of sample and wire in each experiment the values for energies of combustion of individual samples will not be identical. Don't average these values. Report these data in **Table 3**. Also calculate and report in this table:  **$\Delta U$ (Combustion per mole)** for each of your experiments, the average, the standard deviation, the relative standard deviation. The

95 % confidence interval for two values is too large to be useful. You should have two consistent values for the molar energy of combustion of solid succinic acid. {If not, do another experiment.}

Also calculate  $\Delta H$ (Combustion per mole of solid succinic acid, T, K) from Eq. 7 for each experiment, using the balanced combustion reaction, and the uncertainty. Use the average value for the temperature of the reaction. Include these individual values in Table 3.

Compare your values for the heat of combustion with values from NIST {most reliable} or another source (give reference).

Use your values for the heat of combustion of each compound and auxiliary values for  $\Delta H_{\text{For}}\{\text{CO}_2, \text{g}\}$  and  $\Delta H_{\text{For}}\{\text{H}_2\text{O, liq}\}$  – NIST Chemistry WebBook is a reliable source of thermochemical data – and calculate  $\Delta H_{\text{For}}\{\text{Succinic acid, s}\}$  from these data. You will notice that the heat of formation of a compound is a difference between large values. If one assumes that there is negligible error in the heats of formation of water and carbon dioxide, the absolute uncertainty in the heat of formation of a compound is the same as the absolute uncertainty in the heat of combustion of a compound and, therefore, a larger relative uncertainty.

The NIST table gives values nominally at STP, although the details of the corrections from the temperature of the experiment are not given. However, heats of combustion and heats of formation vary only slightly with temperature. The combustion reactions were most probably done around room temperature; so we will neglect any temperature correction. Compare your results for heat of formation of solid succinic acid with the NIST value.

The NIST tables also give a value for the heat of sublimation of solid succinic acid as 120 kJ/mole with a reasonable uncertainty of  $\pm 4$  kJ/mole. Use this value to calculate the heat of formation of gaseous succinic acid,  $\Delta H_{\text{For}}\{\text{Succinic acid, g}\}$ . You will compare your experimental value for  $\Delta H_{\text{For}}\{\text{Succinic acid, g}\}$  with the value calculated using Gaussian.

#### 4. Theoretical Calculations:

There are many ways of estimating heats of formation of compounds when experimental data are not readily available. A group contributions method is often used. {See Exp. 2.} In this method, the heat of formation is considered as being the sum of individual groups within the molecule: -CH<sub>3</sub>, -CH<sub>2</sub>-, -COOH, -NH<sub>2</sub>, etc. Many values are needed for the appropriate groups, but the method does work to give “reasonable values” for complex molecules.<sup>1</sup>

However, we will calculate the heat of formation of gaseous succinic acid using Gaussian. Gaussian is a commercially available (one of several nowadays) software package for modeling chemical systems using current state-of-the-art quantum mechanical methods (algorithms, approximations, etc.). Software such as Gaussian uses quantum mechanics {qm} (CHEM444) to compute wave functions associated with molecular and atomic orbitals (electrons). Quantum mechanics tells us that once we know the wave function, we can compute the internal energy of a molecular system. In the computational complement of this laboratory experiment, you will compute the internal energy of a single succinic acid molecule as well as the energies of the individual atomic species relevant for this molecule. We refer to the values you compute as energies because the quantum mechanical calculations are performed with no consideration of temperature; that is, the temperature is effectively 0 Kelvin if one has to assign a temperature at which the computations are performed.

These quantum mechanical energies will be used in the thermodynamic formulation of the enthalpy of formation of gaseous succinic acid at 298K. In the section above you measured the heat of combustion (enthalpy) of solid succinic acid and with additional data, you calculated the enthalpy of formation of the gaseous species.

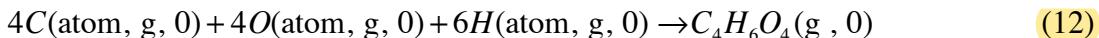
In the following discussion, we will address the theoretical aspects of the calculation, and follow this by a technical discussion about using the Gaussian Software available in the PCHEM Laboratory Macintosh Computers.

We are interested in the following chemical reaction:



where ‘sol’ is used to represent the solid form of the element’s stable state, ‘g’ is the gas phase, and the reaction occurs at 298K. In the following, we will at times drop K and depend on the context to make the meaning clear. Equation (11) is the usual form for the enthalpy of formation of a compound.

As mentioned in the previous paragraph, the Gaussian software computes **energies** of the individual atomic and molecular **gaseous species** at **0 K**. The reaction for the formation of gaseous succinic acid from its gaseous atomic constituents is:



The reverse reaction of Equation (12) is the dissociation energy,  $D_0$ . Thus, the forward reaction as written in Equation (12) entails an energy change represented by  $-D_0$ .

Equations (11) and (12) represent four thermodynamic states (either real or virtual). We are interested in the enthalpy change for the process depicted in Equation (11). But, due to limitations of current state-of-the-art technologies within Gaussian (and other similar software), we are only able to calculate the energies associated with Equation (12).

How can we use the computed data based on Equation (12) to compute the enthalpy change for Equation (11)? The solution is straightforward because enthalpy is a **state function**. To work around our dilemma, we will create a thermodynamic cycle that will connect the 4 states we have defined so far by introducing intermediate bridging states. The changes involved in traversing those states around the cycle will eventually sum to the desired enthalpy change. Thermodynamics places no restrictions on the use of ‘virtual’ states; as long as we can compute changes in thermodynamic quantities between any two states, we can proceed. So the cycle we can use is shown in **Figure 2** below.

We see from **Figure 2** that the process of Equation (11) {depicted in the chemical reaction at the bottom of the cycle with an asterisk (\*)} can be obtained by summing the processes 1, 2, 3, and 4, in the directions indicated. More specifically, processes 1 and 2 are broken down in terms of each element, hence  $1_C$ ,  $1_H$ ,  $1_O$ , etc, with the subscripts indicating the atomic species. Remember, process 3 is that of Equation 12, for which the computations will provide **energies** of the **single atoms** C, H, O, and the single molecule.

If we sum the enthalpy changes for all of the **numbered** steps indicated by arrows (and using  $-D_0$  for the energy change of process 3), we obtain the enthalpy change for our desired reaction as Equation (13) below.

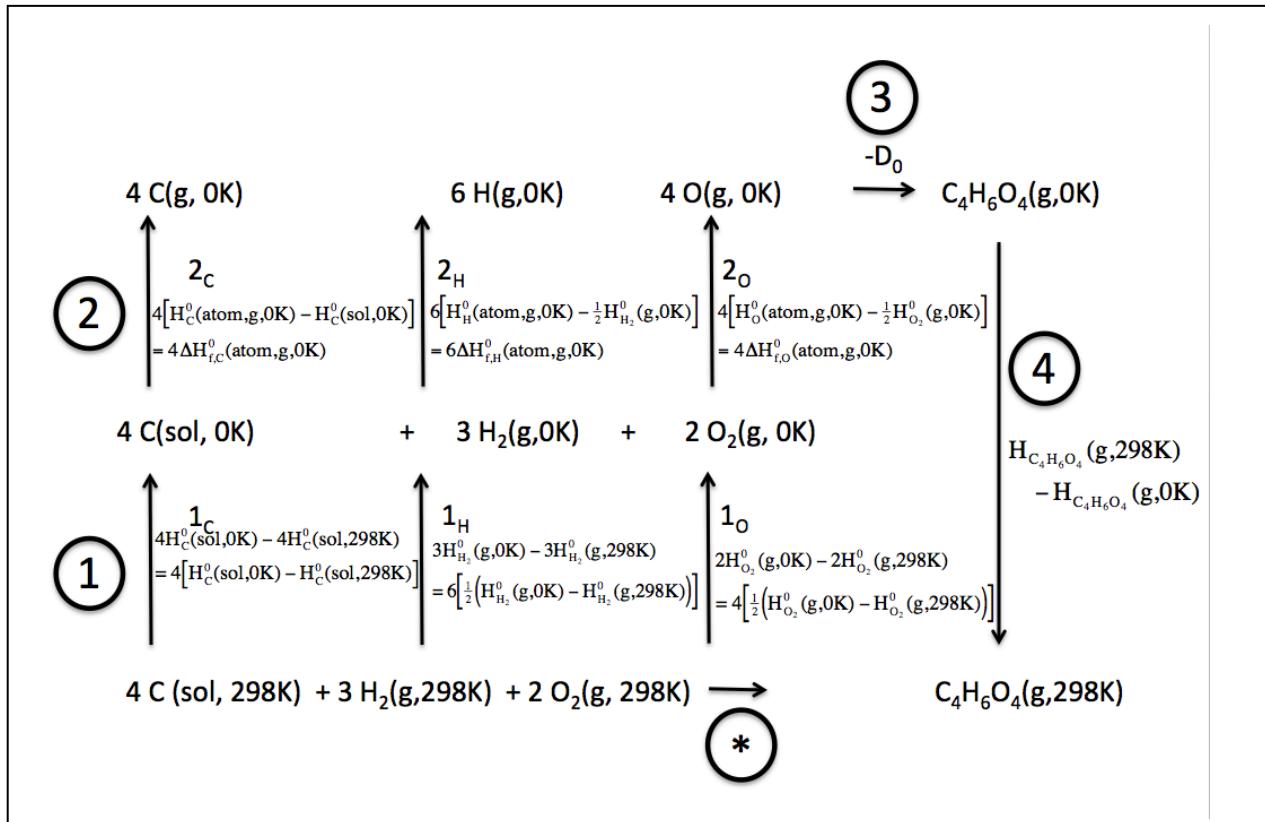


Figure 2. Thermodynamic Cycle for Succinic Acid Formation Enthalpy (gas phase, 298K)

The values for the Energies of the gaseous atoms and succinic acid needed to calculate - D<sub>0</sub> for Step 3 and of the enthalpy change for Step 4 (thermal correction for succinic acid) will be computed using Gaussian in this experiment.

There are three parts to Step 1, the “thermal correction” of the elements or the enthalpy of cooling the elements in their standard states at constant pressure from 298 K to 0 K: [H<sup>o</sup><sub>C(sol, 0K)</sub> - H<sup>o</sup><sub>(C, sol, 298K)</sub>]; [H<sup>o</sup><sub>(H<sub>2</sub>, g, 0K)</sub> - H<sup>o</sup><sub>(H<sub>2</sub>, g, 298K)</sub>]; and [H<sup>o</sup><sub>(O<sub>2</sub>, g, 0K)</sub> - H<sup>o</sup><sub>(O<sub>2</sub>, g, 298K)</sub>]. The value cannot be calculated by Gaussian for solid carbon; consequently, the experimental molar value is given in Table 1. The values in Table 1 are the molar values calculated for the gaseous species, H<sub>2</sub> and O<sub>2</sub>. We will not do the calculations in this experiment, although they were done with Gaussian.

Step 2 shows the dissociation of the elements in their standard states to the atoms at 0 K. The enthalpies of formation for the gaseous atoms are given in Table 1. ΔH<sup>o</sup><sub>F</sub>{C<sub>g</sub>,0K} is the value for the sublimation energy of graphite at 0 K. The values for the hydrogen atom and the oxygen atom are half of the dissociation energies of the molecules at 0 K.

Step 4 is the analogous “thermal correction” for gaseous succinic acid that you will compute using Gaussian. In this case, the correction is from 0 K to 298 K: [H<sup>o</sup><sub>C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>, 298 K</sub> - H<sup>o</sup><sub>C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>,0K</sub>].

You will also compute the Zero Point Energy {ZPE} of gaseous succinic acid using Gaussian – needed in Equation (13).

$$\Delta H_F^0\{C_4H_6O_4,g,298K\} = \{4[H^0_{C,sol,0K} - H^0_{C,sol,298K}] + 3[H^0_{H_2,g,0K} - H^0_{H_2,g,298K}] + 2[H^0_{O_2,g,0K} - H^0_{O_2,g,298K}]\} + \{4\Delta H_f^0\{C_{g,0K}\} + 6\Delta H_f^0\{H_{g,0K}\} + 4\Delta H_f^0\{O_{g,0K}\}\} + \{-D_0\{C_4H_6O_4, g\} - ZPE\{C_4H_6O_4,g\}\} + [H^0_{C4H_6O_4, 298 K} - H^0_{C4H_6O_4,0K}] \quad (13)$$

The first three terms in braces in Equation (13) correspond to Step 1 – the enthalpy of cooling the elements in their standard states from 298 K to 0 K. The second three terms correspond to Step 2 – forming the atoms from the elements in their standard states at 0 K. The next two terms correspond to the formation of gaseous succinic acid  $\{-D_0\{C_4H_6O_4, g\}\}$  from the gaseous atoms and the correction for the vibrational energy in the ground state at 0 K {ZPE}. The last term corresponds to the thermal correction (enthalpy of heating) for gaseous succinic acid from 0 K to 298 K.

**Table 1.** Auxiliary data.

Species, i	v <sub>i</sub>	Spin Multiplicity	$\Delta H_{f,i}^0$ (atom,g,0K) (kJ/mol)	$\Delta H_i^0$ (298K - 0K) (kJ/mol)
C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	1	1	To Be Determined	To Be Determined
C	4	3	710.4	
H	6	2	216.0	
O	4	3	246.8	
C{sol}				1.05
H <sub>2</sub> {g}				8.46
O <sub>2</sub> {g}				8.70

Spin multiplicity values are needed for the Gaussian calculation setup. \*Please be very careful particularly for calculations of individual atoms\*.

### Calculation of Dissociation Energy

The calculation of  $-D_0$  involves computing the quantum mechanical energies of the **atomic species (in gas phase) and the molecular species (in gas phase)**.

Two other quantities that are required (and found in the output/results file from the calculations) are

1.  $[H^0_{C4H_6O_4, 298 K} - H^0_{C4H_6O_4,0K}]$ , the thermal correction for succinic acid

and

2. the ZERO-Point energy, ZPE, of succinic acid at 0K.

The equation for  $-D_0$  is given by:

$$-D_0 = E(C_4H_6O_4,0K) - 4E(C,0K) - 6E(H,0K) - 4E(O,0K) \quad (14)$$

The values for the 'E' in Equation (14) are found in the output file from the Gaussian calculation as will be discussed below.

Finally,  $[H^0_{C4H_6O_4, 298 K} - H^0_{C4H_6O_4,0K}]$  will be found in the Gaussian output file and will be called 'Thermal Correction to Enthalpy'. The ZERO-Point energy, ZPE, of the molecule will also be found in the output file as mentioned above.

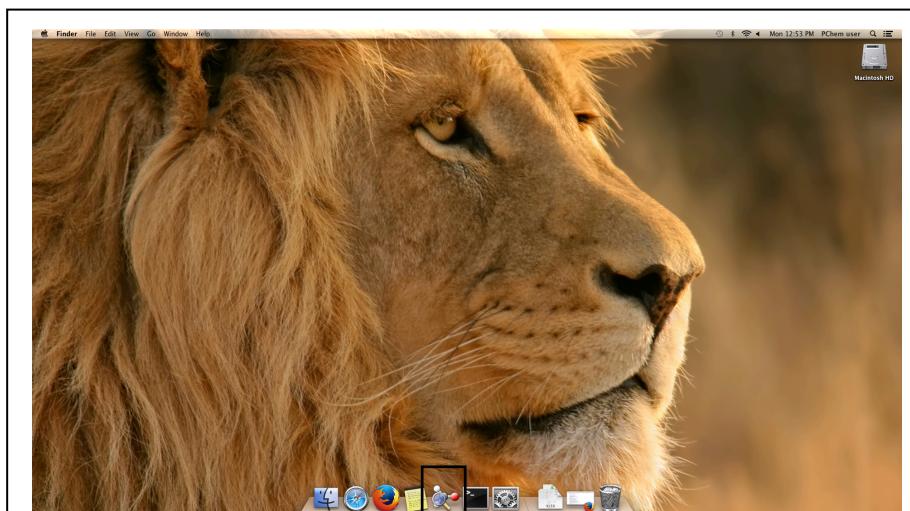
## Running A Gaussian Calculation

A Gaussian calculation is a quantum mechanical calculation. In this sense, the calculation attempts to determine the quantum mechanical wave function of an atom or molecule to describe the electrons associated with the system of interest.

Only a few ‘parameters’ are required as inputs to perform the calculations. In the following, we will discuss these inputs as well as how to set up the calculation, perform the calculations, and retrieve the necessary values from the output file. To reiterate, the necessary values are the energies of the gaseous atoms and gaseous succinic acid, the thermal correction,  $[H^o_{C_4H_6O_4, 298 K} - H^o_{C_4H_6O_4, 0K}]$ , and the ZERO-Point energy of the succinic acid molecule).

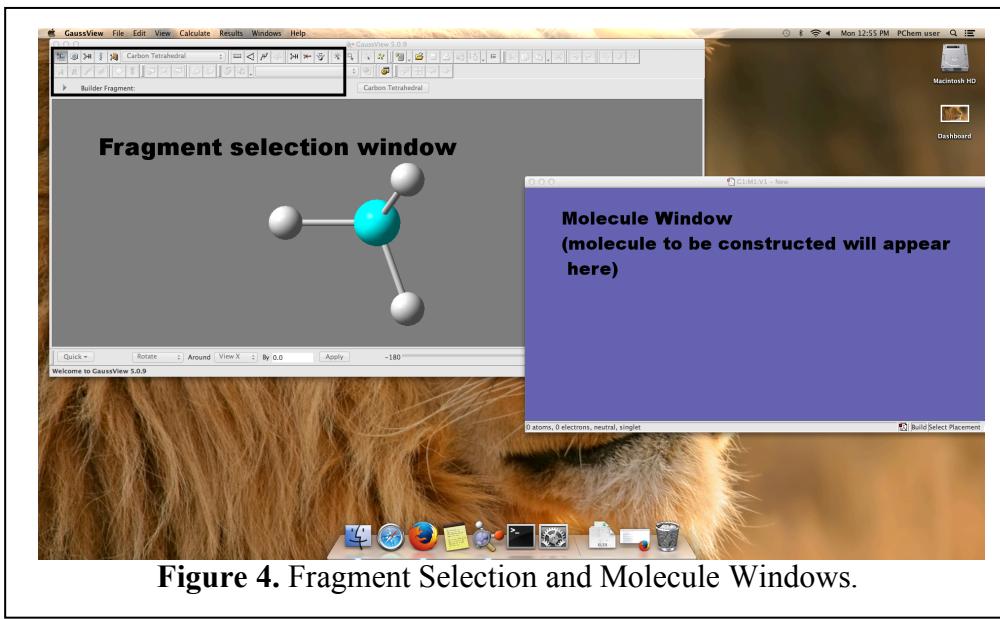
### 1. Starting the Gaussian Program

To start the Gaussian Program (much like starting Microsoft Word or Excel on your computer or laptop), find the GaussView Icon on the Dashboard at the bottom of the screen. Double-click the icon and wait a few seconds for the software to load. The black box in **Figure 3** shows what the icon looks like. The bar at the bottom is the Dashboard.



**Figure 3.** Snapshot of Desktop on PCHEM MacIntosh Computers. Black box shown in the Dashboard at bottom encloses the Icon for Gaussian.

After the software has loaded, you will see two windows. The Grey window is the **Fragment Selection Window** and the Purple window is the **Molecule Window**. Click on the Fragment Selection window shown in Figure 4. This is the main console window for GaussView and we will use some of the tools located in the Tool Bar at the top of the window as shown in Figure 4 (the Tool Bar is highlighted in the black box in the upper left of the Fragment Selection window).



**Figure 4.** Fragment Selection and Molecule Windows.

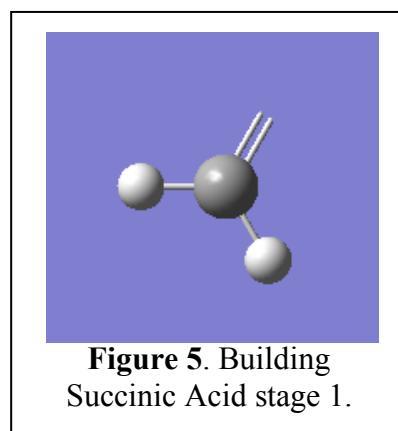
Click on the Fragment selection window shown in Figure 4 to make that window active (it will move to the foreground of the screen if it is not already so).

In the upper left-hand corner, you will see a box with  ${}^6\text{C}$ . Click on that to bring up a Periodic Table of elements. This table will allow you to choose the atoms and hybridization state (tetrahedral,  $\text{sp}^2$ ,  $\text{sp}$ , etc) for the atoms you will need to construct succinic acid. There is a Thumbtack in the upper-left position of this periodic table. Click on it to make it **green** so that it remains active while you are building your succinic acid molecule.

Determine the chemical structure of succinic acid if you have not done so already.

## 2. Building the Succinic Acid Molecule

- In the Periodic Table, select the  $\text{sp}^2$  carbon (2 single bonds, 1 double bond) by clicking on the appropriate button.
- Click on the central carbon atom of the fragment you see in the Fragment Selection window. The carbon atom will turn to a grey color.
- Click a central spot in the Molecule Window. The  $\text{sp}^2$  fragment selected in step b will appear. If you happen to mouse click twice (or more) and more than one fragment appears, you can simply use the “Edit → Undo” sequence of mouse clicks to ‘undo’ your actions. At this point, you should have one fragment in the Molecule Window as shown in **Figure 5**:



**Figure 5.** Building Succinic Acid stage 1.

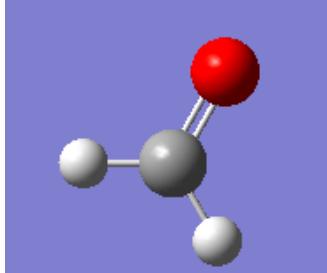
On the Fragment Window, click the central carbon atom again.

d. In the Periodic Table, click on the oxygen atom. What appears to be the water molecule appears in the Fragment Window.

e. Change this water to  $sp^2$  oxygen by selecting the appropriate button at the bottom of the Periodic Table window.

f. Click on the oxygen atom.

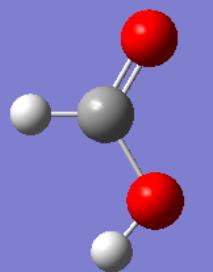
g. Go to the Molecule Window and click on the end of the double bond to carbon where the oxygen should be. The oxygen atom should appear upon your click. It should look something like **Figure 6**:



**Figure 6.** Building Succinic Acid stage 2.

h. In the Periodic Table Window, click on the  $sp^3$  oxygen button; you will see the water molecule in the Fragment Window again. Click on the oxygen atom in the Fragment Window.

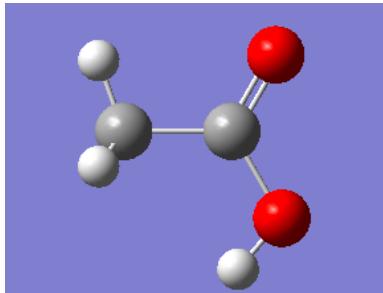
i. In the Molecule Window, click on one of the hydrogen atoms. It should now be an oxygen atom and the fragment in the Molecule Window should be something like **Figure 7**:



**Figure 7.** Building Succinic Acid stage 3.

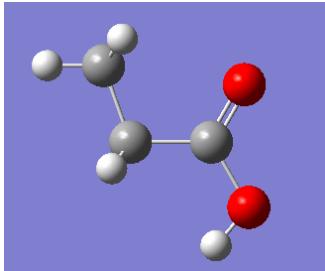
j. Return to the Periodic Table and select the carbon atom. Select the button for an  $sp^3$  carbon atom (tetrahedral carbon). Click on the carbon atom in the Fragment Window.

k. Move to the Molecule Window and click on the non-hydroxyl hydrogen atom (hydrogen atom bonded to the  $sp^2$  carbon). The fragment will look something like **Figure 8**:



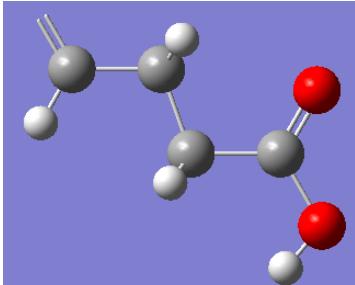
**Figure 8.** Building Succinic Acid stage 4.

**l.** Still in the Molecule Window, click on one of the hydrogen atoms bonded to the sp<sup>3</sup> carbon you just placed in the previous step. The fragment in the Molecule Window will now look something like **Figure 9**:



**Figure 9.** Building Succinic Acid stage 5.

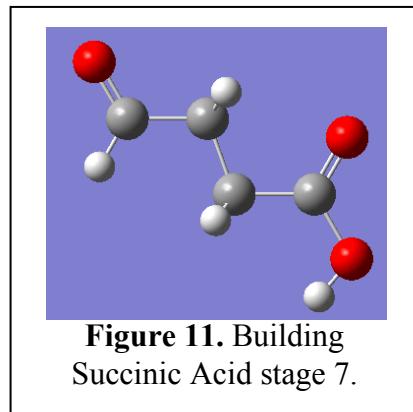
**m.** In the Periodic Table, select the sp<sup>2</sup> carbon by clicking on the appropriate button. Click on the central carbon atom of the fragment present in the Fragment window. Then, in the Molecule Window, click on one of the hydrogen atoms bonded to the second tetrahedral carbon you placed (the one you placed in the previous step). Your fragment in the Molecule Window should look something like **Figure 10**:



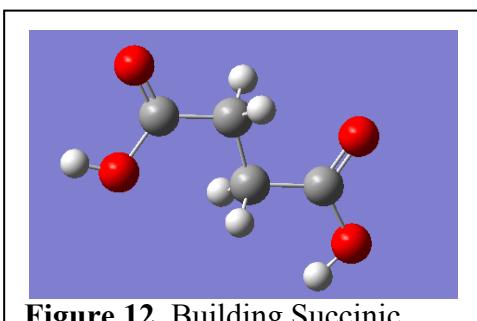
**Figure 10.** Building Succinic Acid stage 6.

**n.** Almost there.

**o.** In the Periodic Table, select the oxygen atom. Click on the button for the sp<sup>2</sup> oxygen in the bottom of that window. Click on the oxygen atom in the Fragment Window. Then go to the Molecule Window and click on the end of the double bond to the second sp<sup>2</sup> carbon you placed in the previous step. The fragment in your Molecule Window now looks something like **Figure 11**:



**p.** Finish by clicking the button for sp<sup>3</sup> oxygen in the Periodic Table. Click on the oxygen atom in the Fragment Window. Then go to the Molecule window and click on the hydrogen atom connected to the carbon atom you placed in step ‘m’. You should now have the full succinic acid molecule in the Molecule Window. Something like **Figure 12**:



### 3. Setting Up the Gaussian Calculation

Once your succinic acid molecule is built proceed to setting up the actual calculation.

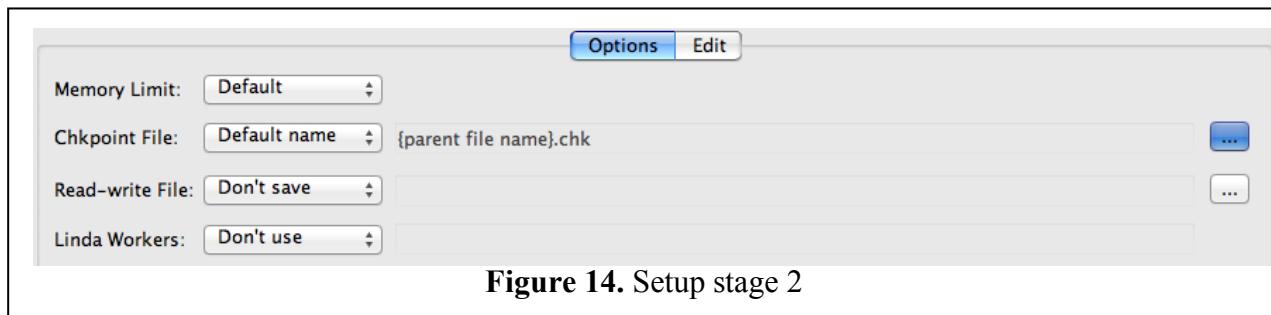
- a.** Click anywhere on the Periodic Table. At the very top of your window, you will see a tab titled ‘Calculate’; it is a pull-down menu. Click on this tab and select ‘Gaussian Calculation Setup’. Another window will pop up. There will be a series of tabs such as “Job Type”, “Method”, “Title”, etc. etc. The next steps will deal with parameters/options in a few of these tabs.
- b.** Click on the “Job Type” tab. Select “Energy” from the available choices in the box on the left. “Energy” should actually already be selected as default.
- c.** Click on the “Method” tab. Choose the appropriate options to match the appearance in **Figure 13**.

**Figure 13.** Setup stage 1.

You will have “Ground State”, “Compound”, “CBS-QB3” selected. The “Charge” will be “0” since we are dealing with neutral species in this lab. The “Spin” selection is very important. The succinic

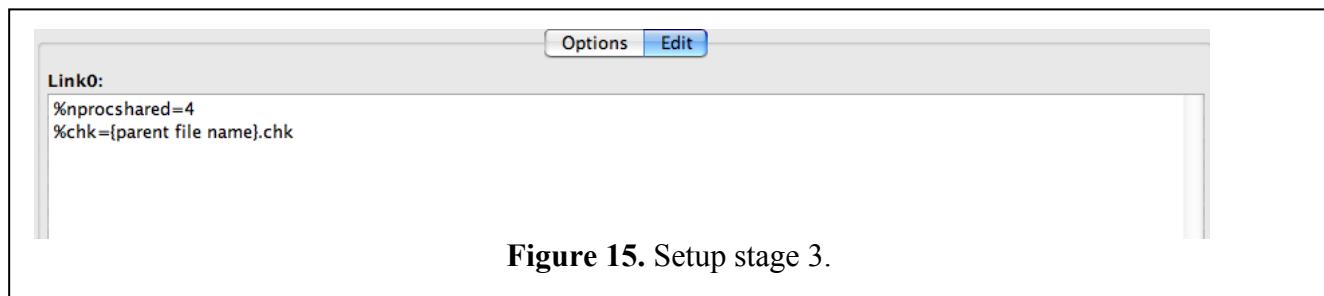
acid molecule and the atoms that make up the molecule are not all singlet (Spin = 1). Refer to Table 1 for the values of Spin Multiplicity to use for each species. Change the “Spin” selection to the appropriate value for the succinic acid MOLECULE. **BE CAREFUL and DO NOT FORGET THIS STEP!**

- d.** Click on the “Title” tab. Enter some text to represent your calculation. This can be something like: “Succinic Acid Molecule Calculation for Energy at 0K” (for the atoms, you will have another appropriate title).
- e.** Click on the “Link 0” tab after completing step 3d.
- f.** Click on the “Options” tab first. Make sure the settings appear as in **Figure 14**:



**Figure 14.** Setup stage 2

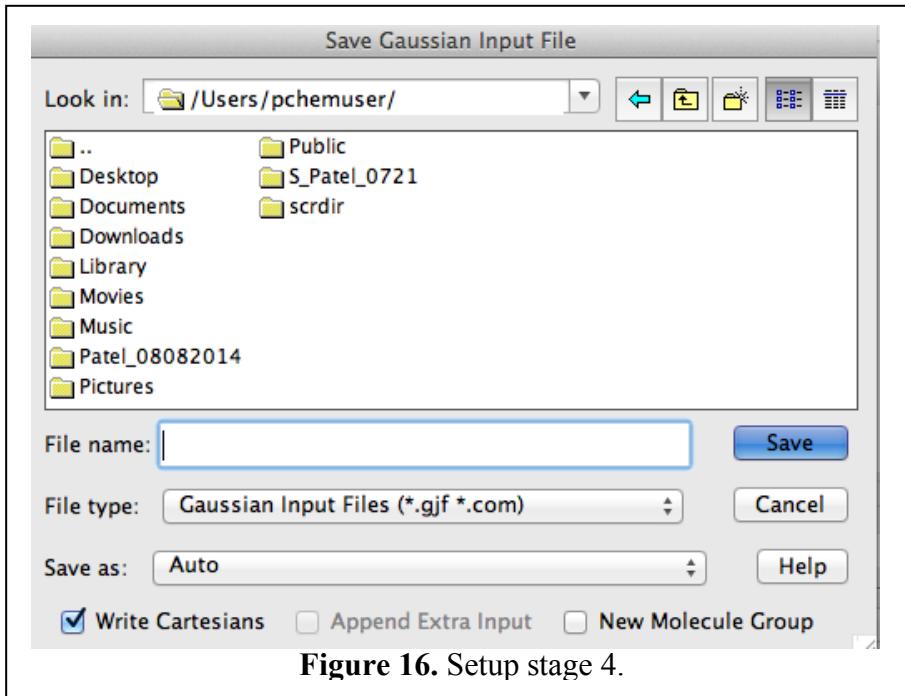
- g.** Click on the “Edit” tab next. Make sure the settings appear as follow (if they do not, then make the appropriate changes to match the following) in **Figure 15**:



**Figure 15.** Setup stage 3.

- h.** Click on the “Submit...” tab in the lower left of the window. You will be asked whether you want to save the file. Click “Yes”. You will then be asked to give a name and location (i.e. what is called a ‘path’) for the file that will contain the parameters and commands that you selected and requested in the previous steps in this section, ‘Setting Up the Gaussian Calculation’.
- i.** In the window with the label (top bar) “Save Gaussian Input File”, you will see a box with the text “Look in:” to its left (there will be a symbol of an open folder there). Delete the text already there and fill in: “/Users/pchemuser” and hit return key. Don’t include the quotation marks (“/Users/pchemuser”), just include what is inside the quotation marks.
- j.** To the right of the box in which you entered text in step 3i, there will be a button with a folder symbol **without an arrow**. Click on the button with the folder symbol without an arrow. You will see a new folder appear in the list of folders displayed in the window with the text “New Folder 1”.

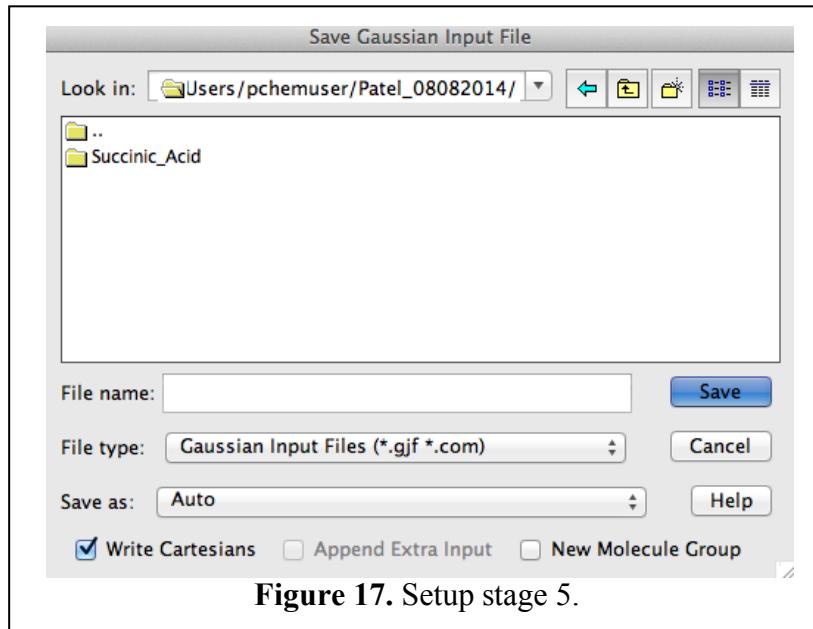
This area will be editable so you can name this new folder. Give it the name of something you will remember (i.e. “yourname\_date\_of\_lab”). In **Figure 16**, the new folder has been given the name “Patel\_08082014”.



To avoid confusion, **WRITE DOWN** the full name of this folder, which is:  
 /Users/pchemuser/yourname\_date\_of\_lab

In the example, the yourname\_date\_of\_lab = Patel\_08082014.

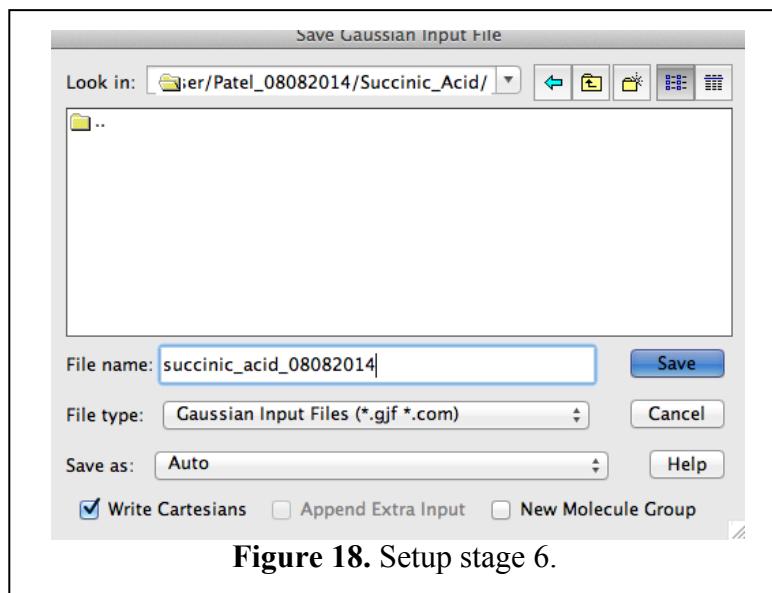
**k.** Next, click on the name of the folder you just created. Now you are in your folder. There are no files yet. Again, use the button at the top of this window to create a new folder. Name this folder “Succinic\_Acid” since we are setting up the calculation for this molecule currently. The completed setup should look like **Figure 17**:



The full name of this folder is: /Users/pchemuser/yourname\_date\_of\_lab/Succinic\_Acid  
**Write this name down.**

**l.** Click on the “Succinic\_Acid” folder to enter that folder.

**m.** The folder will be empty. Now, find the box with the text “File name:” to the left of it. In the box, enter the name of your choice to call the file that will hold the commands and parameters that Gaussian will use to perform the calculations. For succinic acid molecule, a good practical choice would be something like “succinic\_acid\_date\_of\_lab”. The “File Type” should be left as “Gaussian Input Files (\*.gjf \*.com)”. The box may look something like **Figure 18**:



The full name of the file will be:

/Users/pchemuser/yourname\_date\_of\_lab/Succinic\_Acid/succinic\_acid\_date\_of\_lab.com  
**Write this name down.**

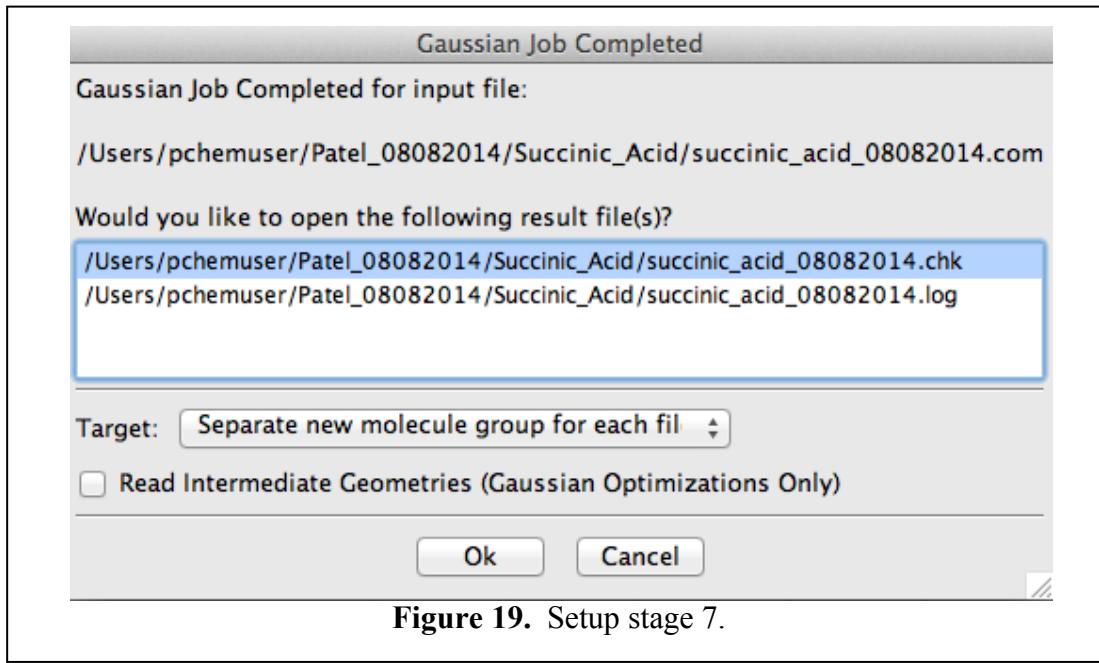
**n.** Hit the “Save” button. A pop-up box asking “Submit the following file to Gaussian?” will appear. Click “Ok” and the calculation will begin. The calculation should take about **40-50 minutes** if everything is set up correctly.

**o.** Perform the above steps for the **ATOMIC species. BE VERY CAREFUL WITH NAMING and SPIN MULTIPLICITIES. DISREGARD FOR THESE DETAILS WILL CAUSE SYSTEMATIC ERRORS (AND PERHAPS FAILURE OF CALCULATION TO PROCEED).**

**These calculations will take only a few minutes or less. They are quick.**

#### **4. Retrieving Necessary Data From Gaussian Calculation**

**a.** Following successful completion of your calculation, you will see a box pop-up (approximately 40-50 minutes or so after you start the calculation of the molecule) that looks something like **Figure 19**:



**Figure 19.** Setup stage 7.

Select the ‘Cancel’ button.

**b.** Click on the Periodic Table Window. Along the top of the screen, you will see the ‘Results’ menu. Click on the “Results” drop –down menu and select “View File”. This will open a file with the name:

**“/Users/pchemuser/yourname\_date\_of\_lab/Succinic\_Acid/succinic\_acid\_date\_of\_lab.log”**

Gaussian invokes another program called ‘TextEdit’ automatically to open this file.

Click anywhere in the window associated with the log file.

At the top of the screen, you will see a Menu item called “Edit”.

Click on the “Edit” menu and select “Find” → “Find” (yes, there are two “Find”’s)

In the box that appears, type “Zero-point correction” and hit the return key.

This will take you to a part of the log file that has the value of the Zero-Point Energy that you will need for **Equation 13**.

Write down this value that is in the units of **Hartrees** (**you will need to convert Hartrees to kJ/mol**).

**c.** Two lines below the zero-point correction data, you will see “Thermal correction to Enthalpy=”. This is the second result you will need for succinic acid. Write the value down. This is in units of **Hartrees**.

**d.** Go back to the top of the window and enter in the search text field “CBS-QB3 (0 K)”

Write down the number associated with this energy again in Hartrees. This is the Energy of the succinic acid molecule at 0K that will be used in **Equation 14** for the evaluation of  $-D_0$ .

**e.** Obtain the analogous results for the atomic species, C, H, O. These calculations will not take long.

Rounding errors can occur because you calculate differences in large numbers. Carry all digits that are given from the calculations to convert from Hartrees to kJ/mole. Use a ridiculous number of digits in the conversion: 1 Hartree = 2625.49962 kJ/mole. **Report values for the individual energies in a table in kJ/mole to a tenth of a kJ/mole: XXXX.X kJ/mole.** The experimental uncertainty in the value for the enthalpy of formation is a few kJ/mole.

To help in this process, set up Table 4 in your report to give the individual values that you calculated with Gaussian in kJ/mole, the other data that are given, and your results for  $-D_0$  and  $\Delta H_F$ {Succinic Acid, g, 298K}.

Hint: The Gaussian calculations give a value for the heat of formation (enthalpy) of **gaseous succinic acid** that is in reasonable agreement with the **NIST value for gaseous succinic acid**, calculated from the heat of formation of the solid and the heat of sublimation. If your results do not agree “reasonably well” with the NIST value check your calculations.

#### Reference:

- <sup>1</sup> Benson, S. W, *Thermochemical Kinetics*, 2<sup>nd</sup> Ed. John Wiley & Sons, New York, 1976  
Benson, S. W., and Buss, J. H., *J. Chem. Phys.* **29**, 546 (1958)

#### Learning Objectives:

Combustion calorimetry; thermochemistry;  $\Delta H$  vs.  $\Delta U$ ; basic Gaussian thermochemical calculations.

There are two data tables for Exp. 4 on Canvas as Excel spreadsheets – one for the experimental data from the combustion experiments and one for the Gaussian calculations. Download each table. Complete all required cells. NO CHANGES. Send these tables as Excel files to the lab instructor grading the experiment. No units in any cell. No additional analyses.

## Partial apparatus for Bomb Calorimetry

