Heat of Combustion and Heat of Formation

CHEM 445-025

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ABSTRACT

Using bomb calorimetry, the thermochemical properties of succinic acid were determined. The average constant volume heat capacity of the system was determined to be C_v^{ave} = 9.86 ± 0.08 kJ/°. Additionally, the average energy of combustion of the gelatin capsule, which was used to contain the succinic acid, was determined to be $\Delta U_{comb,\,cap}^{ave}$ = -18.88 ± 1.69 kJ/g. From there, both the average molar energy and enthalpy of combustion of solid succinic acid were found to be $\Delta U_{comb,\,acid}^{ave}$ = -1593 ± 587 kJ/mol and $\Delta H_{comb,\,acid}^{ave}$ = -1592 ± 587 kJ/mol, respectively. Consequently, the average molar enthalpy of formation of solid succinic acid was calculated to be $\Delta H_{form,\,acid,\,sol}^{ave}$ = -840 ± 587 kJ/mol. This previous value, along with the molar enthalpy of sublimation of the succinic acid found on NIST, was used to find the average molar enthalpy of formation of gaseous succinic acid $\Delta H_{form,\,acid,\,g}^{ave}$ = -720 ± 587 kJ/mol. Furthermore, the molar enthalpy of formation of gaseous succinic acid was also calculated using the Gaussian software package and was found to be -808.4 kJ/mol.

INTRODUCTION

The change in enthalpy of a reaction at constant pressure (ΔH_{rxn}) and the change in energy of a reaction at constant volume (ΔU_{rxn}) are two very important properties in thermodynamic reaction analysis[1]. If they are known, it is possible to calculate many other useful properties (entropy, Gibbs free energy, Helmholtz free energy[2], heat capacities, etc.) that can also be used to describe the thermodynamic system. Furthermore, it is easy to find the change in enthalpy and energy for any reaction with the following formulas $\Delta H_{rxn} = \sum_i v_i \overline{\Delta H_{form,i}}$ and $\Delta U_{rxn} = \sum_i v_i \overline{\Delta U_{form,i}}$ if the formation properties of the pure compounds are known. However, if they are not available, such values need to be determined experimentally, and that can be very complicated.

In this lab, a general procedure for organic compounds was followed to calculate the unknown thermochemical properties of succinic acid ($C_4H_6O_4$) experimentally using bomb calorimetry, heat and energy of combustion of the compound, and heat capacity of the system. To confirm the accuracy of the experiment, a computer software (Gaussian) was also used to predict the heat of formation of the acid based on its functional groups.

PROCEDURE

In order to perform any calculations to determine heat of formation of succinic acid, it was first necessary to determine the heat capacity of the system. In order to do that, a pellet of benzoic acid, wrapped in an iron fuse, was burned inside the bomb calorimeter. The weights of the wire and the pellet wrapped in the wire were measured prior to placing them in the bomb to calculate how much of the wire has burned. The ends of the wire were attached to the electrodes located in the bomb head, and the bomb was then assembled. Next, the bomb was filled with oxygen, to initiate a combustion reaction, until a pressure of 25 atm was reached. The bomb was then placed inside the calorimeter, and 2 liters of water were added inside the can. After the temperature was calibrated, the bomb was ignited and the change in temperature was observed and recorded. The experiment was repeated twice for reproducibility.

Next, the heat of combustion of the gelatin capsule had to be determined, because the succinic acid would be placed in the capsule later on to perform the experiment, and therefore its properties needed to be accounted for. The same steps were followed as with the benzoic acid pellet. The experiment was again repeated twice.

Finally, all the necessary information was obtained to perform the experiment on succinic acid. A small amount of the acid was crushed with a mortar and pestle, and 0.5 - 1 g was placed inside the gelatine capsule. The same procedure was followed as before, and the changes in mass and temperature were recorded.

Aside from collecting experimental data, theoretical calculations were also performed to provide a basis for comparison. In this lab, the Gaussian software package was used. A succinic acid molecule was first constructed, because the program used quantum mechanics and energies of individual atoms in order to compute the enthalpy of formation of a gaseous succinic acid. The Gaussian software provided all the necessary values to perform calculations for dissociation energy and the enthalpy of formation, details and results were presented in the **RESULTS AND DISCUSSION** section.

RESULTS AND DISCUSSION

Table 1. Heat Capacity of Calorimeter Data

Heat Capacity of Calorimeter				
	Wt_{BzA} (g)	**$Wt_{wire,\ burned}$ (g)**	**Temp Rise (°)**	**C_V (kJ/°)**
1	1.0504	0.0022	2.8024	9.91
2	1.0397	0.0086	2.8105	9.80
Average				9.86
Std. Dev.				0.08

Table 1 shows the collection of data involved in calculating the average heat capacity of the system (the calorimeter and all of its contents). To determine the heat capacity of said system, a pellet of benzoic acid was ignited via a wire and the temperature rise was recorded. By rearranging the following equation:

$$\Delta U_{total} = \Delta U_{Comb,\ Benzoic\ Acid} * m_{Benzoic\ Acid} + \Delta U_{Comb,Wire} * m_{Wire,\ Burned} = -C_v \Delta T \quad \text{(Eq. 1)}$$

$$C_v = -\frac{\Delta U_{total}}{\Delta T} = -\frac{\Delta U_{Comb,\ Benzoic\ Acid} * m_{Benzoic\ Acid} + \Delta U_{Comb,\ Wire} * m_{Wire,\ Burned}}{\Delta T} \quad \text{(Eq. 2)}$$

where $\Delta U_{Comb,\ Benzoic\ Acid} = -26.433\ kJ/g$

and $\Delta U_{Comb,\ Wire} = -5.86\ kJ/g$

Using Eq. 2, the heat capacity of each trial was calculated from which the average heat capacity of the system was determined to be 9.86 ± 0.08 kJ/°, which was consistent with the expected value of ≅10 kJ/°[3]. Furthermore, since the error accompanying this calculation was rather small, this shows the high degree of precision with which this part of the experiment was conducted. This value of the heat capacity was used in consequent calculations pertaining to the determination of the energy of combustion of the gelatin capsules and consequently that of the compound, succinic acid.

Table 2. Combustion of Gelatin Capsules

Combustion of gelatin capsules				
	Wt_{cap} (g)	**$Wt_{wire,\ burned}$ (g)**	**Temp Rise (°)**	**ΔU_{Comb} (kJ/g)**
1	0.1153	0.0052	0.2100	-17.68
2	0.1141	0.004	0.2348	-20.07
Average				-18.88
Std. Dev.				1.69

Table 2 shows the collection of data that was used to calculate the energy of combustion of the gelatine capsules, which were used to contain the succinic acid. To determine the energy of combustion, the following equation was rearranged and used:

$$\Delta U_{total} = \Delta U_{Comb,\ Gel} * m_{Gel,\ Burned} + \Delta U_{Comb,Wire} * m_{Wire,\ Burned} = -C_v \Delta T \quad \text{(Eq. 3)}$$

$$\Delta U_{Comb,\ Gel} = (-C_V * \Delta T - \Delta U_{Comb,\ Wire} * m_{Wire,\ Burned}) / m_{Gel,\ Burned} \quad \text{(Eq. 4)}$$

The average value for the heat of combustion of the gelatin capsules was calculated to be -18.88 ± 1.69 kJ/g. This value was a little over the expected range of -12 to -16 kJ/g[3]. This is most likely due to the errors made by students collecting the data; however, this result was not terribly off and was used in consequent calculations. Furthermore, the energy of combustion of the gelatin capsules was reported per gram of the capsule since the weight of each individual capsule may vary.

Table 3. Thermochemical Properties of Succinic Acid

Combustion of Succinic Acid									
	Wt_{cap} (g)	**$Wt_{wire,\ burned}$ (g)**	**Wt_{Succ} (g)**	**Temp Rise (°)**	**ΔU_{Comb} (kJ/g)**	**$\Delta \underline{U}_{Comb}$ (kJ/mol)**	**$\Delta \underline{H}_{Comb}$ (kJ/mol)**	**$\Delta \underline{H}_{Form,\ sol}$ (kJ/mol)**	**$\Delta \underline{H}_{Form,\ g}$ (kJ/mole)**
1	0.1127	0.0073	1.1008	1.3346	-9.98	-1178.12	-1176.88	-1254.65	-1134.65
2	0.1141	0.0107	0.8194	1.6390	-17.01	-2008.41	-2007.17	-424.36	-304.36
Average						-1593	-1592	-840	-720
Std. Dev.						587	587	587	587
R.S.D.*						-37	-37	-70	-82

*Relative Standard Deviation

Table 3 shows the thermochemical properties of succinic acid obtained from experimental data and a consequent series of calculations. These values were reported using the

standard deviation as a measure of the uncertainty. Additionally, the relative standard deviations were calculated as the standard deviations incurred in these measurements were relatively large.

To calculate the energy of combustion of the succinic acid, the following equation was rearranged and used:

$$\Delta U_{total} = \Delta U_{Comb,\,Sample} * m_{Sample} + \Delta U_{Comb,\,Gel} * m_{Gel,\,Burned} + \Delta U_{Comb,\,Wire} * m_{Wire,\,Burned} = -C_v \Delta T \quad \text{(Eq. 5)}$$

$$\Delta U_{Comb,\,Sample} = (-C_V * \Delta T - \Delta U_{Comb,\,Gel} * m_{Gel,\,Burned} - \Delta U_{Comb,\,Wire} * m_{Wire,\,Burned}) / m_{Sample} \quad \text{(Eq. 6)}$$

The value obtained from the above equation is in units of kJ/g; therefore, to obtain the molar energy of combustion this value had to be multiplied by the molar mass of succinic acid (M = 118.09 $\frac{g}{mol}$ [4]). In other words,

$$\Delta \underline{U}_{Comb} = 118.09 \frac{g}{mol} * \Delta U_{Comb} \quad \text{(Eq. 7)}$$

From the molar energy of combustion, the heat (or enthalpy) of combustion can be obtained by utilizing the definition of enthalpy:

$$\Delta H = \Delta U + RT\Delta n_{gas} \quad \text{(Eq. 8)}$$

where R is the universal gas constant R = 0.008314 kJ/mol*K

$$\text{and } \Delta n_{gas} = n_{products,\,gas} - n_{reactants,\,gas} \quad \text{(Eq. 9)}$$

Eq. 8 was written in extensive form. Therefore, the stoichiometry of the chemical reaction had to be taken into account:

$$C_4H_6O_{4(s)} + \tfrac{7}{2}O_{2(g)} \rightarrow 4CO_{2(g)} + 3H_2O_{(l)} \quad \text{(Eq. 9)}$$

From equation 9, it can be seen that the stoichiometry of the succinic acid is $\nu = 1$. Therefore, the value for the molar energy of combustion, for each trial, had to be multiplied by 1. From there, the temperature and Δn_{gas} were the remaining two variables that had to be determined. Since the

experiment was run at near room temperature conditions, T was taken to be 298 K. Furthermore, using Eq. 9, the change in the number of gaseous moles was obtained as follows:

$$\Delta n_{gas} = n_{products,\,gas} - n_{reactants,\,gas} = n_{CO_2} - n_{O_2} = 4 - \tfrac{7}{2} = \tfrac{1}{2}$$

Plugging all the values into Eq. 8, the enthalpy of combustion was obtained for each trial. Additionally, since the previous calculations were done assuming one mole of succinic acid, the molar heat of combustion can be obtained by dividing by the stoichiometry of succinic acid (ν = 1). Looking at the values in Table 3, it can be seen that there is a large degree of uncertainty in the measurements. Namely, the two values obtained from the two respective trials do not agree with one another. This may be due to errors on the students' part (i.e. lack of precision). To gain a better understanding of this high degree of inaccuracy, the values obtained were compared to the literature value of the molar heat of combustion of succinic acid. In the NIST database, this value was found to be $\Delta H_{comb,\,acid,\,sol}$ = -1491 ± 3 kJ/mol[5]. Comparing this value to the average, -1592 ± 587 kJ/mol, it is apparent that the numbers are off by 100 kJ/mol and therefore, rather different. This finding is further emphasized by the large value of standard deviation accompanying the calculation of the average. Another observation to note is that the average molar energy of combustion is almost equal to the average molar enthalpy of combustion. This means that the correction term ($RT\Delta n_{gas}$) is negligible.

From the molar enthalpy of combustion, the enthalpy of formation of solid succinic acid can be obtained (and consequently the enthalpy of formation in the gas phase). Rearranging the following equation,

$$\Delta H_{comb,\,acid} = 4 * \Delta H_{form,\,CO_2} + 3 * \Delta H_{form,H_2O} - \Delta H_{form,\,acid,\,solid} \quad \text{(Eq. 10)}$$

the molar enthalpy of formation of solid succinic acid can be obtained. Since oxygen was at its standard state, its enthalpy of formation was zero. Additionally, the heats of formation of both carbon dioxide and water were obtained from the NIST webbook and recorded as follows:

$$\Delta H_{form,H_2O} = -285.83 \ \tfrac{kJ}{mol}$$ [6]

$$\Delta H_{form,\,CO_2} = -393.51 \ \tfrac{kJ}{mol}$$ [7]

Plugging all the given values into Eq. 10, the molar enthalpy of formation was obtained for each of the two trials and tabulated in Table 3. Once again, looking at results, it is apparent that there is a high degree of inaccuracy which very likely carried over from the previous calculations. Nonetheless, the average value was calculated and determined to be -840. ± 587 kJ/mol. Comparing this value with that obtained from the NIST webbook, -940. ± 2 kJ/mol[5], it is clear that the two values are different by 100 kJ/mol (again), which is a sign of inaccuracy but also of consistency in the calculations.

Lastly, to obtain the molar heat of formation of gaseous succinic acid, the molar heat of sublimation (obtained from NIST)[5] was used. This is dictated in the following set of equations:

$$C_4H_6O_{4(s)} \rightarrow C_4H_6O_{4(g)} \quad \text{(Eq. 11)}$$

$$\Delta H_{subl,\,acid} = \Delta H_{form,\,acid,\,gas} - \Delta H_{form,\,acid,\,solid} \quad \text{(Eq. 12)}$$

$$\Delta H_{form,\,acid,gas} = \Delta H_{subl,\,acid} + \Delta H_{form,\,acid,\,solid} \quad \text{(Eq. 13)}$$

Since the molar enthalpy of formation of the solid was already obtained and additionally, the molar enthalpy of sublimation is known ($\Delta H_{subl,\,acid} = 120 \pm 4$ kJ/mol), the molar enthalpy in the gas phase was easily calculated and tabulated in Table 3. Once again, there is a high degree of spread in the calculated values; nevertheless, the average was calculated and determined to be -720 ± 587 kJ/mol)**.**

Table 4. Determination of Thermochemical Properties via Gaussian Calculations

	kJ/mole
$\mathbf{E_{Succinic\ Acid,\ g}}$	-1198097.3
$\mathbf{E_{C,\ g}}$	-99203.3
$\mathbf{E_{H,\ g}}$	-1312.2
$\mathbf{E_{O,\ g}}$	-196875.5
$\mathbf{-Do_{Succinic\ Acid}}$	-5908.6
Succinic Acid Zero Point Energy	276.4
Succinic Acid Thermal Correction	298.8
Enthalpy of Formation of Succinic Acid, g	-808.4

The values in Table 4 were determined using the Gaussian software package which utilizes quantum mechanics to obtain information about the wave functions of molecular and

atomic orbitals. This software package was specifically used to calculate the molar enthalpy of formation of gaseous succinic acid. The chemical equation for such reaction is stated as follows:

$$4C(sol,\ 298K)\ +\ 2O_2\ (g,\ 298K)\ +\ 3H_2(g,\ 298K) \rightarrow C_4H_6O_4\ (g,\ 298K) \quad \text{(Eq. 14)}$$

Since enthalpy is a state function, it allowed for the calculation of $\Delta\underline{H}_{Form,g}$ of succinic acid in four distinct steps:

1. Change of the thermal state of each species from 298 K to 0 K at standard pressure.
2. Dissociation of each element in its standard state to its atomic counterpart at 0 K.
3. Formation of gaseous succinic acid from its gaseous atoms, denoted by D_0 and correction for vibrational energy in the ground state at 0 K, denoted by ZPE
4. Change of the thermal state of each species from 0 K to 298 K at standard pressure.

The above steps are summarized in the following equation:

$$\begin{aligned}\Delta H_f^o\{C_4H_6O_4,g,298K\} = {} & \{4[H^o(C,s,0K)–H^o(C,s,\ 298K)] + 3[H^o(H_2,g,0K)–H^o(H_2,g,298K)] + 2[H^o(O_2,g,0K)–H^o(O_2,g,298K)]\} \\ & + \{4\Delta H_f^o\{C,g,0K\} + 6\Delta H_f^o\{H,g,0K\} + 4\Delta H_f^o\{O,g,0K\}\} + \{–D_0\{C_4H_6O_4,g) - ZPE\{C_4H_6O_4,g\}\} \\ & + [H^o(C_4H_6O_4,\ 298\ K)–H^o(C_4H_6O_4,0K)] \end{aligned} \quad \text{(Eq. 14)}$$

However, since the Gaussian software only computes the energies of *gaseous* species, some values had to be obtained from other resources. Nonetheless, all the values acquired from running a Gaussian calculation were presented in Table 4. The resulting $\Delta\underline{H}_{Form,g}$ was -808.4 kJ/mol which was very close to the expected value of -817.77 kJ/mol[8]. Furthermore, this shows the level of inaccuracy and imprecision with which trials 1 and 2 were conducted as neither of the two values found were close to that obtained using the software.

CONCLUSIONS

As can be seen from the experimental data collected in this lab, the parts pertaining to the individual combustion of the benzoic acid and the gel capsule produced exceptional results that fell within the ballpark range specified by the lab manual. As for the combustion of succinic acid, it was apparent from the values presented in Table 3, that there was a significant error in the execution of this part of the lab. The results of the two trials greatly differed from each other, yielding a large, unacceptable standard deviation. However, the average values of two thermochemical properties (i.e. the molar enthalpies of combustion and formation) were rather similar to the tabulated values in NIST. Still, the standard deviation was large, nullifying the degree of closeness that those average values exhibited. In other words, there is a high level of systematic error incurred in these results. This error stems from the fact that only two trials were conducted. Therefore, a solution to this problem could be to run more trials such that the student becomes more acquainted with the procedure and has the option to discard outliers.

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