Heat of Combustion and Heat of Formation

CHEM 445 - 025L

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ABSTRACT

Using the specific internal energy of benzoic acid and iron wire (- 26.433 $\frac{kJ}{g}$ and -5.86 $\frac{kJ}{g}$ respectively), two measurements for the heat capacity of the calorimeter system were measured, where the average heat capacity, C_V was determined to be $10.84 \pm 1.55 \frac{kJ}{°}$. Using C_V, the specific internal energy of the gelatin capsule was determined to be $-19.37 \pm 0.74 \frac{kJ}{g}$. The average $\overline{\Delta U_{acid}}$ of succinic acid, determined from C_V, temperature change data, and correcting for the wire and capsule contributions, was $-1672.96 \pm 46.53 \frac{kJ}{mol}$ (2.78 % RSD). From that value, the average $\overline{\Delta_c H_{acid}}$ of succinic acid was determined to be $-1671.72 \pm 46.53 \frac{kJ}{mol}$ (2.78 % RSD). This value was significantly different than the reference data value of $-1492.5 \pm 0.4 \frac{kJ}{mol}$. Other than that, the average $\overline{\Delta_f H_{acid,\,s}}$ of solid succinic acid was determined to be $-759.85 \pm 46.53 \frac{kJ}{mol}$ (6.12 % RSD). This value was significantly different than the reference data value of $-940.0 \pm 2.0 \frac{kJ}{mol}$. Moreover, the average $\overline{\Delta_f H_{acid,\,g}}$ of gaseous succinic acid was determined to be $-639.85 \pm 46.53 \frac{kJ}{mol}$ (7.27 % RSD) experimentally, and $-806.8 \frac{kJ}{mol}$ from Gaussian (estimated at 298K), in which the experimental value was significantly different than the reference data of $817.77 \pm 0.61 \frac{kJ}{mol}$, yet it was in agreement with that of Gaussian.

INTRODUCTION

The heat of formation, $\overline{\Delta_f H}$ of gaseous succinic acid could be determined using bomb calorimetry and comparing the value obtained experimentally to theoretical values determined from Gaussian. Gaussian is a computer software package designed to estimate the chemical systems based on quantum mechanical algorithms. This software is used to model a molecule of succinic acid, and its formation reaction. Through this model we were able to retrieve an estimate for $\overline{\Delta_f H}_{acid, g}$ of gaseous succinic acid, which was compared to the experimentally determined value.

To calculate the $\overline{\Delta_f H}_{acid, g}$ of gaseous succinic acid, a bomb calorimetry experiment was conducted. Due to the calorimeter being nearly adiabatic, any temperature change of the system had to be attributed to the combustion reaction occurring inside the calorimeter. The temperature change values at the initial and final points of the reaction, combined with the heat capacity of the calorimeter system, were enough to determine the $\Delta \widehat{U}_{Comb, acid}$ of solid succinic acid.

An integral step in determining the $\Delta \widehat{U}_{Comb, acid}$ of solid succinic acid was finding the C_V, or heat capacity of the calorimeter system. The C_V was found for a standard compound with a known $\Delta \widehat{U}_{Comb}$ value, in this case benzoic acid. Since the benzoic acid and its products had negligible contributions to the heat capacity of the system, it could be assumed that the C_V of the calorimeter system was constant regardless of the compound being analyzed. The constant value of C_V computed for the calorimeter system was used in determining $\Delta \widehat{U}_{Comb, acid}$ of solid succinic acid.

Using $\Delta \widehat{U}_{Comb, acid}$ of solid succinic acid it was easy to derive $\overline{\Delta_c H}_{acid}$ for solid succinic acid, the $\overline{\Delta_f H}_{acid, s}$ for solid succinic acid, and $\overline{\Delta_f H}_{acid, g}$ of gaseous succinic acid using reference data for the $\overline{\Delta_f H}$ for CO_2 (g) and H_2O (l), and $\overline{\Delta H}_{subl, acid}$ of solid succinic acid. The final value for the $\overline{\Delta_f H}_{acid, g}$ of gaseous succinic acid was then compared to a theoretical value determined using Gaussian.

RESULTS AND DISCUSSION

Table 1: Heat Capacity of The System

Trial	$^1 W_A$ (g)	$^2 W_B$ (g)	$^3 \Delta T$ (∘)	$^4 \Delta U_{Total}$ (kJ)	$^5 C_V$ ($\frac{kJ}{∘}$)
1	1.0321	0.0038	2.8043	-27.304	9.74
2	1.0247	0.0017	2.2704	-27.096	11.93
				Average	**10.84**
				^{6}S.D.	**1.55**

^{1} Weight of benzoic acid ^{2} Weight of burnt wire
^{3} Temperature rise ^{4} Change in total internal energy
^{5} Heat capacity constant volume ^{6} Standard deviation

$$\Delta U_{Total} = \Delta \widehat{U}_{Comb,\,Benzoic\,acid} \times W_A + \Delta \widehat{U}_{Comb,\,Wire} \times W_B \text{ (Eq. 1)}$$

$$C_V = \frac{-\Delta U_{Total}}{\Delta T} \text{ (Eq. 2)}$$

$$^{[1]} \text{ where } \Delta \widehat{U}_{Comb,\,Benzoic\,acid} = -26.433 \tfrac{kJ}{g}, \Delta \widehat{U}_{Comb,\,Wire} = -5.86 \tfrac{kJ}{g}$$

The calculated value of ΔU_{Total} and C_V for each trial were tabulated in Table 1 as shown above. ΔU_{Total} and C_V were calculated by using Eq. 1 and 2 as listed above. The average C_V was obtained to be 10.84 ± 1.55 $\frac{kJ}{∘}$, which fell within the expectation of ~10 $\frac{kJ}{∘}$ [1]. It could be seen that the standard deviation was very significant with respect to the computed value itself, which might have a considerable impact in other calculations, as C_V was used in most of them.

Table 2: Combustion of Gelatin Capsules

Trial	$^1 W_C$ (g)	$^2 W_B$ (g)	$^3 \Delta T$ (∘)	$^5 \Delta \widehat{U}_{Comb,\,Gel}$ ($\frac{kJ}{g}$)
1	0.1182	0.0064	0.2091	-18.85
2	0.1192	0.0074	0.2229	-19.90
			Average	**-19.37**
			^{4}S.D.	**0.74**

^{1} Weight of gelatin capsules ^{2} Weight of burnt wire
^{3} Temperature rise ^{4} Standard deviation
^{3} Specific internal energy change in combustion of gelatin capsules

$$\Delta \widehat{U}_{Comb,\,Gel} = \frac{-C_V \times \Delta T - \Delta \widehat{U}_{Comb,\,Wire} \times W_B}{W_C} \text{ (Eq. 3)}$$

By referring to Table 2, $\Delta\widehat{U}_{Comb,\,Gel}$ for each trial were computed by using Eq. 3. The average of C_V was used in this calculation, as shown in Table 1. The average of $\Delta\widehat{U}_{Comb,\,Gel}$ was $-19.37 \pm 0.74 \frac{kJ}{g}$. Theoretically, the heat of combustion of gelatin capsule should be within the range of -12 and $-16 \frac{kJ}{g}$ [1]. The computed value was not within the expected range due to the significance in error in C_V, which caused this snowball effect in calculation. However, at the surface, it wasn't really far off from the expected range, although it could not be said that it had an agreement with the given range.

Table 3: Thermochemical Data of Succinic Acid

Trial	[1]W_C (g)	[2]W_B (g)	[3]W_D (g)	[4]ΔT ($\circ$)	[7]$\Delta\widehat{U}_{Comb,\,acid}$ ($\frac{kJ}{g}$)	[8]$\overline{\Delta U_{acid}}$ ($\frac{kJ}{mol}$)	[9]$\overline{\Delta_c H_{acid}}$ ($\frac{kJ}{mol}$)	[10]$\overline{\Delta_f H_{acid,\,s}}$ ($\frac{kJ}{mol}$)	[11]$\overline{\Delta_f H_{acid,\,g}}$ ($\frac{kJ}{mol}$)
1	0.1196	0.0064	0.7417	1.1680	-13.89	-1640.06	-1638.82	-792.75	-672.75
2	0.1185	0.0009	0.7339	1.1908	-14.45	-1705.85	-1704.61	-726.96	-606.96
					Average	**-1672.96**	**-1671.72**	**-759.85**	**-639.85**
					[5]**S.D.**	**46.53**	**46.53**	**46.53**	**46.53**
					[6]**R.S.D. (%)**	**2.78**	**2.78**	**6.12**	**7.27**

[1] Weight of capsules   [2] Weight of burnt wire   [3] Weight of succinic acid
[4] Temperature Rise   [5] Standard Deviation   [6] Relative Standard Deviation
[7] Specific internal energy of combustion of succinic acid
[8] Molar internal energy of combustion of succinic acid
[9] Molar enthalpy of combustion of succinic acid
[10] Molar enthalpy of formation of solid succinic acid
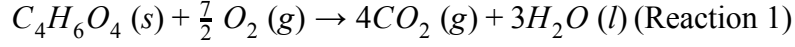[11] Molar enthalpy of formation of gaseous succinic acid

$$\Delta\widehat{U}_{Comb,\,acid} = \frac{-C_V \times \Delta T - \Delta\widehat{U}_{Comb,\,Wire} \times W_B - \Delta\widehat{U}_{Comb,\,Gel} \times W_C}{W_D} \text{ (Eq. 4)}$$

$$\overline{\Delta U_{acid}} = \Delta\widehat{U}_{Comb,\,acid} \times 118.088 \frac{g}{mol} \text{ [2] (Eq. 5)}$$

The data tabulated in both Table 1 and 2 were used to generate the results tabulated in Table 3 above, where it showed the thermochemical data of succinic acid. $\Delta\widehat{U}_{Comb,\,acid}$ was computed by using Eq. 4. By using Eq. 5, $\overline{\Delta U_{acid}}$ was computed by using the molar mass of succinic acid, and the average was $-1672.96 \pm 46.53 \frac{kJ}{mol}$, with an RSD of 2.78 %.

$$\overline{\Delta_c H_{acid}} = \overline{\Delta U_{acid}} + RT\Delta n_{gas} \text{ (Eq. 6)}$$

$$\Delta n_{gas} = n_{products,\,gas} - n_{reactants,\,gas} \text{ (Eq. 7)}$$

$$C_4H_6O_4 \; (s) + \tfrac{7}{2} \, O_2 \; (g) \rightarrow 4CO_2 \; (g) + 3H_2O \; (l) \; \text{(Reaction 1)}$$

The balanced reaction shown in Reaction 1 was the combustion reaction of succinic acid, assuming complete combustion had occurred. By using the stoichiometry of the reaction, $\overline{\Delta_c H_{acid}}$ could be calculated by using the relationship shown in Eq. 6. The correction term, Δn_{gas}, in Eq. 6 could not be ignored since the reactions that occurred involved gases, where it was assumed to be ideal in an isothermal reaction. Δn_{gas} was found by using Eq. 7, which was equal to $\tfrac{1}{2}$. The average of $\overline{\Delta_c H_{acid}}$ was $-1671.72 \pm 46.53 \, \frac{kJ}{mol}$, with an RSD of 2.78 %. In literature, $\overline{\Delta_c H_{acid}}$ is equal to $-1492.5 \pm 0.4 \, \frac{kJ}{mol}$ [3]. The calculated data was greater than the literature value in absolute value by a great significance that it could not be said to be in agreement with each other. The error itself was relatively large in comparison to that of the literature, which impacted the overall value of $\overline{\Delta_c H_{acid}}$. This was likely due to the value used for the heat capacity of the system, as our heat capacity was high, which would cause the $\Delta_c H_{acid}$ to be more negative than the reference data.

$$\overline{\Delta_c H_{acid}} = \sum_i^c \left(v_i \Delta_f H_i \right), v_{i, \, products} > 0, \; v_{i, \, reactants} < 0 \; \text{(Eq. 8)}$$

$$\overline{\Delta_f H_{acid, \, s}} = 4 \times \overline{\Delta_f H_{CO_2}} + 3 \times \overline{\Delta_f H_{H_2O}} - \tfrac{7}{2} \times \overline{\Delta_f H_{O_2}} - \overline{\Delta_c H_{acid}} \; \text{(Eq. 9)}$$

where $\overline{\Delta_f H_{H_2O, \, l}} = -285.83 \, \frac{kJ}{mol}$ [4], $\overline{\Delta_f H_{CO_2, \, g}} = -393.52 \, \frac{kJ}{mol}$ [5], $\overline{\Delta_f H_{O_2, \, g}} = 0 \, \frac{kJ}{mol}$ [6]

From Reaction 1, $\overline{\Delta_f H_{acid, \, s}}$ could be computed by using Eq. 8, where it could be expanded and rearranged to form Eq. 9. It was obtained that the average of $\overline{\Delta_f H_{acid, \, s}}$ equals to $-759.85 \pm 46.53 \, \frac{kJ}{mol}$, with an RSD of 6.12 %. In contrast to the literature value, where $\overline{\Delta_f H_{acid, \, s}}$ is found to be $-940.0 \pm 2.0 \, \frac{kJ}{mol}$ [7], the absolute value of calculated $\overline{\Delta_f H_{acid, \, s}}$ was found to be lower than that of the literature value. As previously mentioned, the error made in an early calculation was already large, that it immensely contributed to greater uncertainty in calculation of $\overline{\Delta_f H_{acid, \, s}}$, causing this large deviation in value from the literature value. It could be seen that they were within each other's proximity, in which the difference was not by ~ 1000's $\frac{kJ}{mol}$, but the significance in difference confirmed that they still did not agree with each other.

The uncertainty in $\overline{\Delta_f H_{acid, \, s}}$ was the same as that of $\overline{\Delta_c H_{acid}}$, due to the assumption made in ignoring the error in $\overline{\Delta_f H_{H_2O, \, l}}$ and $\overline{\Delta_f H_{CO_2, \, g}}$. The literature value obtained online on $\overline{\Delta_f H_{acid, \, s}}$ was at standard room temperature and pressure, where it might pose a relevant reason in such large deviation between it and the experimental data. However, since $\overline{\Delta_c H_{acid}}$ and $\overline{\Delta_f H_{acid, \, s}}$ only vary slightly with temperature, where the combustion reaction might happen at room temperature, any temperature correction on these data could be neglected.

$$C_4H_6O_4 \ (s) \rightarrow C_4H_6O_4 \ (g) \ \text{(Reaction 2)}$$
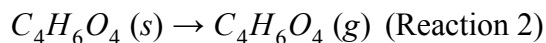
$$\overline{\Delta_f H_{acid,\,g}} = \overline{\Delta H_{subl,\,acid}} + \overline{\Delta_f H_{acid,\,s}} \ \text{(Eq. 10)}$$

The sublimation of succinic acid, from its solid to gas phase, was as shown in Reaction 2. It was obtained online that $\overline{\Delta H_{subl,\,acid}}$ is equal to $120 \pm 4 \ \frac{kJ}{mol}$ [8]. From Eq. 8, a similar equation could be obtained for $\overline{\Delta H_{subl,\,acid}}$. With some rearrangement, one could obtain Eq. 10 as shown below. $\overline{\Delta_f H_{acid,\,g}}$ was computed to be $-639.85 \pm 46.53 \ \frac{kJ}{mol}$, with an RSD of 7.27 %.

Table 4: Thermochemical Data of Succinic Acid by Gaussian Calculations

Data	Values ($\frac{kJ}{mol}$)
E{ $C_4H_6O_4$, g, 0 K}	-1 198 125.0
E{C, g, 0 K}	-99 205.5
E{H, g, 0 K}	-1 312.3
E{O, g, 0 K}	-196 880.0
[1]-D_o{ $C_4H_6O_4$ }	-5 909.2
[2]ZPE{ $C_4H_6O_4$ }	277.2
Thermal Correction{ $C_4H_6O_4$ }	301.8
[3] $\Delta \overline{H_f^{\circ}}${$C, g, 0 \ K$}	710.4
[3] $\Delta \overline{H_f^{\circ}}${$H, g, 0 \ K$}	216.0
[3] $\Delta \overline{H_f^{\circ}}${$O, g, 0 \ K$}	246.8
[4] $\Delta \overline{H^{\circ}}${$C, s, 298 - 0 \ K$}	1.05
[4] $\Delta \overline{H^{\circ}}${$H_2, g, 298 - 0 \ K$}	8.46
[4] $\Delta \overline{H^{\circ}}${$O_2, g, 298 - 0 \ K$}	8.70
[3] $\Delta \overline{H_f^{\circ}}${$C_4H_6O_4, g, 298 \ K$}	**-806.8**

[1] Dissociation energy of succinic acid
[2] Zero point energy of succinic acid
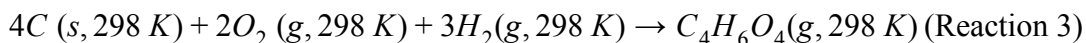[3] Molar enthalpy of formation of species i at T K
[4] Constant pressure molar enthalpy of cooling of species i at standard states

$$-D_0\{C_4H_6O_4, g, 0\,K\} = E\{C_4H_6O_4, g, 0\,K\} - 4E\{C, g, 0\,K\} - 6E\{H, g, 0\,K\} - 4E\{O, g, 0\,K\} \quad \text{(Eq. 11)}$$

$$\Delta H°\{i, s/g, 298 - 0\,K\} = -[H°\{i, s/g, 0K\} - H°\{i, s/g, 298K\}] \quad \text{(Eq. 12)}$$

$$Thermal\ Correction\{C_4H_6O_4\} = H°\{C_4H_6O_4, 298K\} - H°\{C_4H_6O_4, 0K\} \quad \text{(Eq. 13)}$$

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

$$4C\,(s, 298\,K) + 2O_2\,(g, 298\,K) + 3H_2(g, 298\,K) \rightarrow C_4H_6O_4(g, 298\,K)\,\text{(Reaction 3)}$$

$$4C\,(g, 0\,K) + 4O\,(g, 0\,K) + 6H(g, 0\,K) \rightarrow C_4H_6O_4(g, 0\,K)\ \text{(Reaction 4)}$$

To estimate $\Delta \overline{H_f°}\{C_4H_6O_4, g, 298\,K\}$, Gaussian software was used. The software utilized the contribution of individual elements in succinic acid to estimate its heat of formation. The reaction of interest was as shown in Reaction 3. However, Gaussian only took into account the energies of individual atoms in gaseous state to form the constituted compound at 0 K, as shown in Reaction 4. Its reverse reaction absorbed dissociation energy, D_0, where its forward reaction, $-D_0$ could be calculated by using Eq. 11. The energies needed in Eq. 11 were generated from Gaussian, as tabulated in Table 4.

Since enthalpy is a state function, it could be done in many other ways, as long as the reaction of interest could be computed at the end. In order to calculate $\Delta \overline{H_f°}\{C_4H_6O_4, g, 298\,K\}$, it could be done in 4 distinct steps, as listed below.

1. Thermal correction of the elements in their standard states at constant pressure from 298 K to 0 K, as shown in Eq. 12
2. Dissociation of elements in their standard states to their constituent atoms at 0 K
3. Formation of gaseous succinic acid from its gaseous atoms and correction for vibrational energy at ground state at 0 K, denoted as $-D_0$ and ZPE respectively
4. Thermal correction of gaseous succinic acid from 0 K to 298 K, from Eq. 13

By adding up all the energies from these 4 steps, $\Delta \overline{H_f°}\{C_4H_6O_4, g, 298\,K\}$ could be computed, as shown in Eq. 14, resulting in value of -806.8 $\frac{kJ}{mol}$, as tabulated in Table 4. It was found in literature that $\Delta H_f°\{C_4H_6O_4, g, 298\,K\}$ equals to -817.77 ± 0.61 $\frac{kJ}{mol}$ [9], while it was experimentally obtained to be -639.85 ± 46.53 $\frac{kJ}{mol}$. The Gaussian's value was in agreement with the literature's, which was expected, but it was greater in absolute value than experimental value. They were far off from each other due to the same reason mentioned earlier, where this large uncertainty was carried in the calculation from the beginning, resulting in larger deviations.

CONCLUSION

The experimental values obtained for the $\overline{\Delta_c H_{acid}}$ for solid succinic acid and $\overline{\Delta_f H_{acid,g}}$ of gas succinic acid were both significantly different from their literature counterparts. $\Delta_c H_{acid}$ for solid succinic acid was more negative than the reference values, $\overline{\Delta_f H_{acid,s}}$ of solid succinic acid was more positive than the reference value, and $\overline{\Delta_f H_{acid,g}}$ of gaseous succinic acid was significantly different from the theoretical estimate calculated using Gaussian. These results indicate that in our experiment succinic acid released more energy upon combustion and released less energy upon formation than in reality. The large difference between our experimentally determined values and literature values is likely attributed to our poor initial estimate of the heat capacity of the system. C_V was used in nearly all calculations in this experiment, and thus its accuracy had a large potential impact on all results obtained in this experiment. Our experimentally determined C_V varied by nearly 2.5 $\frac{kJ}{°}$ between our first and second trial run, leading to large inaccuracies later in the report. A good inference about our heat capacity estimate is that our estimate for heat capacity was greater than in reality. The major consequence of this was that any temperature difference measured in the calorimeter corresponded to a greater energy difference than reality; for each degree K that our system increased, a larger amount of energy was theoretically required. Since we were calculating the $\Delta_c H_{acid}$ for solid succinic acid based on temperature differences, it makes sense that our estimate for $\Delta_c H_{acid}$ was more negative than the reference value if the C_V of our system was overestimated. The effects of this then propagated to the $\Delta_f H_{acid,s}$ of solid succinic acid being too positive due to the equation used to determine $\Delta_f H_{acid,s}$.

REFERENCES

[1] Cruz, Frederico. Heat of Combustion and Heat of Formation; Lab Manual, 2018.

[2] Butanedioic acid. https://webbook.nist.gov/cgi/cbook.cgi?ID=110-15-6 (accessed May 2, 2020).

[3] Enthalpy of Combustion - Butanedioic acid. https://webbook.nist.gov/cgi/cbook.cgi?ID=C110156&Type=HCOMBS#ref-1 (accessed May 2, 2020).

[4] Heat of Formation - Water. https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Mask=2 (accessed May 2, 2020).

[5] Heat of Formation - Carbon dioxide. https://webbook.nist.gov/cgi/inchi?ID=C124389&Mask=1 (accessed May 2, 2020).

[6] Sandler, S. I. *Chemical, biochemical, and engineering thermodynamics*; John Wiley: Hoboken, NJ, 2017.

[7] Heat of Formation - Butanedioic acid. https://webbook.nist.gov/cgi/cbook.cgi?ID=C110156&Mask=2#Thermo-Condensed (accessed May 2, 2020).

[8] Heat of Sublimation - Butanedioic acid. https://webbook.nist.gov/cgi/cbook.cgi?ID=C110156&Mask=4#Thermo-Phase (accessed May 2, 2020).

[9] Ruscic, B.; Bross, D. H. Selected ATcT [1, 2] enthalpy of formation based on version 1.122 of the Thermochemical Network [3]. https://atct.anl.gov/Thermochemical Data/version 1.122/species/?species_number=1169 (accessed May 3, 2020).