

DETERMINING ENTHALPY CHANGES WITH USE OF HESS' LAW



Aspect	Design	DCP	CE
1			
2			
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INTRODUCTION

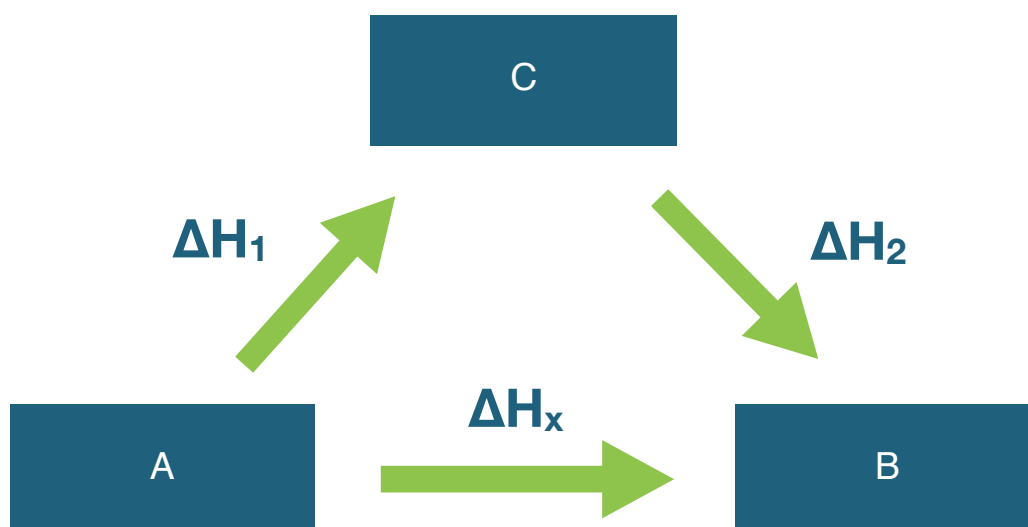
Determining enthalpy change by direct measurement, in a lot of reactions, is almost impossible or very difficult to achieve. This is also the case of thermal decomposition of sodium hydrogencarbonate [NaHCO_3] - the objective of my experiment. The First Law of thermodynamics and Hess' Law derived from it, can make us do it differently just thanks to these laws. The first law states:

“ that energy in the set system cannot be created or destroyed”¹

The second law states that:

“ the total energy change occurring during the conversion of a given set of reactions into a particular set of products is constant, irrespective of the pathway ”²

It means that in reality we have a set of reactions which looks like this:



And we cannot directly determine the value of ΔH_x it can be done by using the path of ΔH_1 and afterwards ΔH_2 by which ΔH_x can be determined with the equation: $\Delta H_x = \Delta H_1 + \Delta H_2$. This method of determining enthalpy change will be used in this investigation.

¹ Damji, S. Green, J. *CHEMISTRY*. Victoria, IBID Press, 2007, p 141.

² Damji, Green p 141

DESIGN

RESEARCH QUESTION

What is the enthalpy change of thermal decomposition of sodium hydrogencarbonate [NaHCO_3]?

VARIABLES

Table 1 | Variables in the investigation

Independent Variables	Units
1. Mass of sodium hydrogencarbonate 2. Mass of Anhydrous Sodium Carbonate 3. Indirect: Enthalpy change for the decomposition of sodium hydrogencarbonate	
Dependent Variables	
Direct: Temperature changes occurring during reactions Indirect: Amount of energy absorbed/evolved during reactions	kJ mol^{-1}
Controlled Variables	
Volume of Hydrochloric acid (HCl)	cm^3
Concentration of Hydrochloric acid (HCl)	mol dm^{-3}
Mass of NaHCO_3 used	g
Mass of anhydrous Na_2CO_3 used	g
temperature of the sample	$^{\circ}\text{C}$
temperature of the surrounding	$^{\circ}\text{C}$
time length of reactions	s
Uncontrollable Variables	
Contamination of the Apparatus	
Pressure	atm
Contamination of Substrates	
Heat exchange with outer environment	J

APPARATUS AND CHEMICALS

- ❖ 2 x polystyrene cups of atleast 130 cm³ volume
- ❖ 1 x measuring cylinder 100 cm³ ± 0.1 cm³
- ❖ 250 cm³ of 2 mol dm⁻³ hydrochloric acid [HCl]
- ❖ Mass Balance ± 0.001 g
- ❖ 14 g of sodium hydrogencarbonate [NaHCO₃]
- ❖ 8 g of anhydrous sodium carbonate [Na₂CO₃]
- ❖ Laboratory Data Logger for temperature
- ❖ iPhone stopwatch ± 1s
- ❖ 2M HCL Standard Solution

RISK ASSEMENT

Some chemicals and techniques used may be hazardous so the experimental should wear an apron, protective gloves, goggles and pay extra attention will conducting the experiment.

METHOD:

1. Measure out, using a measuring cylinder of 100 cm³ ± 0.1 volume, twice by 50 and 50, 100 cm³ of 2 mol of dm⁻³ hydrochloric acid and pour it into the polystyrene cup of 200 cm³ volume.
2. Weight out accurately about 14g of sodium hydrogencarbonate into the mass balance with a uncertainty of 0.001g. Record the exact mass used.
3. Record the tempratue of the surroundings using the data logger with accuracy of ± 0.1°C.
4. Start the iPhone stopwatch.
5. Using the data logger record the temprature of the acid in the cup every 30 seconds. After a few reasings start adding solid to it, and mixing it, do it little at a time, and slow mixing, otherwise the evolution of gas may cause liquids to overflow.
6. Continue taking temprature readings until you have ten readings after the temprature has reached its maximum/minimum.
7. Repeast points 1-6 but taking 8g of anhydrous sodium carbonate, instead of sodium hydrogencarbonate.

RAW DATA

Room temperature recorded was: 20.0 °C

Mass of sodium hydrogencarboante [NaHCO_3] = 14.000 ± 0.001 g

Table 2 | Temperature measurements of the sample with NaHCO_3 added, raw data:

Time / s ± 1	Temperature / °C ± 0.1
0	20.5
30	20.5
60	20.5
90	20.5
120	14.9
150	11.1
180	11.2
210	11.3
240	11.4
270	11.6
300	11.7
330	11.9
360	12.0
390	12.1
420	12.2
450	12.2
480	12.2
510	12.5
540	12.6
570	12.8
600	12.9

In the sample above the whole power didn't get into the cup with acid, a bit of it remained on the walls of the bottle.

Room temperature recorded was: 21.0 °C

Mass of anhydrous sodium carbonate (Na_2CO_3) = 7.999 ± 0.001 g

Table 3 | Temperature measurements of the sample with added Na_2CO_3 , raw data:

Time / s ± 1	Temperature / °C ± 0.1
0	21.5
30	21.5
60	21.5
90	21.5
120	23.6
150	24.7
180	25.7
210	25.5
240	25.3
270	25.0
300	24.8
330	24.7
360	24.7
390	24.6
420	24.5
450	24.5
480	24.3
510	24.4
540	24.4
570	24.4
600	24.5

Note | Temperature at the start of the timing and the room temperatures were a bit different because the other part of the experiment was concluded later in the day

DATA PROCESSING

Table 4 | Temperature measurements of the sample with NaHCO₃ added, **processed data***:

Time / s ± 1	Temperature / °C ± 0.1
0	20.5
30	20.5
60	20.5
90	20.5
120	14.9
150	11.1
180	11.2
210	11.3
240	11.4
270	11.6
300	11.7
330	11.9
360	12.0
390	12.1
420	12.2
450	12.2
480	12.2
510	12.5
540	12.6
570	12.8
600	12.9

Graph 1 | Temperature of the sample with NaHCO₃ added:

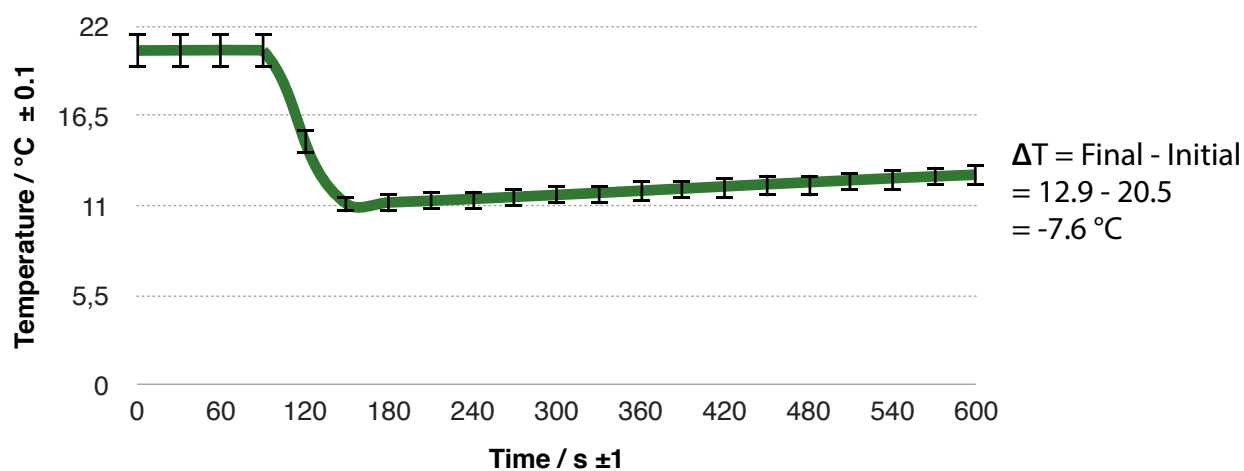
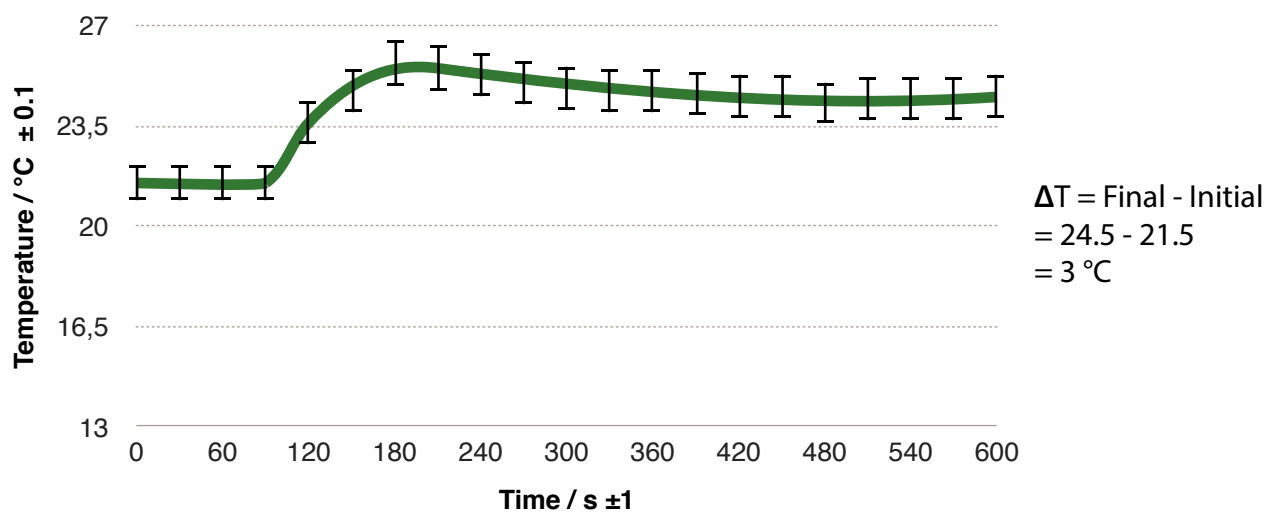


Table 5 | Temperature measurements of the sample with Na₂CO₃ added, **processed data***:

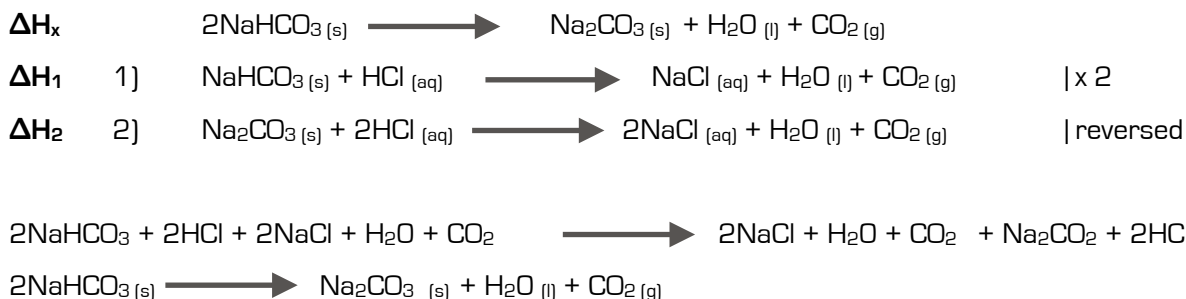
Time / s ±1	Temperature / °C ± 0.5
0	21.5
30	21.5
60	21.5
90	21.5
120	23.6
150	24.7
180	25.7
210	25.5
240	25.3
270	25.0
300	24.8
330	24.7
360	24.7
390	24.6
420	24.5
450	24.5
480	24.3
510	24.4
540	24.4
570	24.4
600	24.5

Graph 2 | Temperature of the sample Na₂CO₃ with added:



CALCULATIONS

Thermal decomposition of sodium hydrogencarbonate:



So to calculate enthalpy change the following equation must be applied:

$$\Delta H_x = 2\Delta H_1 - \Delta H_2$$

Assumptions:

$$m_s = m_{\text{H}_2\text{O}}$$

$$c = c_{\text{H}_2\text{O}}$$

$$d = d_{\text{H}_2\text{O}}$$

$$\Delta H = Q \div n$$

$$n = m \div M$$

$$Q = m \times c \times \Delta T$$

Calculations for sodium hydrogencarbonate - ΔH_1 :

$$M_1 = 22.99 + 1.01 + 12.01 + (3 \times 16.00) = 84.01 \text{ g mol}^{-1}$$

$$\Delta M_1 = 0$$

$$m_1 = 13.999 \text{ g}$$

$$\Delta m_1 = 0.001 \text{ g}$$

$$n_1 = m \div M = 13.999 \div 84.01 \approx 0.1666 \text{ mol}$$

$$\text{uncertainty: } \Delta n_1 = n \times (\Delta m \div m + \Delta M \div M) = 0.1666 \times (0.001 \div 13.999 + 0) \approx 1.190 \times 10^{-5} \text{ mol}$$

Number of moles in 13.999 g of sodium hydrogencarbonate is (0.1666 ± 0.00001) mol

$$Q_1 = m_s \times c_1 \times \Delta T_1$$

$$m_s = 100.0 \text{ g}$$

$$\Delta m_s = 0.5 \text{ g}$$

$$c_1 = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$$

$$\Delta c_1 = 0$$

$$\Delta T_1 = 20.5\text{ }^{\circ}\text{C} - 12.9\text{ }^{\circ}\text{C} = 11.5\text{ }^{\circ}\text{C} = 7.6\text{ K}$$

$$\Delta(\Delta T_1) = 0.5 + 0.5 = 1.0\text{ }^{\circ}\text{C} = 1.0\text{ K}$$

$$Q_1 = 100.0\text{ g} \times 4.18\text{ Jg}^{-1}\text{K}^{-1} \times 7.6 = \mathbf{3177\text{ J}}$$

$$\text{uncertainty} = \Delta Q_1 = Q_1 \times (\Delta m \div m + \Delta c \div c + \Delta(\Delta T) \div \Delta T) = 3177 \times (0.5 \div 100 + 0 + 0.1 \div 7.6) = \mathbf{43.8\text{ J}}$$

Heat absorbed (as the sample got cooler in this reaction) in this reaction is equal to 3177 ± 434 Joules

$$\Delta H_1 = Q \div n = 3177 \div 0.1666\text{ mol} \approx + 19069\text{ J mol}^{-1}$$

$$\text{uncertainty: } \Delta(\Delta H_1) = \Delta H_1 \times (\Delta Q_1 \div Q_1 + \Delta n_1 \div n_1) = 19069 \times (43.8 \div 3177 + 1.190 \times 10^{-5} \div 0.1666) \approx 27.3\text{ J mol}^{-1}$$

Enthalpy change of this reaction is $+ 19069 \pm 2606\text{ J mol}^{-1}$

Calculations for sodium carbonate - ΔH_2 :

$$M_2 = 2 \times 22.99 + 12.01 + (3 \times 16.00) = 105.99\text{ g mol}^{-1}$$

$$\Delta M_2 = 0$$

$$m_2 = 8.001\text{ g}$$

$$\Delta m_2 = 0.001\text{ g}$$

$$n_2 = m \div M = 8.001 \div 105.99 \approx 0.07549\text{ mol}$$

$$\text{uncertainty: } \Delta n_2 = n \times (\Delta m \div m + \Delta M \div M) = 0.07549 \times (0.001 \div 8.001 + 0) \approx 1 \times 10^{-5}\text{ mol}$$

Number of moles in 8.001 g of sodium carbonate is $0.07549 \pm 1 \times 10^{-5}\text{ mol}$

$$Q_2 = m_s \times c_2 \times \Delta T_2$$

$$m_s = 100.0\text{ g}$$

$$\Delta m_s = 0.5\text{ g}$$

$$c_2 = 4.18\text{ Jg}^{-1}\text{K}^{-1}$$

$$\Delta c_2 = 0$$

$$\Delta T_2 = 24.5\text{ }^{\circ}\text{C} - 21.5\text{ }^{\circ}\text{C} = 3.0\text{ }^{\circ}\text{C} = 3.0\text{ K}$$

$$\Delta(\Delta T_1) = 0.1\text{ }^{\circ}\text{C}$$

$$Q_2 = 100.0\text{ g} \times 4.18\text{ Jg}^{-1}\text{K}^{-1} \times 3.0 = \mathbf{1254\text{ J}}$$

$$\text{uncertainty} = \Delta Q_2 = Q_2 \times (\Delta m \div m + \Delta c \div c + \Delta(\Delta T) \div \Delta T) = 1254 \times (0.5 \div 100 + 0 + 0.1 \div 3.0) = \mathbf{43.9\text{ J}}$$

Heat evolved (as the sample got hotter) in sodium carbonate reaction is equal to $- 1254 \pm 43.9$ Joules

$$\Delta H_2 = Q \div n = 1254 \div 0.07549 \text{ mol} \approx 16611 \text{ J mol}^{-1}$$

$$\text{uncertainty: } \Delta(\Delta H_2) = \Delta H_2 \times (\Delta Q_2 \div Q_2 + \Delta n_2 \div n_2) = 16611 \times (43.9 \div 1254 + 1 \times 10^{-5} \div 0.07549) \approx 11.6 \text{ J mol}^{-1}$$

Enthalpy change of this reaction is $-16611 \pm 11.6 \text{ J mol}^{-1}$

Temperature increase = Reaction is Exothermic = Enthalpy Change is Negative

Therefore the overall enthalpy change of thermal decomposition of sodium hydrogencarbonate when Hess' Law is applied is:

$$\Delta H_x = 2\Delta H_1 - \Delta H_2$$

$$\Delta H_x = 2 \times 19069 - (- 16611) = 54749 \text{ J mol}^{-1} = 54.75 \text{ kJ mol}^{-1}$$

$$\text{uncertainty: } \Delta(\Delta H_x) = 2\Delta(\Delta H_1) - \Delta(\Delta H_2) = 2 \times 27.3 - 11.6 = |-43| \text{ J mol}^{-1}$$

$$\Delta(\Delta H_x) = 43 \text{ J mol}^{-1} \approx 0.43 \text{ kJ mol}^{-1}$$

Enthalpy change for thermal decomposition of sodium hydrogencarbonate is

$$\mathbf{54.75 \pm 0.43 \text{ kJ mole}^{-1}}$$

Percentage Error

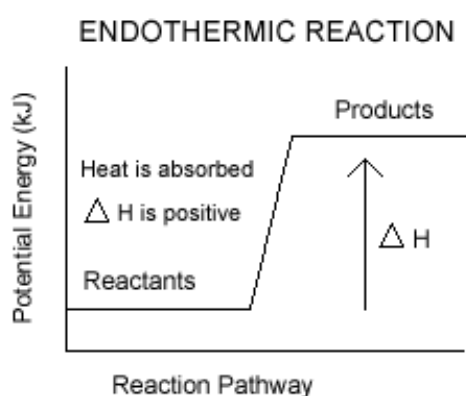
% Error = Accepted Value - Experimental Value

$$\frac{\quad \quad \quad}{\text{Accepted Value}} \times 100 \% = 85 - 54.75 = 30.25/85 = \mathbf{35\%}$$

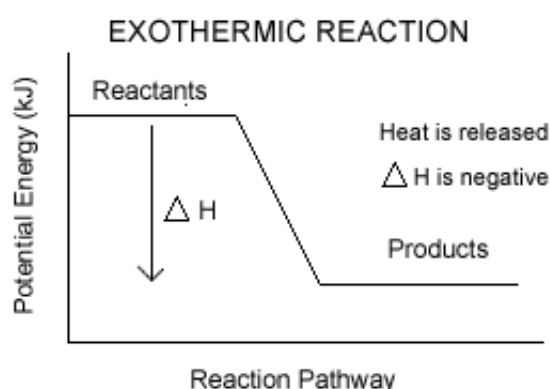
CONCLUSION

Hess' Law is a very important subject and a crucial tool in determining the values of enthalpy changes, as it was stated in the introduction earlier. The importance of the law was and can be observed during the investigation presented above. It was actually unreal and impossible to resolve enthalpy change of thermal decomposition of sodium hydrogencarbonate (NaHCO_3). This led to using a different method, which was carrying out two independent reactions, and observing and recording them. Thanks to those results, overall enthalpy change could have been calculated.

In the first sample acid's temperature was $20.5\text{ }^{\circ}\text{C}$. After the addition of sodium hydrogencarbonate it decreased to 12.9 and further started increasing due to the compensation of room temperature which was $20.0\text{ }^{\circ}\text{C}$. The fact that the sample got colder, we can clearly state, and know that it absorbed energy from the surroundings area hence the reaction was endothermic and enthalpy change was positive as shown in picture 1. After calculations the obtained ΔH_1 was $19069 \pm 27.3\text{ J mol}^{-1}$.

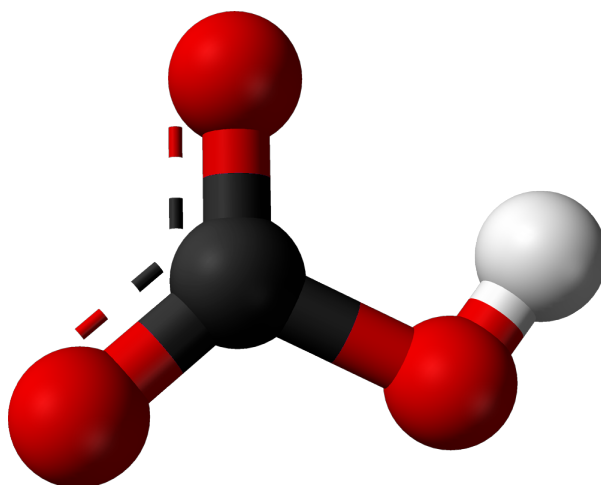


Picture 1 | Describing the Endothermic Reaction

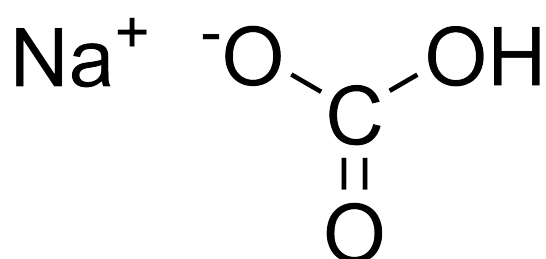


Picture 2 | Describing the Exothermic Reaction

In the second sample it was very much the opposite reaction. At the beginning its temperature of hydrochloric acid was $20.5\text{ }^{\circ}\text{C}$. When the sodium carbonate was added it increased to $24.5\text{ }^{\circ}\text{C}$ and then again like the previous one, steadily was changing, and begun to decrease also due to room temperature compensation. As the sample got warmer during the course of the reaction we can conclude, that it evolved some energy so it was an exothermic reaction with negative enthalpy change as shown in picture 2. The obtained value of it was $\Delta H_2 = -16611 \pm 11.6\text{ J mol}^{-1}$



Picture 3 | Sodium Hydrogencarbonate 3



Picture 4 | Sodium Hydrogencarbonate 4

Using this data provided, we are able to calculate that for this white solid presented, when powder commonly used as a baking soda product, or in some medicine, energy change of this decomposition occurs the most effectively at 200 °C, equals to about 96.64 ± 0.43 kilojoules per one mole of the substance. This is not compatible and the widely accepted value of **+85** per kJ per mole ⁵, which is the accepted value, implying some errors in the procedure, overall results, and its main realization.

The percentage error, as calculated earlier was seen to be 35%. This means that about 1/3 of the experiment could have been misplaced in the procedures and results. However, the percentage error isn't significant enough to exclude any statements being made from the experiment.

³ <http://www.kentchemistry.com/links/Kinetics/PEDiagrams.htm> Accessed: 19/04/2014

⁴ <http://www.groent.org/blog/wp-content/uploads/2013/12/SodiumBicarbonate.png> Accessed: 19/04/2014

⁵ <http://www.nationalstemcentre.org.uk/elibrary/resource/10686/try-this-the-thermal-decomposition-of-sodium-hydrogen-carbonate> Accessed: 19/04/2014

EVALUATION AND IMPROVEMENTS

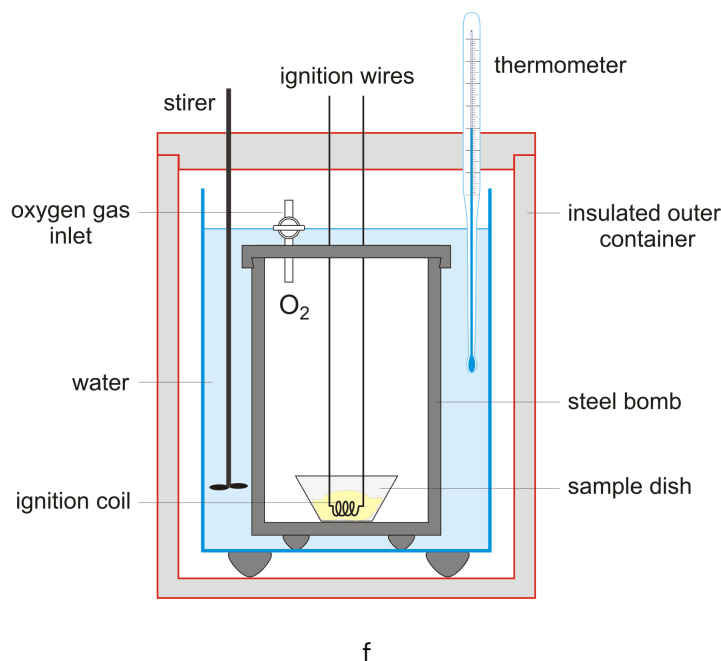
Results clearly show us that there were some inaccuracies in the procedure and the methods used to its fulfillment. The value given, 54.75 ± 0.43 kilojoules per one mole of the substance is not as close, somewhat quite distant from the expected +85 kilojoules per mole, so this indicates that there were some errors which did occur. That sets up a strong base on evaluation and finding improvements.

In the experiment, a simple method was used, using the polystyrene cups and using the data logger to measure the temperature. Instead, a calorimetry, a technique used to measure the enthalpy associated with a particular change⁶, could and should have been used. It is particularly useful in such experiments when energy changes in the system are monitored. The technique has its conditions as well, such as that to have it done an object which assures that no energy will be added or will escape the system during the measurements is added. The object is called calorimeter.

In the experiment, polystyrene cup acts very slightly like one, because it fills most of the requirements of the sort of calorimeter apparatus, it had a low heat capacity and a very proper insulator. It is very important, these traits, because when creation or destruction of energy from the original system is not desired. If a calorimeter does not have these characteristics, then a change in temperature of the calorimeter and its content is observed and reaction continues with heat loss or gain from the surroundings, which is not a wanted effect. As it was mentioned earlier, such changes are usually a major source of faults in the results. It could have been the same in this case especially that cups lacked lids or other kinds of covers which could have allowed for free energy exchange with the surroundings via the upper part of the cup.

Besides that, Polystyrene is a good insulator and has a low heat capacity, it is still able to release or gain a significant amount of energy via its walls which do not have heat capacity equal to 0 and do not provide energy sealing and covering. To get rid of these problems, and avoid such errors, a professional laboratory calorimeter should be used in the experiment.

⁶ <http://www.science.uwaterloo.ca/~cchieh/cact/c120/calorimetry.html> Accessed 20/04/2014



Picture 5 | Shows a professional calorimeter ⁷

Due to the well insulating double walls with vacuum between them and the proper lid, experimenter can be sure that there is no energy exchange with the surroundings. This would ensure more precise, proper results, and less disturbed results.

The usage of the thermometer is not accurate enough to conclude all the data needed, that is why a data logger was used which helped the experiment a lot. The Logtag Temperature Recorder, which did allow for much more precise and frequent readings and records resulting in more accurate and valuable view on the course of the reaction and further data analysis.

In the Raw Data area, it was clearly marked that in the first sample with sodium hydrogencarbonate, not all the powder was added to HCl solution. Some of it remained in the slight wall and the plate of the weighing transparent glass plate. This could have somehow strongly influences the obtained results depending how much NaHCO_3 has remained in the bottle used as it is the reason for the occurrence of the reaction the more distorted the results were. The reason for that could have been the mildness of sodium hydrogencarbonate hence the adhesion to the instruments walls. Mildness can also make a

⁷ <http://www.periodni.com/gallery/calorimeter.png> Accessed 20/04/2014

problem, causing graining of the power accompanied, by the decrease in the surface area of fragmented substance and affected the efficiency of the reaction.

So to avoid that substances should be kept in closed and sealed containers and be mechanically fragmented before used in the experiment, for example using the mixer and the mortar equipment.

What has probably influenced my calculations and thus results much are high uncertainty of apparatus followed by high uncertainties of calculations and the final results. This can be easily eliminated by the use of more accurate apparatus, which would definitely increase the validity of the general result.

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