

To what extent do the reactions
between NaOH and HCl
through different pathways
agree with Hess's Law

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1 Introduction

1.1 Definition for Terminologies

1.1.1 Enthalpy Change

An enthalpy change describes the change in enthalpy observed in the constituents of a thermodynamic system when undergoing a transformation or chemical reaction. It is the difference between the enthalpy after the process has completed, i.e. the enthalpy of the products, and the initial enthalpy of the system, i.e. the reactants. These processes are reversible and the enthalpy for the reverse process is the negative value of the forward change. [1]

1.1.2 Hess's Law

Hess's law states that the change of enthalpy in a chemical reaction is independent of the pathway between the initial and final states. [2]

1.1.3 Coffee-cup Calorimeter

Coffee-cup calorimeter, which is constructed from a styrofoam cup and a lid with one hole, allows the insertion of a thermometer through the hole. The styrofoam cup holds a known amount of a solvent, usually water, that absorbs the heat from the reaction. When the reaction occurs, the cup provides insulation. [3]

1.2 Lab Introduction

In this lab, I will be measuring the enthalpy changes for different pathways of the reaction between sodium hydroxide (NaOH) and hydrochloric acid (HCl) and compare the enthalpy changes.

2 Methodology

2.1 Experiment Design

In this experiment, I separate the different possibilities of pathways into three different parts:

2.1.1 Part A

In part A, the reaction is between aqueous NaOH and aqueous HCl. 50ml $1\text{mol} \cdot \text{L}^{-1}$ NaOH solution are poured into 50ml $1\text{mol} \cdot \text{L}^{-1}$ HCl solution in the coffee-cup calorimeter. A digital thermometer is submerged into the liquid and a magnetic stirrer is put into the calorimeter to make sure that the heat is evenly distributed inside the solution.

2.1.2 Part B

In part B, the reaction is between NaOH solid and aqueous HCl. 2 grams of NaOH solid are added into 50ml $1\text{mol} \cdot \text{L}^{-1}$ HCl solution in the coffee-cup calorimeter. A digital thermometer is

submerged into the liquid and a magnetic stirrer is put into the calorimeter to make sure that the heat is evenly distributed inside the solution.

2.1.3 Part C

In part C, the reaction is between NaOH solid and water. 2 grams of NaOH solid are added into 50ml water in the coffee-cup calorimeter. A digital thermometer is submerged into the liquid and a magnetic stirrer is put into the calorimeter to make sure that the heat is evenly distributed inside the solution.

The three parts each contains two trials with the same procedure, aiming at decreasing random uncertainty.

2.2 Data Collection

The variable we are looking at in the three parts are temperature change, which is measured by the digital thermometer. The digital thermometer is connected to Logger Pro¹. The software provides us with a temperature-time graph, like figure 1 below:

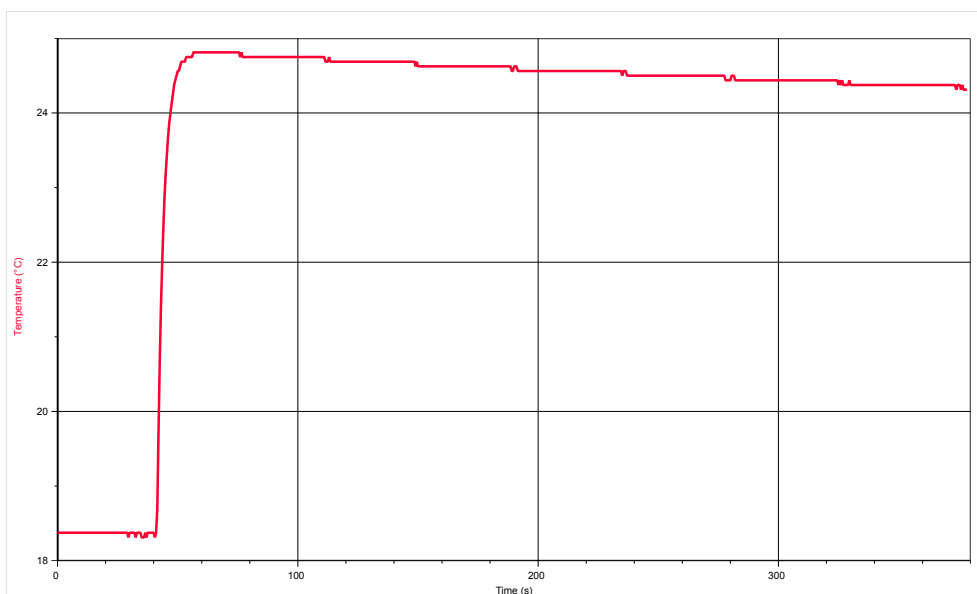


Figure 1: Temperature-time graph (A-1)

2.2.1 Graph Processing

From the graph, we can see that the reaction starts at around 40 second and finishes at around 60 second. After 60 second, the temperature started to drop since the coffee-cup calorimeter does not have perfect heat insulation. This means that we need to consider the heat loss through the calorimeter during the reaction.

By finding the equation for the line of best fit of the section starting from around 80 second, I get the rate of heat loss for the coffee-cup calorimeter, which is the same when the reaction happen.

¹ A premier data-collection software from Vernier Software & Technology.

When restoring the ideal temperature with no heat loss, we should add the temperature to the curve according to the rate of heat loss we got from the fit. An equivalent approach is to extend the fitted line backwards and the value on the line at the time when the reaction starts is the ideal final temperature. This is because a temperature addition of (time of reaction \times rate of heat lost) is added to the original peak on the graph. Refer to figure 2 for the processing above:

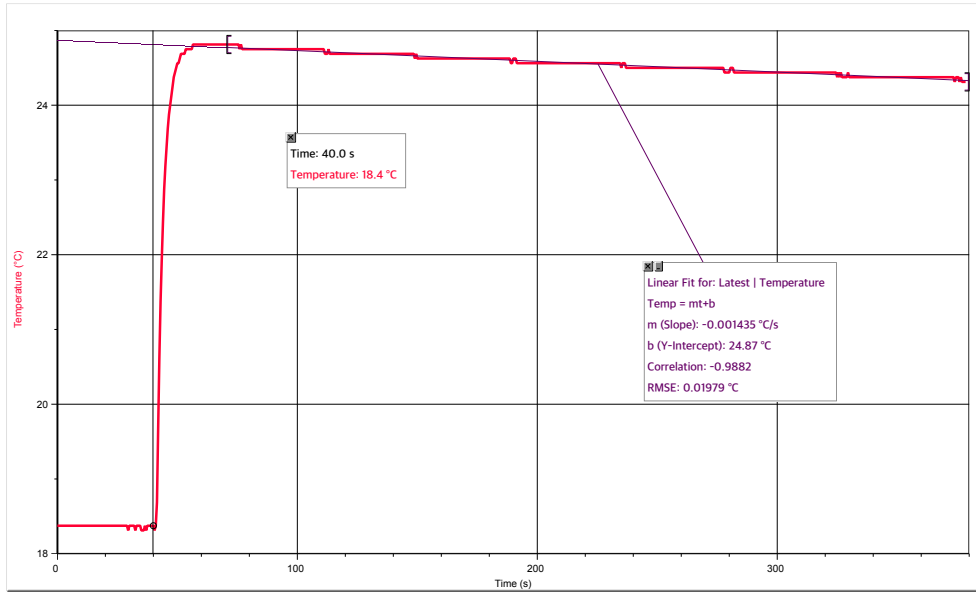


Figure 2: Temperature-time graph (A-1, processed)

In this case, we can see that the fitted line has equation $\text{Temp} = -0.001435 \cdot \text{Time } ^\circ\text{C} + 24.87 ^\circ\text{C}$, indicating that the rate of heat loss is $0.001435 ^\circ\text{C}$ every second. From figure 2, we know that beginning of the reaction is at 40 second sharp with initial temperature at $18.4 ^\circ\text{C}$. By inserting the time into the equation, we get the ideal final temperature:

$$T_{\text{final}} = -0.001435 \times 40 + 24.87 = 24.81 ^\circ\text{C}$$

The ideal change of temperature ΔT is:

$$\Delta T = 24.81 - 18.4 = 6.4 ^\circ\text{C} = 6.4 \text{ K}^2$$

² This is because the difference between Celsius and Kelvin is the starting point. The change rate of these two units are the same.

3 Data and Analysis

3.1 Calculation of ΔH for Each Trial

3.1.1 Defining Function $\Delta H(\Delta T, m)$

Now I am going to define a function $\Delta H(\Delta T, m)$ that calculates the ΔH for each trial with two variables: ΔT and m , where ΔT is the change of temperature in Kelvin for the trial and m is the mass of the solution for the trial.

ΔH Value

$$\begin{aligned}\Delta H &= -Q = -cm\Delta T \\ &= -4.18 \text{ kJ kg}^{-1} \text{ K}^{-1} \cdot m \text{ kg} \cdot \Delta T \text{ K} \\ &= -4.18 \cdot m \cdot \Delta T \text{ kJ}\end{aligned}$$

Uncertainty

c

This is the specific heat capacity of water from the data booklet. [4] With very precise measurement, this value has no uncertainty.

m

This is the mass of the solution. The volumetric flask I used was 50ml, with the minimum scale value as 1ml. This means that every time 50 grams of solution measured, there is an addition of uncertainty as 0.5 grams. The absolute uncertainty of m can be written as:

$$\frac{m}{50} \times 0.5 = \frac{m}{100}$$

So the relative uncertainty can be written as:

$$\frac{\frac{m}{100}}{m} = \frac{1}{100}$$

ΔT

ΔT is calculated in 2.2 by subtracting the ideal final temperature by the initial temperature. Since the digital thermometer gives the value with one decimal, the absolute uncertainty is 0.2 K, so the percentage uncertainty is:

$$\frac{0.2}{\Delta T}$$

Absolute Uncertainty

The absolute uncertainty is the product of the ΔH value and the sum of all relative uncertainty:

$$(4.18 \cdot m \cdot \Delta T) \left(\frac{0.2}{\Delta T} + \frac{1}{100} \right) \text{ kJ}$$

Finally, we get the function $\Delta H(\Delta T, m)$:

$$\Delta H(\Delta T, m) = -4.18 \cdot m \cdot \Delta T \pm (4.18 \cdot m \cdot \Delta T) \left(\frac{0.2}{\Delta T} + \frac{1}{100} \right) \text{ kJ}$$

3.1.2 Using the Function

Through similar process as 2.2, we get the six ΔT values for the three different parts, along with the corresponding m value.

$\Delta T(\text{K})$	Trial 1	Trial 2	$m(\text{kg})$
Part A	6.4	6.5	0.100
Part B	21.9	22.2	0.050
Part C	9.9	10.4	0.050

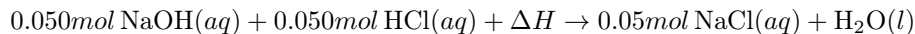
We can input the information in the table above into the function $\Delta H(\Delta T, m)$ and get the enthalpy changes for the six trials:

$\Delta H(\text{kJ})$	Trial 1			Trial 2		
	value	rel.	abs.	value	rel.	abs.
Part A	-2.68	0.04125	± 0.11	-2.72	0.04077	± 0.11
Part B	-4.58	0.01913	± 0.09	-4.64	0.01901	± 0.09
Part C	-2.07	0.03020	± 0.06	-2.17	0.02923	± 0.06

3.2 Calculation of ΔH for Reactions

3.2.1 Part A

In part A, the equation of reaction is:



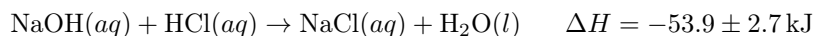
However, for the ΔH for a reaction, its unit is kJ mol^{-1} . So we need to expand the size of the reaction so that the number moles reaction is 1:

$$\Delta H_A = \frac{\Delta H_{A1/2} \text{ kJ}}{0.050 \text{ mol}} = 20.0 \cdot \Delta H_{A1/2} \text{ kJ mol}^{-1}$$

However, the way we get the value 0.050 is through the volume of the NaOH solution. The relative uncertainty for that, as mentioned in 3.1.1, is $\frac{1}{100}$. We can get the final enthalpy change of this reaction by considering this uncertainty:

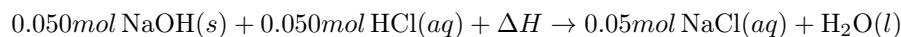
(kJ)	Trial 1	Trial 2
ΔH_A	-53.5	-54.3
Rel.	0.05125	0.05077
Abs.	± 2.7	± 2.8

By averaging the result from the two trials, we finally get:



3.2.2 Part B

In part B, the equation of reaction is:



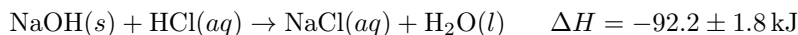
However, for the ΔH for a reaction, its unit is kJ mol^{-1} . So we need to expand the size of the reaction so that the number moles reaction is 1:

$$\Delta H_B = \frac{\Delta H_{B1/2} \text{ kJ}}{0.050 \text{ mol}} = 20.0 \cdot \Delta H_{B1/2} \text{ kJ mol}^{-1}$$

However, the way we get the value 0.050 is through the mass of NaOH solid. The absolute uncertainty for that is 0.001grams, so the relative uncertainty is $0.001 \div 2.000 = 0.0005$. We can get the final enthalpy change of this reaction by considering this uncertainty:

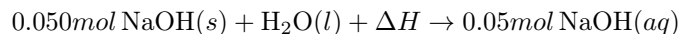
(kJ)	Trial 1	Trial 2
ΔH_B	-91.5	-92.8
Rel.	0.01963	0.01951
Abs.	± 1.8	± 1.8

By averaging the result from the two trials, we finally get:



3.2.3 Part C

In part C, the equation of reaction is:



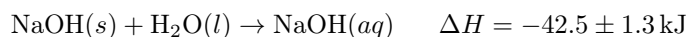
However, for the ΔH for a reaction, its unit is kJ mol^{-1} . So we need to expand the size of the reaction so that the number moles reaction is 1:

$$\Delta H_C = \frac{\Delta H_{C1/2} \text{ kJ}}{0.050 \text{ mol}} = 20.0 \cdot \Delta H_{C1/2} \text{ kJ mol}^{-1}$$

However, the way we get the value 0.050 is through the mass of NaOH solid. The absolute uncertainty for that is 0.001grams, so the relative uncertainty is $0.001 \div 2.000 = 0.0005$. We can get the final enthalpy change of this reaction by considering this uncertainty:

(kJ)	Trial 1	Trial 2
ΔH_C	-41.4	-43.5
Rel.	0.03070	0.02973
Abs.	± 1.3	± 1.3

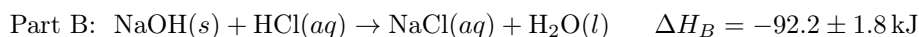
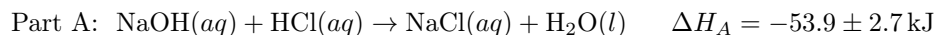
By averaging the result from the two trials, we finally get:



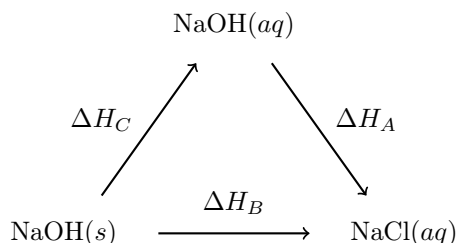
4 Conclusion

4.1 Conclusion

In 3.2, we get the following result:



By analyzing the two different pathways, we can get this illustration cycle below:



We find out that part C and part A together is equivalent to part B when we only focus on reactants and products. According Hess's Law, $\Delta H_C + \Delta H_A = \Delta H_B$. When we do the calculation, we find out that:

$$\begin{aligned} \Delta H_C + \Delta H_A &= -53.9 \pm 2.7 \text{ kJ} - 42.5 \pm 1.3 \text{ kJ} \\ &= -96.4 \pm 4.0 \text{ kJ} \end{aligned}$$

which does overlap with the range of ΔH_B considering the uncertainty. Thus, the lab does agree with the Hess's Law.

4.2 Evaluation

We are going to look into the reproducibility of this experiment.

According to information on the Internet, we find the literature value for enthalpy change of aqueous NaOH reacting with aqueous HCl, $\Delta H_A = -57.9 \text{ kJ mol}^{-1}$ [5], while the literature value for the enthalpy change of NaOH solution is $\Delta H_C = -44.51 \text{ kJ mol}^{-1}$ [6]. We can see that the numeric value of the two literature values are both a bit bigger than the enthalpy change we get. There are two possible reasons for this:

- For part C, NaOH is hygroscopic, very easy to absorb moisture from air. This is cause the surface of NaOH solid to dissolve and release heat, so it will be less available to react and release heat when we are actually measuring temperature change. This makes ΔT smaller, leading to smaller numeric value of ΔH . A possible solution to this is to act faster when weighing and try to do the experiment in a dryer place.
- For part A and C, the prediction of heat loss by the line of best fit might not be so accurate. It's possible that the ideal final temperature we get is lower than the actual value. That also lease to a smaller ΔT and thus ΔH with a smaller numeric value. The way we might be able to fix this is to upgrade the calorimeter to, for instance, a bomb calorimeter, which is better at heat insulation.

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