

Experiment 1: Hot & Cold

Section 2, Group 3: (names omitted)

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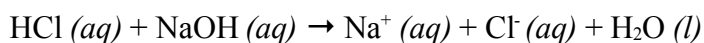
Introduction

This report covers the investigation of temperature changes that were observed by the technicians at a small chemical manufacturing company during their acid-base neutralization reactions (1). The goal was to determine the causes of the temperature changes and report a full explanation of the behavior of these synthesis reactions, including an assessment of whether these reactions offered any potential economic benefits to the company.

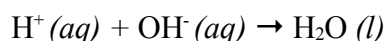
The technicians' procedures were reviewed, and it was determined that their synthesis reactions were non-combustion reactions being carried out under constant pressure conditions. Under such conditions, the total enthalpy is equal to the change in heat (ΔH) of the reaction. Typically, these heat changes are measured using a constant pressure calorimeter (2).

Because a commercial calorimeter was not available a much simpler constant pressure calorimeter was constructed from commonly available materials. To meet the requirement that the calorimeter be a good insulator, it was decided to construct the calorimeter from two nested styrofoam cups with a cardboard lid, based upon a suggestion from Cooper (1).

The acid-base neutralization reaction investigated was hydrochloric acid in aqueous solution mixed with sodium hydroxide, also in aqueous solution. The balanced equation for this reaction is:



However, since the Na^+ and Cl^- ions are spectator ions, the reaction of interest is given by:



The accepted, standard heat of neutralization for this reaction carried out under constant pressure is -56.2kJ per mole of H^+ ions (2). The negative sign on this heat is an indication that the

reaction is *exothermic* (gives off heat). For an ideal calorimeter the heat exchange between the system (the reaction, the solution and the calorimeter) and the surroundings should be effectively zero. Since energy is conserved, the change in heat of the system plus the change in heat of the surroundings must equal zero. Therefore the overall change in heat of the system equals zero, and thus the change in heat of all the system components must sum to zero:

$$\Delta H_{\text{rxn}} + \Delta H_{\text{soln}} + \Delta H_{\text{calorimeter}} = 0$$

And:

$$\Delta H_{\text{rxn}} = -(\Delta H_{\text{soln}} + \Delta H_{\text{calorimeter}})$$

To calculate the heat of reaction, ΔH of the solution and the ΔH of the calorimeter must be determined. The change in heat for a given object or container is given by the heat capacity of the object multiplied by the change in temperature ΔT (2):

$$\Delta H = C\Delta T$$

For the water solution, the heat capacity is given by the specific heat of water multiplied by the mass of water present:

$$C_{\text{water}} = s_{\text{water}} * m_{\text{water}}$$

For the calorimeter, however, the heat capacity must be determined experimentally. For this calibration procedure, it was decided to measure the temperature change when cold water was added to hot in the calorimeter. For this reaction, the heat lost by the hot water plus the heat lost by the calorimeter (it is equilibrated initially with the hot water) should equal the heat gained by the cold water(1):

$$\Delta H_{\text{hot water}} + \Delta H_{\text{cold water}} + \Delta H_{\text{calorimeter}} = 0$$

Or:

$$-\Delta H_{\text{calorimeter}} = \Delta H_{\text{hot water}} + \Delta H_{\text{cold water}}$$

Again, the heat change of the hot and cold water is given by the heat capacity of water times their respective temperature changes. Therefore, the heat capacity for the calorimeter is given by:

$$\Delta H_{\text{calorimeter}} = C_{\text{calorimeter}} \cdot \Delta T \quad (2)$$

So:

$$C_{\text{calorimeter}} = \Delta H_{\text{calorimeter}} / \Delta T$$

Once $C_{\text{calorimeter}}$ is known, $\Delta H_{\text{rxn}} = -(\Delta H_{\text{calorimeter}} + \Delta H_{\text{solution}})$ can be calculated for any experiment as:

$$\Delta H_{\text{rxn}} = -(C_{\text{calorimeter}} + C_{\text{solution}})\Delta T,$$

where $C_{\text{solution}} = s_{\text{water}} \cdot m_{\text{solution}}$, since all the solutions are primarily water.

Experimental

Two identical calorimeters were constructed. Each used two nested styrofoam cups, a ringstand, two rings, two 10cm x 10cm corrugated cardboard lids, a standard laboratory funnel, and a *Vernier* temperature probe connected to a *Vernier Lab Pro* Interface as shown in figure 1:

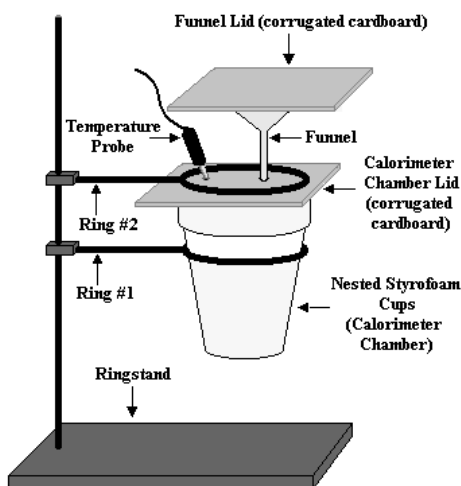


Figure 1: Calorimeter Assembly

Notes:

1. Ring #1 holds calorimeter chamber in place
2. Ring #2 holds calorimeter chamber lid in place
3. Funnel and temperature probe penetrate calorimeter chamber lid to enter calorimeter

For the calibration procedure, a mass of hot water was added to the calorimeter chamber and the temperature allowed to stabilize. Once the temperature had stabilized, a mass of cold water was added to the calorimeter, the calorimeter was agitated slightly, again the temperature was allowed to stabilize and the temperature was taken again. From these figures, the changes in heat of both the hot and cold water were calculated and used to calculate the heat capacity of the calorimeter.

For the acid-base neutralization reactions, it was decided to use 1.0M hydrochloric acid and 1.0M sodium hydroxide for the first reaction, and 6.0M hydrochloric acid and 6.0M sodium hydroxide for the second reaction. It was further decided that the hydrochloric acid would be the limiting reagent, so that the volume of sodium hydroxide was measured to equal or exceed the volume of the hydrochloric acid, with equal molarity solutions chosen to eliminate calculations involving relative conversions of concentrations.

For each trial, the sodium hydroxide was added to the calorimeter chamber, the temperature was measured, and then an equal or lesser volume of hydrochloric acid was added and the calorimeter chamber was agitated slightly. The temperature changes were logged using *Logger Pro* software.

Results

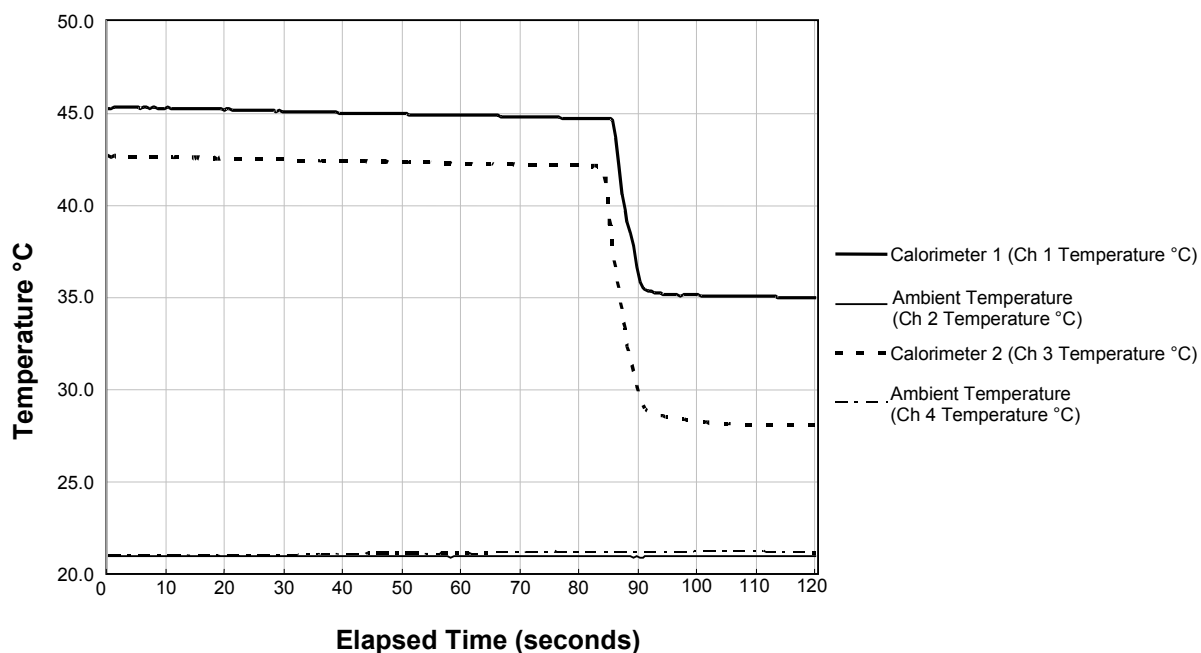
Calorimeter Calibration

Trial 1

Initially, 50.93g of hot water at 45.2°C was added to calorimeter 1, and 65.05g of hot water at 42.7°C was added to calorimeter 2. Between the onset of measurement (time 0.0) and 84.5s, the water in the calorimeters showed a slow but steady decline in temperature. At 84.5s into the trial

the temperature of calorimeter 1 had stabilized at 44.7°C, and the temperature of calorimeter 2 had stabilized at 42.1°C, whereupon 50.54g of water at 19.73°C was added to calorimeter 1 and 83.28g of water at 19.73°C was added to calorimeter 2. At that point, the temperatures of both calorimeters dropped sharply, stabilizing at 35.0°C for calorimeter 1 and 28.0°C for calorimeter 2 (see figure 2).

Figure 2: Calorimeter Calibration - Trial 1



Density of Water 1.00g/cm³ (1)

Specific Heat of Water: 4.184 J/g · °C (1)

Mass of Water in RXN = Mass of Water + Beaker – Mass of Empty Beaker
 (trial 1, calorimeter 1, hot) = 149.43g – 98.50g
 = 50.93g

ΔT = Temperature_{final} - Temperature_{initial}
 (trial 1, calorimeter 1, hot) = 35.2°C - 44.7°C
 = -9.5°C

$$\begin{aligned} \Delta H_{\text{hot water}} &= (\text{specific heat of water}) \times (\text{mass of hot water}) \times (\Delta T) \\ (\text{trial 1, calorimeter 1}) &= (4.184 \text{ J/g} \cdot ^\circ\text{C})(50.93\text{g})(-9.5^\circ\text{C}) \\ &= -2.0 \times 10^3 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{cold water}} &= (\text{specific heat of water}) \times (\text{mass of water}) \times (\Delta T) \\ (\text{trial 1, calorimeter 1}) &= (4.184 \text{ J/g} \cdot ^\circ\text{C})(50.54\text{g})(15.47^\circ\text{C}) \\ &= 3.271 \times 10^3 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{calorimeter}} &= -(\Delta H_{\text{cold water}} + \Delta H_{\text{hot water}}) \\ (\text{trial 1, calorimeter 1}) &= -(3.271 \times 10^3 \text{ J} + (-2.0 \times 10^3 \text{ J})) \\ &= -1.3 \times 10^3 \text{ J} \end{aligned}$$

$$\begin{aligned} C_{\text{calorimeter}} &= \Delta H_{\text{calorimeter}} / \Delta T \\ (\text{trial 1, calorimeter 1}) &= \text{heat gained by calorimeter} / \Delta T \\ &= -1.27 \times 10^3 \text{ J} / -9.5^\circ\text{C} \\ &= 1.3 \times 10^2 \text{ J} / ^\circ\text{C} \end{aligned}$$

Table 1: Calorimeter Calibration, Trial 1

Trial 1		
	Calorimeter 1	Calorimeter 2
Mass of Hot Water plus Beaker	149.43g	177.23g
Mass of Empty Beaker	98.50g	112.18g
Hot water added to RXN:	50.93g	65.05g
Initial Temperature of Hot Water	45.2°C	42.7°C
Reaction Temperature of Hot Water	44.7°C	42.1°C
Final Temperature of Hot Water	35.2°C	28.1°C
$\Delta T_{\text{hot water}}$	-9.5°C	-14.0°C
$\Delta H_{\text{hot water}}$	$-2.0 \times 10^3 \text{ J}$	$-3.81 \times 10^3 \text{ J}$
Mass of Cold Water plus Beaker	162.73g	147.50g
Mass of Empty Beaker	112.19g	64.22g
Cold Water added to RXN:	50.54g	83.28g
Initial Temperature of Cold Water	19.73°C	19.73°C
Final Temperature of Cold Water	35.2°C	28.1°C
$\Delta T_{\text{cold water}}$	15.47°C	8.37°C
$\Delta H_{\text{cold water}}$	$3.3 \times 10^3 \text{ J}$	$2.92 \times 10^3 \text{ J}$
$\Delta H_{\text{calorimeter}}$	$1.3 \times 10^3 \text{ J}$	$-8.9 \times 10^2 \text{ J}$
$C_{\text{calorimeter}}$	$1.3 \times 10^2 \text{ J} / ^\circ\text{C}$	$-6.4 \times 10^1 \text{ J} / ^\circ\text{C}$

It was decided based on the large heat capacities calculated plus the negative sign on the heat capacity for calorimeter2 to discard the data from calibration trial 1. It was decided at the

time that the likely cause for this result was that somehow there was a leak of heat from the calorimeter, most likely because of the high initial hot water temperature.

Trial 2

Trial 2 ran very similarly to trial 1. 24.80g of hot water at 38.1°C was added to calorimeter 1 and 32.35g of hot water at 36.6°C was added to calorimeter 2. Again, the temperatures in both calorimeters dropped sharply when the cold water was added. The temperature of the final mix in calorimeter 1 was 29.8°C and the temperature of the mix in calorimeter 2 stabilized at 29.5°C (see figure 3).

Figure 3: Calorimeter Calibration - Trial 2

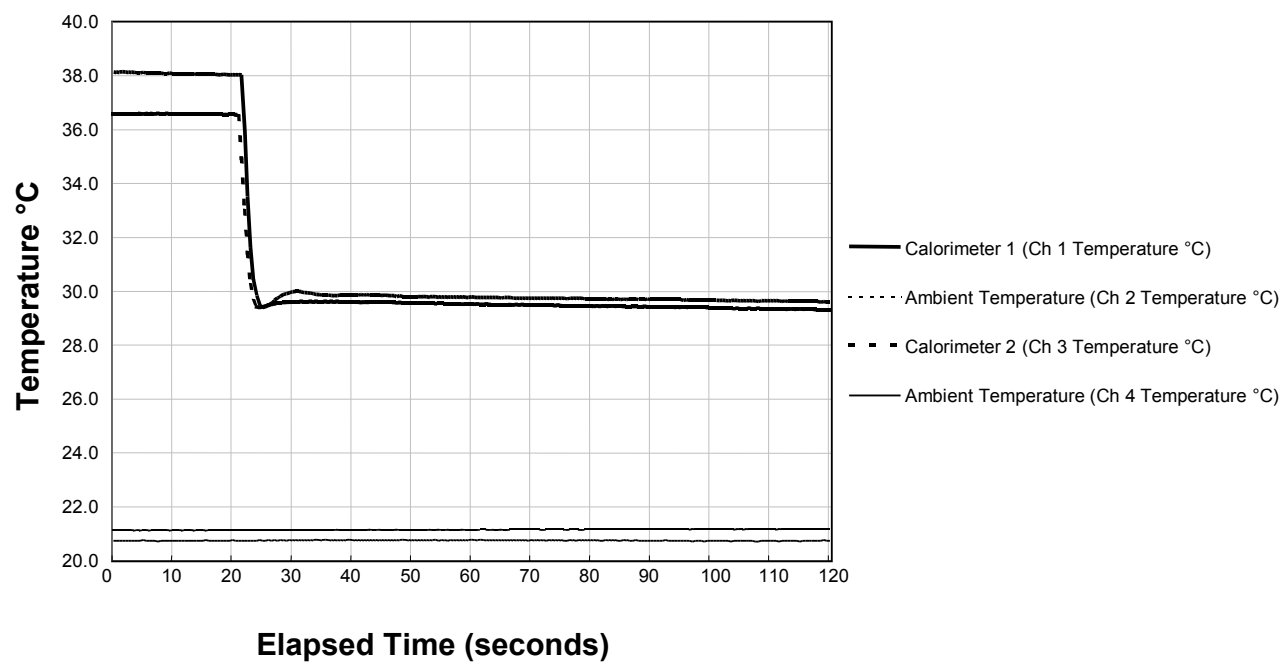


Table 2: Calorimeter Calibration, Trial 2

Trial 2	Calorimeter 1	Calorimeter 2
Mass of Hot Water plus Beaker	54.97g	57.23g
Mass of Empty Beaker	30.17g	24.88g

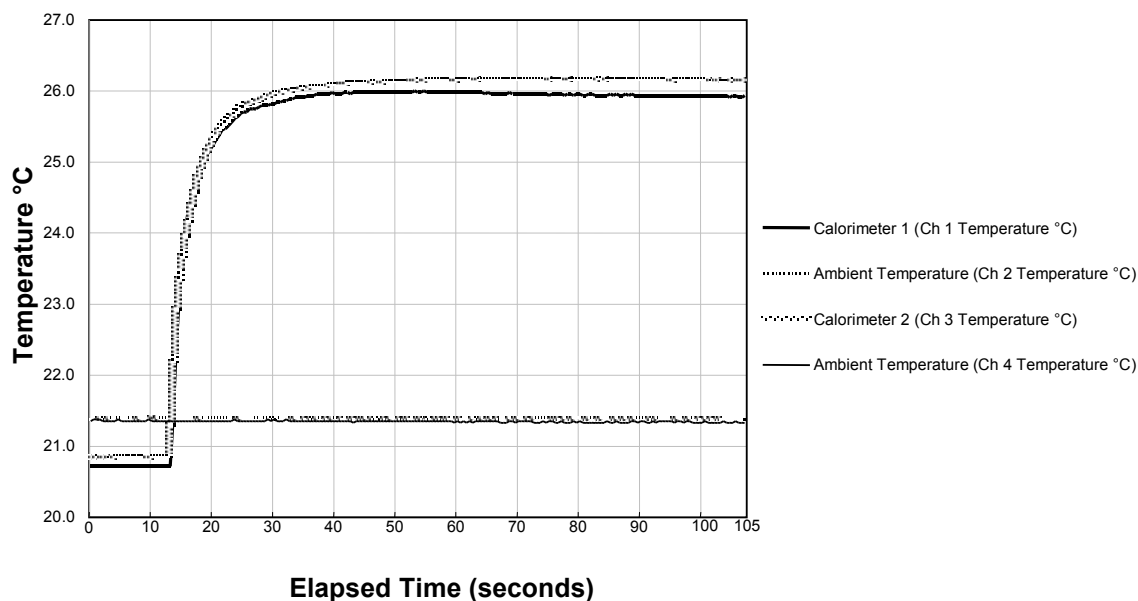
Hot water added to RXN:	24.80g	32.35g
Initial Temperature of Hot Water	38.1°C	36.6°C
Reaction Temperature of Hot Water	38.0°C	36.6°C
Final Temperature of Hot Water	29.8°C	29.5°C
$\Delta T_{\text{hot water}}$	-8.2°C	-7.1°C
$\Delta H_{\text{hot water}}$	$-8.5 \times 10^2 \text{ J}$	$-9.6 \times 10^2 \text{ J}$
Mass of Cold Water plus Beaker	90.93g	87.50g
Mass of Empty Beaker	62.66g	64.07g
Cold Water added to RXN:	28.27g	23.43g
Initial Temperature of Cold Water	20.0°C	20.2°C
Final Temperature of Cold Water	29.8°C	29.5°C
$\Delta T_{\text{cold water}}$	9.8°C	9.3°C
$\Delta H_{\text{cold water}}$	$1.2 \times 10^3 \text{ J}$	$9.1 \times 10^2 \text{ J}$
$\Delta H_{\text{calorimeter}}$	$-3.5 \times 10^2 \text{ J}$	$4.9 \times 10^1 \text{ J}$
$C_{\text{calorimeter}}$	$4.3 \times 10^1 \text{ J}$	$-6.9 \times 10^0 \text{ J}$

It was still troubling that the heat capacity figure for calorimeter 2 was negative. This data, however, was retained, due to time constraints. The magnitude of the heat capacities for both calorimeter 1 and calorimeter 2 were much less extreme than in trial 1.

Acid Base Reaction #1 – 1.0M HCl + 1.0M NaOH

The reaction profile in the acid base experiments was the opposite of that for the calibration of the calorimeter. Initially the 1.0M Sodium Hydroxide placed in the calorimeter was near ambient temperature, 20.7°C in calorimeter 1 and 20.9°C in calorimeter 2. When the 1.0M Hydrochloric Acid was added to the 1.0M Sodium Hydroxide solution, the temperature quickly rose to and stabilized at 26.0°C in calorimeter 1 and 26.1°C in calorimeter 2. The temperature rise in the solution indicated that the reaction was exothermic (the reaction gave off heat to its surroundings) (see Figure 4, next page)

Figure 4: Acid-Base Reaction - 1.0M HCl + 1.0M NaOH



$$\begin{aligned} \text{Mass}_{\text{soln}} &= (49.0\text{mL})(1\text{g}/1\text{mL})(1.00\text{g}) \\ \text{(from acid base reaction 1)} &= 49.0\text{g} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{soln}} &= (49.0\text{g})(4.184\text{ J/g} \cdot ^\circ\text{C})(5.3^\circ\text{C}) \\ \text{(from acid base reaction 1)} &= 1.1 \times 10^3\text{J} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{rxn}} &= -(1.1 \times 10^3\text{J} + (4.3 \times 10^1\text{J}/^\circ\text{C})(5.3^\circ\text{C})) \\ \text{(from acid base reaction 1)} &= -1.3 \times 10^3\text{J} \end{aligned}$$

$$\begin{aligned} \text{mol}_{\text{limiting reagent}} &= (24.0\text{mL})(1\text{L } 1.0\text{M HCl}/1000\text{mL})(1\text{mol HCl}/1\text{L } 1.0\text{M HCl}) \\ \text{(from acid base reaction 1)} &= 0.0240\text{mol HCl} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{rxn}}/\text{mol}_{\text{limiting reagent}} &= -1.3 \times 10^3\text{J}/0.0240\text{mol HCl} \\ \text{(from acid base reaction 1)} &= 5.4 \times 10^4\text{J/mol HCl} \end{aligned}$$

Table 3: Acid Base Neutralization Reaction – 1.0M HCl + 1.0M NaOH

Acid Base Reaction #1 – 1.0M HCl + 1.0M NaOH		
	Calorimeter 1	Calorimeter 2
Volume of NaOH	25.0mL	25.5mL
Volume of HCL	24.0mL	24.4mL
Total Volume of Solution	49.0mL	49.9mL
Initial Temperature of Solution	20.7°C	20.9°C
Final Temperature of Solution	26.0°C	26.1°C
ΔT of solution	5.3°C	5.2°C
Mass _{soln}	49.0g	49.9g

ΔH_{soln}	$1.1 \times 10^3 \text{ J}$	$1.1 \times 10^3 \text{ J}$
C_p calorimeter	$4.3 \times 10^1 \text{ J/}^\circ\text{C}$	$-6.9 \times 10^0 \text{ J/}^\circ\text{C}$
$\Delta H_{\text{calorimeter}}$	$2.3 \times 10^2 \text{ J}$	$-3.6 \times 10^1 \text{ J}$
ΔH_{rxn}	$-1.3 \times 10^3 \text{ J}$	$-1.0 \times 10^3 \text{ J}$
Moles _{limiting reagent}	$2.4 \times 10^{-2} \text{ mol}$	$2.44 \times 10^{-2} \text{ mol}$
$\Delta H(\text{rxn})/\text{mol}_{\text{limiting reagent}}$	$-5.5 \times 10^4 \text{ J/mol}$	$-4.3 \times 10^4 \text{ J/mol}$

Acid Base Reaction #2 – 6.0M HCl + 6.0M NaOH

The reaction profile in the 6.0M reaction was similar to that for the 1.0M reaction, except that the temperature increase in the solution was significantly greater as should be expected for the greater concentration (and hence greater number of moles reacting) of acid and base present. (see figure 5)

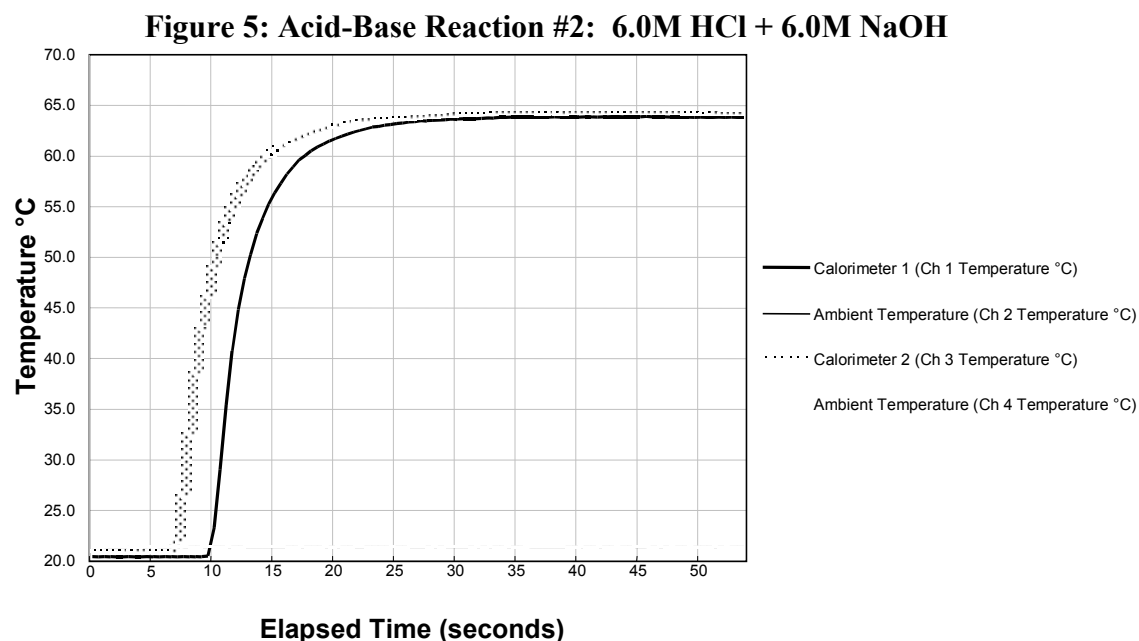


Table 4: Acid Base Reaction – 6.0M HCl + 6.0M NaOH

Acid Base Reaction #2 – 6.0M HCl + 6.0M NaOH	Calorimeter 1	Calorimeter 2
Volume of NaOH	25.0mL	25.0mL
Volume of HCL	24.9mL	25.0mL
Total Volume of Solution	49.9mL	50.0mL
Initial Temperature of Solution	20.4°C	21.0°C
Final Temperature of Solution	63.8°C	64.2°C

ΔT of solution	43.4°C	43.2°C
Mass _{soln}	49.9g	50.0g
ΔH_{soln}	$9.06 \times 10^3 \text{ J}$	$9.04 \times 10^3 \text{ J}$
C_p calorimeter	$4.3 \times 10^1 \text{ J/}^\circ\text{C}$	$-6.9 \times 10^0 \text{ J/}^\circ\text{C}$
$\Delta H_{\text{calorimeter}}$	$1.9 \times 10^3 \text{ J}$	$3.0 \times 10^2 \text{ J}$
ΔH_{rxn}	$-1.09 \times 10^4 \text{ J}$	$-8.7 \times 10^3 \text{ J}$
Moles _{limiting reagent}	$1.50 \times 10^{-1} \text{ mol HCl}$	$1.50 \times 10^{-1} \text{ mol HCl}$
$\Delta H(\text{rxn})/\text{mol}_{\text{limiting reagent}}$	$-7.3 \times 10^4 \text{ J/mol HCl}$	$-5.8 \times 10^4 \text{ J/mol HCl}$

The final step in the process was to take the results from each of the trials and calculate a mean ΔH_{rxn} for each mole of HCl:

Table 5: Mean $\Delta H_{\text{rxn}}/\text{mol HCl}$

Trial	$\Delta H_{\text{rxn}}/\text{mol HCl}$
1.0M HCl + 1.0M NaOH (calorimeter 1)	$-5.5 \times 10^4 \text{ J/mol HCl}$
1.0M HCl + 1.0M NaOH (calorimeter 2)	$-4.3 \times 10^4 \text{ J/mol HCl}$
6.0M HCl + 6.0M NaOH (calorimeter 1)	$-7.3 \times 10^4 \text{ J/mol HCl}$
6.0M HCl + 6.0M NaOH (calorimeter 2)	$-5.8 \times 10^4 \text{ J/mol HCl}$
Mean $\Delta H_{\text{rxn}}/\text{mol HCl}$	$-5.7 \times 10^4 \text{ J/mol HCl}$

Note that both of the 1.0M reactions were below the mean and both of the 6.0M reactions were above the mean.

Discussion

Despite the troublesome negative heat capacity for calorimeter 2 in the calibration runs, there was a reasonable correspondence between the average of -57kJ/mol for heat of neutralization for a reaction of hydrochloric acid and sodium hydroxide and the -56.2kJ/mol figure in Chang.(2) The most likely cause is that compared to the overall heat of reaction, the heat capacity of the calorimeters was small; thus the effect of the heat capacities on the final ΔH_{rxn} was minimal. Other potential sources of error include measurement error when measuring volumes of reagents, compromise of the insulating capacity of the calorimeter by unseen structural defects in the construction of the styrofoam cups, or a possible ‘chimney’ effect from either the temperature

probe or the funnel. The chimney effect should be considered improbable, however, as the penetrations of the lid were small in total proportion to the total lid area, and for a chimney effect to occur, some sort of 'heat current' would have to be established (to specifically direct the heat to the probe or funnel. There is nothing to suggest that any such current existed. A review of other thermochemistry studies is only suggested, if the heat loss persists after other more obvious corrections to experimental flaws have been corrected.

A suggestion to improve upon the calibration, is to better insulate the top of the calorimeter by making it from an insulator such as styrofoam. A plug of styrofoam cut to fit the calorimeter would be a good start. In addition, it is recommended that a stirrer be added to the assembly for agitating the solutions. Better mixing of the solutions without disturbing the calorimeter itself could improve results. Another possible improvement would be to use larger styrofoam cups so more solution could be employed without jeopardizing the insulating capacity of the calorimeter, as larger solutions are more likely to be forgiving of small errors.

The more interesting result was that the calculated heat of neutralization was much higher in the 6.0M hydrochloric acid plus 6.0M sodium hydroxide reactions. This suggests that higher concentrations of either the hydrochloric acid or the sodium hydroxide may yield heat independently of the neutralization reaction. A simple method of testing this hypothesis would be to simply dilute high concentration solutions of each reagent in distilled, de-ionized water and measure the enthalpy change.

These reactions are unlikely to have significant potential as an energy source. This can be demonstrated by comparison. As observed the figure obtained for the neutralization reaction was – 57 kilojoules per mole of hydrochloric acid. Given that one mole of hydrochloric acid has a mass of 36.46g (not counting its water solution), that means that approximately 1.6 kilojoules of heat is

generated per gram of hydrochloric acid. By way of comparison, glucose which is one of the poorer fuels (used by animals as a bodily source of energy), generates approximately 15.6 kilojoules per gram of glucose, and other fuels have much higher heat values (3)

References Cited

- (1) Cooper, Melanie M., *Cooperative Chemistry Laboratory Manual*, Third Edition; McGraw Hill, New York; 2006 , p 121-123
- (2) Chang, Raymond *General Chemistry: The Essential Concepts*, Fourth Edition; McGraw Hill, New York; 2006, p 183-186
- (3) Gutow, J; Matsuno, N.; Mihalick, J; *Enthalpy and Combustion*, revised 9/07; University of Wisconsin-Oshkosh; Oshkosh, Wisconsin