

Hess' Law and Heats of Neutralization

Objective: To determine the quantity of heat evolved in a series of acid-base reactions and use these ΔH values to calculate ΔH for another reaction.

Concept to be Tested: To show that neutralization reactions obey Hess' Law.

Text References: McMurray and Fay: Chapter 8.1-8.9.

Laboratory Techniques References: *General Lab Procedures* including *Safety in the Laboratory*

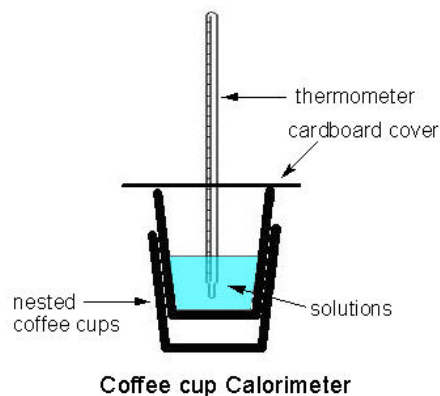
Introduction

Hess' Law states that *the heat evolved or absorbed in a chemical reaction is the same whether the reaction takes place as one or several reactions*. This law is also known as the Law of Constant Heat Summation and or simply as the Law of Summations. Stated another way, if a given chemical equation can be written as the sum of several other chemical equations, the enthalpy change, ΔH , of the first chemical equation equals the sum of the enthalpy changes of the other chemical equations.

This is explained by thermodynamic theory, which holds that enthalpy is a state function. Chemists have made great use of Hess' Law in establishing the heats of formation of compounds that are not easily formed from their constituent elements. This will be a key part of the experiment today. In this experiment, you will determine the heats of neutralization for three different acid-base reactions. Using this data you will calculate the heat of neutralization for a fourth acid-base reaction. Then you will compare your results to literature values.

The Coffee Cup Calorimeter

In today's experiment you will use a simple but highly efficient set up called a coffee cup calorimeter. Your calorimeter will consist of two nested Styrofoam[®] coffee cups, a thermometer, and a cover (cardboard is more efficient than foil as a cover). It is important that you note which cup is used as the inner cup and maintain this arrangement through the entire experiment. You must also use the same thermometer in the calorimeter throughout the experiment. (You cannot switch to the second thermometer without having to recalibrate your calorimeter.)



Thermometers and Temperature

The thermometers you use in the laboratory are reasonably precise and can be used to accurately measure changes in temperature. However, these same thermometers have not

been calibrated, so while a single thermometer may be highly precise when determining the temperature of the room or a solution, this temperature reading is probably not very accurate. Fortunately, this experiment only requires an accurate determination of the temperature changes involved and the laboratory thermometers perform this function very well.

There is one small catch in this. You will be required to use of two thermometers during this experiment. Before you can calibrate the calorimeter, you must first “calibrate” the two thermometers that you will use during the experiment. This is done by placing the two thermometers in a beaker of water and allowing them to equilibrate (come to a stable temperature reading). **While the thermometers are still in the beaker of water**, you will compare their temperature readings. **If** the two thermometers give **identical** temperature readings, **no correction** will be needed. If the two thermometers give **different** temperature readings, **a temperature correction will be necessary** before proceeding.

As previously stated, the laboratory thermometers are accurate and precise at measuring the magnitude of change in temperature (within 0.1 °C to 0.5 °C depending upon the skill of the observer). Since the energy lost or gained also depends upon the initial temperature reading of both liquids, it is necessary to “correct” the thermometer readings so that both thermometers produce the same temperature reading. It produces much less confusion if you use the thermometer in the calorimeter as the “master” thermometer and adjust the reading of the other thermometer accordingly.

Thermometer correction (if needed). The temperature correction is not as difficult as it sounds. If the two thermometers produce different readings, **while the thermometers are still in the beaker of water** clearly identify one of the thermometers (marker, string, tape, different color of liquid, etc.), record whether this thermometer reads higher or lower than the other, and what the difference in temperature reading is between these two thermometers. Now determine which thermometer you wish to use with the calorimeter.

- **If you use the thermometer with the higher reading in the calorimeter**, you will need to add the temperature difference you measured in your thermometer trial to the temperature reading of the second thermometer, the one with the lower reading (used for measuring the temperature of a second solution outside the calorimeter).
- **If you use the thermometer with the lower reading in the calorimeter**, you will need to subtract the temperature difference you measured in your thermometer trial to the temperature reading of the second thermometer, the one with the higher reading (measuring the temperature of a second solution outside the calorimeter).

Again, this is only necessary if the two thermometers you use in your experiment do not initially produce the same temperature reading for a beaker of water.

Calibration of Calorimeter

You are going to determine the heat of neutralization by measuring the temperature change of the resultant solution. When the neutralization takes place, the heat evolved is absorbed by the solution. This solution will be contained by the calorimeter and some of

the heat is “lost” to the calorimeter (the coffee cups, the thermometer, the air above the solution, and even the cardboard lid). Therefore you will need to determine the **calorimeter constant** before you proceed with the neutralization reactions.

Make certain to note which coffee cup is the inner cup and which thermometer you use in the calorimeter. You must use this arrangement for each of your experimental trials. If you use a lid, you must use that lid throughout the experiment. Otherwise, your calorimeter constant you calculate is invalid and a new calorimeter constant must be determined.

There are two assumptions that are made before determining this calorimeter constant:

1. The calorimeter constant is linear over the temperature range involved in this experiment.
 2. The calorimeter cools at a constant rate under the laboratory conditions.
- Barring any significant change in the technique you use (leaving the cover off the calorimeter, altering the construction of the calorimeter, etc.) or sudden dramatic change in the temperature of the laboratory ($> 30\text{ }^{\circ}\text{C}$) these assumptions are valid.

Determination of the calorimeter constant is relatively simple and it allows you to practice all the measurements and most of the calculations you will need for the neutralization experiments. This determination will be made by mixing hot water and cold (room temperature) water. In an ideal situation, the energy lost by the hot water should exactly equal the energy gained by the cold water. In fact, what should be seen is that more energy is lost by the hot water than is gained by the cold water. This “missing” energy was gained by the calorimeter when it was heated to the same final temperature as the cold water.

***Important!* When performing this part of the experiment make certain to run a quick check to make certain that the change in temperature of the hot water, ΔT_{hot} , is larger than the temperature change of the cold water, ΔT_{cold} . If this is not the case you must re-run the determination of the calorimeter constant.**

The “target” measurement is T_0 , the temperature at the “instant” of mixing. Unfortunately, this value cannot be measured directly and must be extrapolated from a graph of your data. There are a variety of reasons for this. The most significant of these is that the mixing is not instantaneous and both hot and cold spots exist for a short time within the calorimeter. Even if the mixing were perfect, the thermometer cannot to instantly produce the temperature of mixing. Waiting a minute or two for the system to equilibrate after mixing cannot be guaranteed to produce a good T_0 because the calorimeter and its contents are constantly losing heat to the surroundings (cooling off).

To determine the **temperature at mixing**, T_0 , you will need to record the temperature over roughly a 3 minute time period. A stopwatch will be needed for timing the reaction.

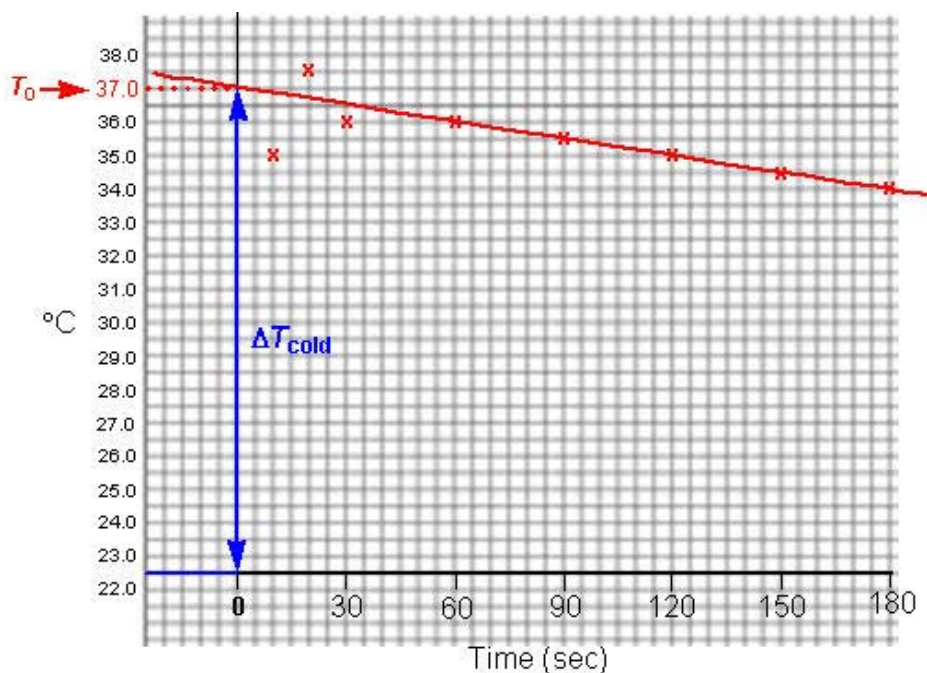
You will need to record the temperature (without removing the thermometer from the calorimeter) at 10-second intervals following the initial mixing. When the temperature remains constant *or* begins to cool extend the time interval to 30 seconds and continue this for a total of 3 minutes following the initial mixing. Since you are measuring the energy gained by the cold water *and* the calorimeter, the initial temperature (prior to mixing) is the temperature of the water in the calorimeter.

The best way to demonstrate the determination of T_0 is by working an example. This example will also demonstrate how to calculate the calorimeter constant.

Example 1. You place 50.0 mL of water into your clean and **dry** calorimeter. The temperature reading of the water in the calorimeter is determined to be 22.5 °C. The initial temperature of the 50.0 mL of hot water is 53.0 °C. You remove the lid of the calorimeter and rapidly pour in the hot water, quickly replace the lid, and record the following temperature readings:

| Time (sec) | Temp °C | Time (sec) | Temp °C |
|------------|---------|------------|---------|
| 10 | 35.5 | 90 | 35.5 |
| 20 | 37.5 | 120 | 35.0 |
| 30 | 36.0 | 150 | 34.5 |
| 60 | 36.0 | 180 | 34.0 |

Use this data to plot the temperature change. Use a ruler and position it to draw a **straight line** that *best* fits the data. The temperature at the point where this line intersects 0 sec is T_0 .



Plotting this data shows that $T_0 = 37\text{ °C}$.

Calculation of the Calorimeter Constant. Once you have established T_0 , the calculation of the calorimeter constant is relatively straightforward. First, you will use T_0 to calculate the ΔT_{hot} and ΔT_{cold} .

$$\text{Initial temp hot water} = 53.0\text{ }^{\circ}\text{C}$$

$$\text{Initial temp cold water} = 22.5\text{ }^{\circ}\text{C}$$

$$T_0 = 37.0\text{ }^{\circ}\text{C}$$

$$\Delta T_{\text{hot}} = 53.0\text{ }^{\circ}\text{C} - 37.0\text{ }^{\circ}\text{C} = 16.0\text{ }^{\circ}\text{C}$$

$$\Delta T_{\text{cold}} = 37.0\text{ }^{\circ}\text{C} - 22.5\text{ }^{\circ}\text{C} = 14.5\text{ }^{\circ}\text{C}$$

The energy lost by the hot water equals the energy gained by the water and the calorimeter. It is possible to calculate the energy lost by the hot water since the mass of water and ΔT_{hot} is known. It is also possible to calculate the energy gained by the cold water since both the mass of water and ΔT_{cold} are also known. The difference in these two values is the energy gained by the calorimeter (and the surroundings).

These energy values are calculated by the simple formula:

$$q = mC\Delta T$$

Assume that the density of water is 1.00 g/mL. The specific heat of water is 4.184 J/g \cdot $^{\circ}$ C.

$$\text{Energy lost by hot H}_2\text{O} = 50.00\text{ g} \times 4.184\text{ J/g}\cdot^{\circ}\text{C} \times 16.0\text{ }^{\circ}\text{C} = 3347.2\text{ J}$$

$$\text{Energy gained by cold H}_2\text{O} = 50.00\text{ g} \times 4.184\text{ J/g}\cdot^{\circ}\text{C} \times 14.5\text{ }^{\circ}\text{C} = 3033.4\text{ J}$$

$$\text{Difference in Energy} = 3347.2\text{ J} - 3033.4\text{ J} = 313.8\text{ J}$$

This difference is the amount of energy gained by the calorimeter. The calorimeter constant is determined by dividing this value by the temperature change of the calorimeter. **The ΔT of the calorimeter is equal to the ΔT of the cold water.**

$$\text{Calorimeter constant} = \frac{313.8\text{ J}}{14.5\text{ }^{\circ}\text{C}} = 21.6\text{ J/}^{\circ}\text{C}$$

This constant will be used throughout your calculations.

Heat of Neutralization

Since you have already determined the calorimeter constant, this portion of the experiment is relatively easy. You will need to clean and dry your calorimeter and reassemble it exactly as it was when you determined the calorimeter constant (same thermometer, same inner cup, etc.). You will now measure the heat evolved in the neutralization reactions.

You will need to record the molarity of each of the acids and bases that you use. You must also make certain that the initial temperatures of the acids and bases are identical. Typically you will use a clean and dry graduated cylinder to measure 50.0 mL of acid

solution. This solution will be placed into the calorimeter and the lid and thermometer replaced. Rinse and dry the graduated cylinder and then obtain 50.0 mL of the base. Place the second thermometer into the base and determine its temperature. You must adjust the temperature of this base to match that of the acid in the calorimeter. Remember to account for any thermometer correction that is needed. If your base is too cool, you can use the warmth of your hands to warm it or alternately hold it under cold water to cool it.

Once the temperature of the base matches that of the acid remove the lid of the calorimeter and rapidly add the base to the acid (*avoid splashing if at all possible*). Put the cover back onto the calorimeter and begin recording the temperature readings at 10-second intervals. After one minute record the temperature at 30-second intervals for 2 more minutes (3 min total).

You will need to plot this data as you did for the calorimeter constant in order to determine the T_0 for each of the neutralization reactions. Again, the calculations involved can best be demonstrated with an example.

Example 2. Fifty mL of a 3.0 M solution of a weak monoprotic acid, HA, is placed into a coffee cup calorimeter. This solution is initially at 23.0 °C. To this is added 50.0 mL of a 3.0 M NaOH solution initially at 23.0 °C. Assume that the density of all solutions and their mixture to be 1.00 g/mL and also assume that the specific heat of the mixture is 4.184 J/g·°C. The calorimeter constant was determined to be 21.6 J/°C. A plot of the temperature changes observed during the reaction indicated that T_0 for this reaction was 29.2 °C. Determine the energy liberated in this reaction and the molar heat of the neutralization.



mmol HA = 50.0 mL × 3.0 M = 150.0 mmol = 0.150 mol
mmol NaOH = 50.0 mL × 3.0 M = 150.0 mmol = 0.150 mol
(there is no limiting reagent in this reaction)

Total volume of solution = 50.0 mL acid + 50.0 mL base = 100.0 mL

Mass of solution = 100 mL × 1.00 g/mL = 100.0 g

$$\Delta T = T_0 - T_{\text{initial}} = 29.2 \text{ °C} - 23.0 \text{ °C} = 6.2 \text{ °C}$$

Energy absorbed by solution = 100.0 g × 4.184 J/g·°C × 6.2 °C = 2594 J

Energy absorbed by calorimeter = 21.6 J/°C × 6.2 °C = 134 J

Total energy produced by neutralization = 2594 J + 134 J = 2728 J

$$\text{molar heat of neutralization} = \frac{2728 \text{ J}}{0.150 \text{ mol}} = 1.82 \times 10^4 \text{ J/mol} = 18.2 \text{ kJ/mol}$$

Experimental Procedure

Calibration of Thermometers

Obtain two (2) 110 °C thermometers and a 250 mL beaker. Mark one of the thermometers so that it may easily be identified (tape, marker, color of liquid, etc.). Fill the beaker approximately half full with distilled water and place both thermometers into the beaker. Wait about 2 minutes and read the thermometers to the nearest 0.1°C while they are still immersed in the water. Record these readings on your data sheet. If there is no difference in the temperature, no correction will be necessary. Discard the water in the beaker and carefully dry the beaker.

If there is a difference in the reading, you will need to use the difference in values as a correction factor so that the two thermometers have “equivalent” readings.

Determination of Calorimeter Constant

Obtain two (2) Styrofoam[®] coffee cups, a cardboard lid, a 50 mL graduated cylinder, and a stopwatch. Assemble the calorimeter by placing cup inside the other (make certain to mark the inner cup). Carefully measure 50.0 mL of water in the graduated cylinder and pour this into the ***dry*** calorimeter. Place one of thermometers through the hole in the cardboard lid and place this onto the calorimeter. Make certain the bulb of the thermometer is submerged in the water. Allow this system to equilibrate while you are preparing the hot water.

Measure 50.0 mL of water into the graduated cylinder and place this in the ***dry*** 250 mL beaker. You will need to heat this sample of water to produce at least a 10-20 °C increase in temperature (an initial temperature of 50 °C or higher is good). If your laboratory has a microwave, heat the water in the microwave for 20 to 25 seconds. If there is no microwave, you will need to heat the water on a hot plate for a few minutes. After heating the water, removed the beaker from the microwave or hot plate, and place the beaker on a folded paper towel (or some other form of insulation) on the bench. Place the second thermometer into the beaker and with occasional gentle stirring with the second thermometer allow the water to “equilibrate” for 2 minutes.

Make certain you have everything in place to record data. Decide who will read the thermometer, who records the data, and who will handle the stopwatch. Make certain the stopwatch works and that you know how to work it. You may wish to practice while waiting for the heated water to stabilize.

Record the thermometer reading of the “cold” water in calorimeter and also record the thermometer reading of the “hot” water. In a smooth motion, remove the lid (and thermometer) of the calorimeter, pour in the hot water (***avoid splashing if possible***), replace the lid with thermometer **and** start the stopwatch. Record the readings of the thermometer in the calorimeter at 10-second intervals until the temperature begins to

decrease then increase the interval to 30-second readings. Record the temperature for a total of 3 min.

Make a quick *estimate* of T_0 – you do not need to be exact for this estimate. Then use this estimate to make certain that the ΔT_{hot} is larger than the ΔT_{cold} . If ΔT_{cold} is larger, you will need to repeat this part of the experiment.

Heats of Neutralization

NaOH is a strong corrosive that is especially hazardous to your eyes. HCl, acetic acid (CH_3COOH), and ammonia (NH_3) are also corrosive and each also has very irritating vapors. Take care when handling these solutions.

Part 1 Neutralization of HCl with NaOH

Rinse, dry, and reassemble the calorimeter. Measure 50.0 mL of 3.00 M HCl in a clean *dry* graduated cylinder and add it to the calorimeter. Replace the lid and thermometer. Clean and dry the graduated cylinder and obtain 50.0 mL of 3.00 M NaOH. Place the second thermometer into the NaOH. Record the volume and molarity of both the HCl and NaOH. Record the temperature of the HCl in the calorimeter. This is the initial temperature. Adjust the temperature of the NaOH so that it matches the temperature of the HCl in the calorimeter. You may warm the NaOH by using the warmth of your hand. If you need to cool the NaOH, you can do this by running cool water over the outside of the graduated cylinder.

Make certain the stopwatch is cleared and ready. Make certain that everything is in place to record temperature and time.

In a smooth motion, remove the lid (and thermometer) of the calorimeter, pour in the 50.0 mL of NaOH solution into the calorimeter (*avoid splashing if possible*), replace the lid with thermometer **and** start the stopwatch. Record the readings of the thermometer in the calorimeter at 10-second intervals for 1 minute then increase the interval between readings to 30-seconds. Record the temperature for a total of 3 min. This data will allow you to calculate the heat evolved in the reaction and the molar heat of this neutralization reaction. The solution in the calorimeter may safely be discarded in the sink. Rinse, dry, and reassemble the calorimeter. Rinse and dry the graduated cylinder.

Part 2 Neutralization of Acetic Acid with NaOH

Measure 50.0 mL of 3.00 M acetic acid, CH_3COOH in a clean *dry* graduated cylinder and add it to the calorimeter. Replace the lid and thermometer. Clean and dry the graduated cylinder and obtain 50.0 mL of 3.00 M NaOH. Place the second thermometer into the NaOH. Record the volume and molarity of both the CH_3COOH and NaOH. Record the temperature of the CH_3COOH in the calorimeter. This is the initial temperature. Adjust the temperature of the NaOH so that it matches the temperature of the CH_3COOH in the calorimeter. You may warm the NaOH by using the warmth of your hand. If you need to

cool the NaOH, you can do this by running cool water over the outside of the graduated cylinder.

In a smooth motion, remove the lid (and thermometer) of the calorimeter, pour in the 50.0 mL of NaOH solution into the calorimeter (*avoid splashing if possible*), replace the lid with thermometer **and** start the stopwatch. Record the readings of the thermometer in the calorimeter at 10-second intervals for 1 minute then increase the interval between readings to 30-seconds. Record the temperature for a total of 3 min. This data will allow you to calculate the heat evolved in the reaction and the molar heat of this neutralization reaction. The solution in the calorimeter may safely be discarded in the sink. Rinse, dry, and reassemble the calorimeter. Rinse and dry the graduated cylinder.

Part 3 Neutralization of Acetic Acid with Ammonia

Measure 50.0 mL of 3.00 M acetic acid, CH₃COOH in a clean *dry* graduated cylinder and add it to the calorimeter. Replace the lid and thermometer. Clean and dry the graduated cylinder and obtain 50.0 mL of 3.00 M ammonia, NH₃. Place the second thermometer into the ammonia solution. Record the volume and molarity of both the CH₃COOH and NH₃. Record the temperature of the CH₃COOH in the calorimeter. This is the initial temperature. Adjust the temperature of the NH₃ so that it matches the temperature of the CH₃COOH in the calorimeter. You may warm the NH₃ by using the warmth of your hand. If you need to cool the NH₃, you can do this by running cool water over the outside of the graduated cylinder.

In a smooth motion, remove the lid (and thermometer) of the calorimeter, pour in the 50.0 mL of NaOH solution into the calorimeter (*avoid splashing if possible*), replace the lid with thermometer **and** start the stopwatch. Record the readings of the thermometer in the calorimeter at 10-second intervals for 1 minute then increase the interval between readings to 30-seconds. Record the temperature for a total of 3 min. This data will allow you to calculate the heat evolved in the reaction and the molar heat of this neutralization reaction. The solution in the calorimeter may safely be discarded in the sink.

You will use this data to calculate the molar heat of neutralization of HCl with ammonia.

Cleanup

Clean and dry the coffee cups. Return the coffee cups, the cardboard lid, and the stopwatch to the appropriate supply bin. Rinse and dry the graduated cylinder, thermometers, and the beaker and return them to the appropriate storage areas. All solutions may safely be discarded down the drain.

Safety

All of the solutions are corrosive irritants. The NaOH is particularly hazardous to your eyes. Eye protection must be worn at all times you are in the laboratory. Acetic acid, HCl and ammonia also have highly irritating fumes. If you are wearing contact lenses, you must wear completely enclosed goggles – do not remove your goggles during the laboratory. All solutions may safely be discarded down the drain. Wash your hands before leaving the laboratory.

