

Thermochemistry

Background

Most all chemical reactions give off or absorb some form of heat. It is usually of great interest to know precisely how much, and the determination of heats of reactions (by two different methods) is what this lab will illustrate.

Determination of heats of reaction by calorimetry

It is impossible to measure the heat of a reaction directly. That is, we can't just stick some kind of probe into a burning fire (for example) and have the probe tell us that the reaction is giving off 5000 joules of heat. Instead, we have to measure it indirectly, via its effect on its surroundings. You'll be doing that in the lab today.

How do we do that? Well, for the lab today (and in general), we need to know a couple of things before we start:

- Energy can be neither created nor destroyed in an ordinary chemical reaction. This is the First Law of Thermodynamics.
- The amount of heat that something of constant mass has evolved or absorbed is given by the formula $q = m S \Delta T$. Here, q is the heat evolved or absorbed (in Joules), m is the mass of the object, S is its "specific heat capacity" (the amount of heat required to raise the temperature of one gram of the object by 1°C), and ΔT is the change in temperature the object experiences. ΔT is *always* taken to be T_f (final temperature of the object) - T_i (initial temperature of the object).

How do the above two facts help us determine a heat of reaction? Well, the First Law of Thermodynamics tells us that whatever heat the reaction produces or consumes (this is also called the "Enthalpy of Reaction") has to go somewhere or come from somewhere. Where does it come from or go to? The surroundings, of course, and we can calculate the amount of heat the surroundings absorbed or gave off using the second fact above, given that our surroundings have a constant mass (they will for the lab today).

In addition, because there can be no net creation or destruction of heat, the heat absorbed or donated by the surroundings must exactly match the amount of heat evolved or absorbed by the reaction. We write this in mathematical terms as $q_{\text{rxn}} + q_{\text{surr}} = 0 \text{ J}$. Here, q_{rxn} is the heat evolved or absorbed by the reaction, and q_{surr} represents the same thing for the surroundings.

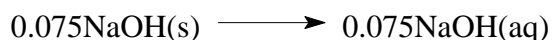
So, using all of the above, we could drop (say) 3 grams of sodium hydroxide in 100 grams of water and watch the sodium hydroxide dissolve. The reaction here (such as it is) would be the dissolution of three grams of sodium hydroxide. By the time the reaction has finished, the heat it evolved or absorbed would be being absorbed by not only the 100 grams of water used, but by the three grams of sodium hydroxide as well. We would say, therefore, that our surroundings consisted of 103 grams of solution and calculate q_{surr} using that mass.

Once we'd calculated q_{surr} (using $mS\Delta T$), we could then calculate q_{rxn} , the heat the reaction gave off, by using the relation that $q_{\text{rxn}} + q_{\text{surr}} = 0 \text{ J}$.

But what to do with that? We want ΔH for the reaction, not q_{rxn} . We start out by noting that, when carried out at constant pressure, the heat a reaction absorbs or evolves *is* ΔH for that reaction. Easy enough.

But what reaction? The ΔH we've just determined is for 3 grams of NaOH dissolving. That, in and of itself, is not really a useful piece of information; chemical equations use *moles* and not grams. It's easy enough to convert 3 grams of NaOH to moles (it's 0.075 moles), so now we know how much heat is associated with the dissolution of 0.075 moles.

Thing is, though, that you'll very rarely see a chemical reaction written like:



Instead, you're used to seeing



This latter equation (and others like it, of course) is what we're after in the lab today. How do we get from one to the other? Divide both sides of the first equation by 0.075. When you do that, be *sure* to divide the ΔH by 0.075 as well, to keep it consistent.

Verification of Hess' Law Using an Acid/Base Reaction

It's not always practical to determine a heat of reaction by throwing the chemicals together and hoping for the best. You might get side products or explosions, or the reaction might occur so slowly it's impossible to measure its enthalpy accurately.

What to do then? The lab today illustrates one solution to that problem, that being Hess' Law. Hess' Law says, very simply, that if two reactions add to give a third, then the enthalpy of reaction for the third reaction is the sum of the enthalpies of reaction for the first two reactions. As an example, have a look at

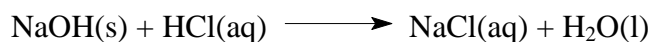


The two reactions above add to give



Since the two reactions above add to give the third, their enthalpies add to give the enthalpy of reaction for the third as well, namely -10 kJ .

You will be determining the ΔH values for three reactions in the lab today:



These three reactions are interesting in that any two of them (given suitable rearrangement) will add to give the third (you can verify this for yourself). Because of this, the enthalpies for the two reactions being added should (after suitable modification) add to give the enthalpy of reaction for the third reaction.

Useful Data

In the lab today, all experiments are being carried out at constant pressure (we don't get many tornados passing through), so all q_{rxn} 's calculated in the lab today may be safely assumed to be equal to a ΔH as outlined above.

We are also assuming that the surroundings consist only of the solution in which the reaction is carried out, and ignore any heat being absorbed or given off by the calorimeter that you are using as the reaction vessel.

In addition (and finally), we assume that the density of all solutions used is 1.00 g/mL (which makes determining their mass a simple task), and that the specific heat capacity of the HCl and NaOH solutions is the same as that of water, namely 4.184 J/g-°C.

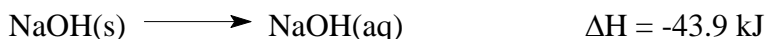
Pre-Lab Exercises

- 1) In one experiment, 3.00 grams of NaOH (molar mass 40.00 grams) was mixed with 75.0 mL of 1.00 M HNO₃. If the initial temperature of the HNO₃ was 21.6°C and the final temperature of the solution 43.4°C, determine ΔH for the reaction



[Ans: -94.9 kJ]

- 2) The following experimental enthalpy of reaction values were determined:



Two of the reactions above add, without modification, to give the third.

- Which two?
- What ΔH do they predict for the third reaction?
- Is the value predicted within five percent of what was determined experimentally?

Equipment Required

To do the lab today, you will need:

- Two Styrofoam cups and one lid
- One 250-mL beaker
- One 150-mL (or similar size) beaker
- One thermometer
- A triple-beam balance
- One small weigh boat
- One scoop
- A 50- or 100-mL graduated cylinder

Procedure

You are to work in pairs today. Each partner will do each of the experiments once.

For all experiments, assemble the calorimeter by stacking one Styrofoam cup inside the other, then putting the two cups inside the 250-mL beaker. Put the thermometer through the hole in the centre of the plastic lid (if there isn't a hole at the centre of your plastic lid make one, but *not* with the thermometer), and put the lid on the Styrofoam cup.

Part 1: Determination of the Heat Capacity of the Calorimeter

- 1) Assemble your calorimeter (two cups stacked inside the 250-mL beaker). Record the mass of the empty assembly.
- 2) Using a graduated cylinder, pour 50.0 mL of water into your calorimeter. Record the mass of this assembly (using the triple-beam balance).
- 3) Determine the initial temperature of the water in the calorimeter.
- 4) Obtain two pieces of ice and wipe them dry. Quickly place them in the calorimeter (with the water) and cover the calorimeter with a lid.
- 5) When the ice has melted, swirl the water gently to achieve thermal equilibrium then record the temperature of the water in the calorimeter.
- 6) Remove the lid and reweigh the calorimeter and water (to determine the mass of ice added).
- 7) Pour the water out of your calorimeter and dry it.
- 8) Repeat steps 1 – 7 one additional time (for a total of two runs).

Part 2: Enthalpy of solution of solid sodium hydroxide

- 1) Record the mass of your empty calorimeter.
- 2) Pour 100.0 mL of water into your calorimeter (use a graduated cylinder to measure it). Record the mass of the water and calorimeter.
- 3) Swirl the water gently to achieve thermal equilibrium then record the temperature of the water as precisely as your thermometer allows (the precision will vary depending on the type of thermometer you have).
- 4) Determine the mass of a small weigh boat using the triple-beam balance.
- 5) Add about three grams of sodium hydroxide pellets to the weigh boat. Record the mass of NaOH and weigh boat.
- 6) Lift the lid from the apparatus enough so that you can add the NaOH pellets into the water. Add the pellets, and then replace the lid. Swirl the apparatus and watch the thermometer. Record the highest stable temperature the thermometer reads. Afterwards, remove the lid and check to make sure that all the sodium hydroxide has dissolved. If some remains visible, replace the lid and continue swirling and re-read the highest stable temperature.
- 7) Remove the lid and thermometer.

- 8) Empty and clean your calorimeter.
- 9) Repeat steps 1 – 8 for one additional sample of NaOH (for a total of two runs).

Part 3: Enthalpy of neutralization of solid sodium hydroxide by hydrochloric acid

- 1) Record the mass of your empty calorimeter.
- 2) Use a graduated cylinder to dispense 50.0 mL of 0.500 M HCl and 50.0 mL of water into the (now cleaned) calorimeter.
- 3) Record the mass of your calorimeter and contents.
- 4) Replace the lid and thermometer, swirl, and allow the mixture to come to a constant temperature.
- 5) Record the temperature of the solution as accurately as your thermometer allows.
- 6) Determine the mass of a small weigh boat using the triple-beam balance.
- 7) Add about one gram of sodium hydroxide pellets to the weigh boat. Determine the mass of the weigh boat and pellets and record the mass.
- 8) Lift the lid from the apparatus enough so that you can add the NaOH pellets into the water. Add the pellets, and then replace the lid. Swirl the apparatus and watch the thermometer. Record the highest stable temperature the thermometer reads.
- 9) Remove the lid and thermometer.
- 10) Empty and clean your calorimeter.
- 11) Repeat steps 1 – 10 for one additional sample of NaOH (for a total of two runs).

Part 4: Enthalpy of neutralization of aqueous sodium hydroxide by hydrochloric acid

- 1) Record the mass of your empty calorimeter.
- 2) Dispense 50.0 mL of 0.500 M HCl into your calorimeter. Record the temperature of this solution as precisely as your thermometer allows.
- 3) Record the mass of the calorimeter and HCl solution.
- 4) Rinse and dry your thermometer.
- 5) Obtain a clean and dry 150-mL beaker.
- 6) Use a graduated cylinder to dispense 50.0 mL of 0.500 M NaOH into a clean, dry beaker. Record the temperature of this solution as precisely as your thermometer allows.
- 7) Rinse and dry your thermometer and replace it in the calorimeter assembly.
- 8) Add the NaOH solution to the HCl solution and replace the lid on the calorimeter. Swirl the calorimeter and watch the temperature. Record the highest stable temperature the thermometer shows.
- 9) Empty and clean your calorimeter.

10) Repeat steps 1 – 9 for one additional sample of NaOH (for a total of two runs).

Treatment of Data

Using the data from part 1, calculate the heat capacity of the calorimeter. For each of your trials in parts 2, 3, and 4 (there should be six in total), calculate:

1) The heat evolved or absorbed by the surroundings (the solution and calorimeter).

2) ΔH for each of the three reactions:



3) Two of the reactions above add, without modification, to give the third.

a) Which two?

b) What ΔH do they predict for the third reaction?

c) Is the value predicted within five percent of what was determined experimentally?

Discussion

State Hess' Law in your own words. Do the results you obtained in this lab support Hess' Law? Give one possible source of error (beyond your reasonable control) that might cause your results to not support Hess' Law. Explain its effect on your results.