

Calorimetry and the Heat of Neutralization of Acid-Base Reactions

INTRODUCTION

In this experiment, you will determine the molar heats of reaction ($\Delta H_{\text{neutralization}}$) of four acid-base neutralization:

- Strong acid/strong base HCl / NaOH
- Strong acid/weak base HCl / NH_4OH
- Weak acid/strong base $\text{HC}_2\text{H}_3\text{O}_2$ / NaOH
- Weak acid/weak base $\text{HC}_2\text{H}_3\text{O}_2$ / NH_4OH

BACKGROUND

Acid-Base Reactions

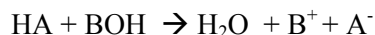
When acids and bases combine with one another in a neutralization reaction, heat energy is produced and liberated. We can measure the amount of heat energy released (q) by use of a simple calorimeter. The heat produced by the reaction can then be used to determine the molar heat of neutralization (ΔH_{neut}), which is the heat released per mole of acid or base reacting.

The Bronsted-Lowry concept for an acid is any molecular species which increases the concentration of H^+ ions in aqueous solution. Bases increase the hydroxide ion (OH^-) concentration in aqueous solution.

A strong acid is an acid which easily and frequently dissociates, *i.e.*, easily generates protons (H^+ ions) in solution. Hydrochloric acid is an example of a strong acid. HCl nearly completely dissociates into H^+ and Cl^- ions in solution. A weak acid infrequently dissociates in solution. Acetic acid is an example of a weak acid. It dissociates according to the reaction: $\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$. The equilibrium lies far to the left. At any given moment, there are only a small percentage of acid molecules dissociated.

In a similar manner, we can speak of bases as strong or weak depending on their tendency to separate into a positive ion and OH^- . Sodium hydroxide (NaOH) is a strong base that completely dissociates into Na^+ and OH^- ions when dissolved in water. Ammonium hydroxide (NH_4OH), produced when ammonia (NH_3) dissolves in water only partially dissociates into ammonium and hydroxide ions: $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$. This equilibrium lies far to the left; therefore, a small percentage of the hydroxide ions are released into solution.

When an acid and base are combined, water and a salt are produced. We will consider only monoprotic acids and bases with a single hydroxide in this experiment. Therefore, our general reaction will be:

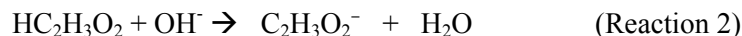


Heat is generated as the hydrogen ion and hydroxide ion combine to form water. The bond between H^+ and OH^- in water is strong, generally stronger than the bonds in weak acids or bases, causing the reaction to be exothermic. Because of the great excess of water solvating the ions, the attraction of B^+ toward A^- is weak, at this point we will assume it is zero

When both the acid and the base are strong, or fully dissociated into ions, the net ionic equation for the neutralization reaction follows. The energy released is high.

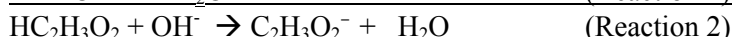


When the acid or the base is weak, the net ionic equation must show the weak acid or weak base together, and not dissociated.



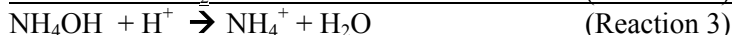
Additional energy is required to pull the H^+ from the rest of the weak acid (reaction 2), or OH^- from the rest of the weak base (reaction 3). We would expect less heat released in the neutralization, as some heat is required to break the bond in the acid or the base.

We can refer to the energy of the neutralization reaction as a difference of *the energies of bond making minus the energies of bond breaking*. For a strong acid and strong base; the energy of reaction is the energy of formation of H_2O only. For a weak acid reacting with a strong base we have to consider two reactions:



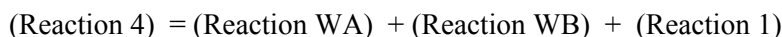
The energy of reaction will be the energy released to form water – the energy required to break $\text{HC}_2\text{H}_3\text{O}_2$
 (Reaction 2) = (Reaction WA) + (Reaction 1)

For a weak base reacting with a strong acid, we also have two reactions:



The energy of the reaction will be the energy to form water minus the energy to break NH_4OH .
 (Reaction 3) = (Reaction WB) + (Reaction 1)

If we have a weak acid and a weak base, we must consider three energies: the energy to form water minus the energy to break apart the weak acid and the energy to break apart the weak base.



We can put all of this together in Hess's Law: "If a reaction is the sum of two or more other reactions, the enthalpy change for the overall process is the sum of the enthalpy changes for the constituent reactions."

If we know the enthalpy change for a strong acid and strong base, strong acid/weak base, weak acid/strong base and weak base/weak acid, we can separate out the various enthalpies of reaction, as shown above. Note: The energy required to break the bond for the weak acid or weak base is positive (energy required = endothermic). The energy produced from the formation of water (reaction 1) is negative (energy produced = exothermic).

Measuring the heats of neutralization by calorimetry

Heat is generated by our reacting system. We will assume all of this heat goes into two functions – heating the liquid in the system and heating the calorimeter. We can express the heat of the reaction as follows:

$$-q_{\text{system}} = q_{\text{surroundings}}$$

Our reaction is the system being studied. The reaction transfers the heat it produces to the surroundings: the calorimeter and the solution.

$$-q_{\text{reaction}} = q_{\text{solution}} + q_{\text{calorimeter}}$$

The “solution” in this equation is the mixture of the solutions of acid and base. The solutions are not “pure” water. Use the density of 1.03 g/mL and specific heat of 4.05 J/g•C° in calculations. The mass of the solution is just the combined masses of the acid and base solutions. For the calorimeter, you will have already determined its heat capacity.

In each neutralization reaction, you will be working with 50.0 mL of 2.00 M acid and base. From these values, you can determine the moles of acid or base reacting. You can then use the heat of the reaction previously determined to calculate the molar heat of neutralization:

$$\Delta H_{\text{neut}} = \frac{q_{\text{reaction}}}{\text{mol}_{\text{acid}}}$$

PROCEDURE

Determining the Heats of Neutralization for various acid-base reactions:

You will examine the following combinations of acids and bases:

- Strong acid/strong base HCl / NaOH
- Weak acid/strong base HC₂H₃O₂ / NaOH
- Strong acid/weak base HCl / NH₄OH
- Weak acid/weak base HC₂H₃O₂ / NH₄OH

1. Prepare a table for the four reactions, listing volume acid, volume base, and initial and final temperatures. The initial temperature of acids and bases should be the same (room temperature). Note: When the acid and base are combined, there will be an increase in temperature.

For each acid/base combination, you will carry out the following steps:

2. Measure 50.0 mL of the 2.0 M acid and place in the calorimeter.
3. Measure and record the temperature.
4. Measure 50.0 mL of the 2.0 M base.
5. Pour the base into the calorimeter and very carefully stir the acid and base with your thermometer. Record the highest observed temperature.
6. The solutions are no longer "pure" water. Use the density of 1.03 g/mL and specific heat of 4.05 J/g•C°.
7. Calculate the heat produced by the reaction (q) and the molar ΔH_{neut} for the acid / base combination.
8. Report your data to your instructor to provide to the full class for interpretation.
9. Obtain full class data.

Thermochemistry (Acid-Base Neutralizations) Experiment • Assignment & Report Guidelines

READING Experiment – Lab Manual Pages
Chemistry, 5th ed. by Silberberg: Chapter 6

PRE-LAB Begin the prelab on a new page of your laboratory notebook. **ALL elements of the pre-lab MUST be completed before an experiment is started.**

Heading

- Title of experiment and number, your name, the dates of the experiment.

Purpose

- Briefly, but specifically explain the purpose of the experiment. In this experiment, there is more than one.

Chemical Reactions

- **In your notebook, provide both the MOLECULAR and the NET IONIC equations for each reaction we will carry out.**
- *Note:* Treat strong acids and bases as being completely dissociated in water, and weak acids and weak bases as if they do not dissociate as reactants (but will be dissociated after the reaction). For example:

$\text{H}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$ for hydrochloric acid as a reactant.
 $\text{CH}_3\text{COOH}_{(\text{aq})}$ for acetic acid as a reactant.

Strong Acid / Strong Base: $\text{HCl}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow$

Weak Acid / Strong Base: $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow$

Strong Acid / Weak Base: $\text{HCl}_{(\text{aq})} + \text{NH}_4\text{OH}_{(\text{aq})} \rightarrow$

Weak Acid / Weak Base: $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{NH}_4\text{OH}_{(\text{aq})} \rightarrow$

General Strategy

- **Summarize** the procedure of the experiment, and **explain** how you will use the data you measure to determine the quantities you want to find. Showing the important equations can be helpful.

Data Table

- On a **NEW** page, prepare a table for each part of the experiment that includes space for recording each quantity you will measure in the lab.

Answers to Pre-Lab Questions

MINI-LAB REPORT Begin the lab report section on a new page of the lab notebook.

Heading

- Title of experiment and number, your name, name of any lab partner(s), and the date(s) of the experiment.

Data / Observations / Results

- ORIGINAL Quantitative & Qualitative DATA (signed data pages from your lab notebook).

Calculations / Results

- Show calculations for the ΔH of the acid-base reactions in your report. Use the proper format for labeling and showing calculations in a formal report. **Show a full calculation for at least one system.**
- In your notebook, summarize the full results for the ΔH of the four reaction systems that you determined in the lab.

Discussion & Conclusions / Answers to Post-Lab Questions

- **No formal discussion is needed in the lab manual. The post-lab / discussion question worksheet asks for an analysis of your data and the class data.**

PRELAB QUESTIONS

Buffy carries out a neutralization reaction in her Styrofoam cup calorimeter, with a heat capacity of $41 \text{ J/}^\circ\text{C}$. She mixes 25.0 mL of 3.0 M acid solution and 25.0 mL of 3.0 M base solution at $22.3 \text{ }^\circ\text{C}$. (Assume the density and the heat capacity of her solutions are the same as those in your experiment.) The temperature rose to $36.5 \text{ }^\circ\text{C}$.

- 1) Calculate the heat energy absorbed by the solution (q_{solution}).
- 2) Calculate the heat energy absorbed by the calorimeter. ($q_{\text{calorimeter}}$).
- 3) Calculate q_{reaction} .
- 4) Calculate the number of moles of acid reacting.
- 5) Calculate the ΔH_{neut} of the reaction in Joules/mole
- 6) How does the q_{reaction} value differ from $\Delta H_{\text{neutralization}}$? Which value is an intensive property? Explain.

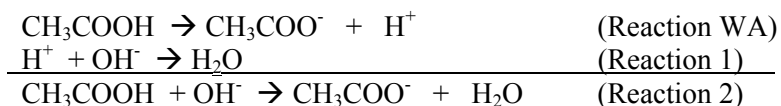
POSTLAB QUESTIONS – *Discussion of Individual & Class Data and Application of Hess's Law*

1. Complete the following table:

System	Molecular Equation	ΔH (kJ) <i>(your data)</i>	ΔH (kJ) <i>(class average)</i>
	Net Ionic Equation		
#1 SA/SB			
#2 WA/SB			
#3 SA/WB			
#4 WA/WB			

2. Do *your* values of ΔH for each reaction follow the expected trend? Do the *class average* values of ΔH for each reaction follow the expected trend? Briefly explain.

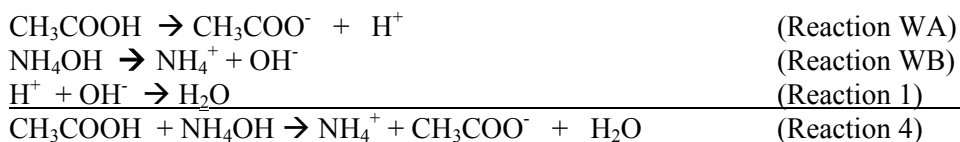
3. Given Hess's Law, you should now be able to determine the ΔH for Reaction WA below, and Reaction WB.



$$\Delta H_2 = \Delta H_{\text{WA}} + \Delta H_1$$

Using the *class average* values above, calculate the value for ΔH_{WA} .

4. In a similar manner, and using *class average* values, calculate ΔH_{WB} . Show the setup of the Hess's law determination, as in #3 above.
5. Does it take more or less energy to break the weak acid bond or the weak base bond (compare ΔH_{WA} & ΔH_{WB})? Are the reactions endothermic or exothermic? Discussing bond breaking / forming, explain why.
6. You should now be able to verify that your experimental ΔH_4 agrees with ΔH_4 calculated from the weak acid dissociation, weak base dissociation, and the reaction of hydrogen and hydroxide ions:



Calculate a value for $\Delta H_{4,\text{calc}}$?

Determine the % difference between your *calculated* and *experimental* values for the ΔH_4 .