1 Thermochemistry: Hess' Law

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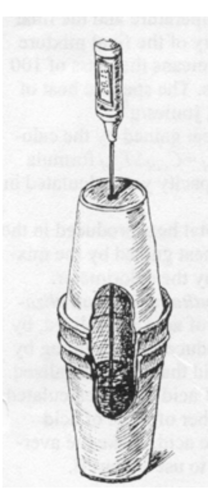
- **Measure temperature changes that take place in a calorimeter during neutralization reactions and use the measurements to calculate enthalpy of reaction.**
- **Compare the enthalpy of neutralization of a strong acids and the enthalpy of solution of a solid base, and use these measured values to illustrate the validity of Hess' Law**
- **Use Hess' Law to calculate the enthalpy values for steps in a reaction that were not measured.**



DISCUSSION

In this experiment, you will measure the enthalpy of neutralization for hydrochloric acid both with aqueous sodium hydroxide and with solid sodium hydroxide. You will also measure the enthalpy of solution when solid sodium hydroxide is dissolved in water. From the results you will verify Hess' Law.

You will use two simple calorimeters, each one made from four plastic foam cups, and you will also need two thermometers. Note the diagram below that illustrates a cross section of the apparatus

Heat Capacity of the Calorimeter

First you will determine how much heat is gained by the calorimeter when the temperature increases inside it. This heat gain divided by the temperature change is called the *heat capacity* of the calorimeter. The following equation illustrates the relation between the heat capacity and the change in temperature of the calorimeter.

$$q_{cal} = C_{cal}\Delta T_{cal}$$

or

$$C_{cal} = \frac{q_{cal}}{\Delta T_{cal}}$$

where

q_{cal} =the heat gained by the calorimeter
C_{cal}=the heat capacity of the calorimeter
ΔT_{cal}=the change in temperature of the calorimeter

Enthalpy of Neutralization of a Strong Acid and a Strong Base

Next you will measure the enthalpy of reaction when aqueous hydrochloric acid neutralizes aqueous sodium hydroxide. Both of these compounds are strong electrolytes, and in 1.0 *M* solutions they are completely ionized.

Notice from the following equations that the driving force for the reaction is simply the formation of water from the hydrogen and hydroxide ions. There are no covalent bonds to be broken before water is formed.

molecular equation

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

ionic equation

H^+ + ~~Cl^-~~ + ~~Na^+~~ + OH^- → ~~Na^+~~ + ~~Cl^-~~ + $H_2O(l)$

net-ionic equation

$$H^+ + OH^- \rightarrow H_2O(l)$$

Enthalpy of Solution of Solid Sodium Hydroxide

In this step you will measure the amount of heat that is released when solid sodium hydroxide is dissolved in water.

$$NaOH(s) \rightarrow NaOH(aq)$$

Enthalpy of Neutralization of a Strong Acid and a Solid Strong Base

In this step, you will measure the enthalpy of reaction when solid sodium hydroxide is neutralized by 1.0 *M* hydrochloric acid. This is a combination of two of the steps above.

For this and each of the preceding steps, you will be able to calculate heat absorbed or lost by any solution in the calorimeter by using the equation:

$$q = m\,C\Delta T$$

where

q=the heat lost or gained by the solution
m=the mass of the solution
C=the specific heat of the solution
ΔT=the change in temperature of the solution.

Hess' Law

Reactions seldom proceed exactly as they are written in a balanced chemical equation.

Instead, the reactants pass through a number of intermediate steps before they become the indicated products. Hess' Law says that the enthalpy of the overall reaction is the sum of the enthalpies of the intermediate steps.

The neutralization of solid sodium hydroxide with hydrochloric acid can be considered as a two-step process. First, the sodium hydroxide dissolves. Then the hydrochloric acid reacts with the aqueous sodium hydroxide. The enthalpies of these two steps should add up to the enthalpy of the combined process. Since you will measure all three of these enthalpies individually, you will be able to verify Hess' law.

PROCEDURE

A. Heat Capacity of the Calorimeter

1. Place two thermometers in tap water for one minute, and compare their readings to the nearest 0.1°C. Record the difference in the readings. If this difference is non-zero, remember to correct the recorded temperature of one of the thermometers throughout the experiment.

Select one of these thermometers as the main thermometer to be used for all temperature changes. Label it.

Also select two calorimeters from the desk at the front of the laboratory room. Label one of these calorimeters as the main calorimeter.

2. Place 50.0 mL of cold tap-water (20°C to 24°C) in the main calorimeter. Measure and record the water's temperature.

3. Then place 50.0 mL of hot tap-water (40°C to 44°C) in the other calorimeter. Measure and record this temperature.

4. Quickly mix the two by placing the warm water into the main calorimeter (with the cold water). Replace the lid and the thermometer and slowly swirl the water inside. Watch the temperature for the next minute. Record the highest temperature that you observe.

For Steps 5 and 6 that follow, use $q=mC\Delta T$ to calculate the heat. The final temperature for both the warm and for the cold water is the highest reading that you observed when you mixed the two together. Use 1.0 g/mL as the density of water and 4.18 joules/g·˚C as the specific heat of water.

5. Now calculate the amount of heat that has been lost by the warm water.

6. Calculate the amount of heat gained by the cold water.

7. Find the difference between the heat lost by the warm water and the heat gained by the cold water. This equals the heat gained by the calorimeter (q_{cal}).

8. Finally, divide the heat gained by the calorimeter by the change in temperature of the cold water, and calculate the heat capacity for the calorimeter (C_{cal}):

$$C_{cal} = \frac{q_{cal}}{\Delta T_{cal}}$$

- **For Parts B and D, use 1.02 g/mL as the density of the final mixture and 4.02 J/g^o C as its specific heat.**
- **For Part C, use 52 g as the mass of the solution and 3.93 J/g^{o}C as its specific heat.**
- **The enthalpy of the overall reaction is the sum of the enthalpies of the intermediate steps.**

B. Enthalpy of Neutralization of a Strong Acid and a Strong Base

Place 50.0 mL of 1.0 *M* HCl*(aq)* in the main calorimeter, and then place 50.0 mL of 1.0 *M* NaOH*(aq)* in the other calorimeter. Place the lids and the thermometers in the calorimeters, and measure the temperatures after about a minute.

9. Record the temperature of the HCl*(aq)*.
10. Record the temperature of the NaOH*(aq)*.
11. Take the average of these two temperatures as your starting temperature.
12. Pour the NaOH solution into the HCl solution, and mix them together. Replace the lid and the thermometer, and watch the temperature for about two minutes or until it reaches a high point and then starts to fall. Record the highest temperature as the final temperature.
13. Calculate the heat gained in the mixture of solutions by using the $q=mC\Delta T$ formula. For the ΔT value, take the difference between the starting temperature and the final temperature. The density of the final mixture will be **1.02 g/mL**; this means the mass of 100 mL would be 102 grams. The specific heat of the final mixture is **4.02 J/g·˚C**.
14. Calculate the heat gained by the calorimeter by using the $q_{cal} = C_{cal}\,\Delta T_{cal}$ formula and the average heat capacity you calculated in Part A.
15. Calculate the total heat produced in the reaction by adding the heat gained by the mixture to the heat gained by the calorimeter.
16. Calculate the *enthalpy of neutralization*, in kilojoules per mole of acid neutralized, by taking the total heat produced and dividing by the number moles of acid that was neutralized. The number of moles of acid can be calculated by multiplying the number of liters of acid times the molarity of the acid.

C. Enthalpy of Solution of a Solid Strong Base

17. Pick up a vial of solid NaOH pellets from the stockroom. There will be about 2 grams of NaOH*(s)* in the vial. Weigh the vial and its contents to the nearest 0.001 g.
18. Place 50.0 mL of distilled water in the calorimeter, and put the lid and thermometer in place. Watch the temperature for about a minute, and record the lowest temperature as the starting temperature.
19. Place the NaOH pellets in the water, and replace the lid and thermometer. Swirl the contents of the calorimeter to allow the NaOH*(s)* to dissolve as quickly as possible. Watch the temperature until it reaches a peak and starts down again. Record the highest temperature as the final temperature.
20. Reweigh the empty vial within 0.001 g.
21. Calculate the mass of the NaOH pellets that were placed in the calorimeter.

22-26. Calculate the enthalpy of solution in kilojoules per mole of NaOH. The total mass of the solution will be about **52 grams** and the specific heat of the solution is **3.93 joules/g^{o}C**. Average your trial results.

D. Enthalpy of Neutralization of a Strong Acid and a Solid Base

27. Place 53 mL of 1.0 *M* HCl*(aq)* in a 100-mL graduated cylinder, and then add enough distilled water to bring the final volume up to 100 mL. Place the solution in the calorimeter, and measure the temperature.
28. Pick up another vial of NaOH pellets, and weigh it.
29. Add the pellets to the calorimeter, and replace the lid and the thermometer. Swirl the contents of the calorimeter to allow the NaOH*(aq)* to dissolve and neutralize the acid. You should have a slight excess of HCl*(aq)*. Verify this by adding a drop of phenolphthalein to the solution; it should remain colorless. (If it turns pink, all the NaOH was not neutralized, and the results will not be correct. Repeat this part.) Record the final temperature.
30. Reweigh the empty vial.
31. Calculate the mass of NaOH*(s)* used .

32-36. Calculate the enthalpy of reaction in kilojoules per mole of NaOH. The density of the final solution is **1.02 g/mL** and the specific heat is **4.02 joules/g^{o}C**. Average your trial results.

E. Enthalpy of Neutralization of a Weak Acid and a Strong Base

Follow the same procedure here as you did with the strong acid and the strong base, only substitute acetic acid ($HC_2H_3O_2$) for HCl. The density and specific heat in the final solution are the same as they were in Part B.

F. Hess' Law

37-39. Write the molecular equations for Parts C, B and D, respectively. Use the labels *(s), (l)* and *(aq)* to show the physical states of the reactants and products. Show that the sum of the equation in Part C and the equation in Part B equals the equation in Part D by crossing out the products in Part C that is consumed as a reactant in Part B.

40-42. Copy down the average enthalpies you measured from Parts C and B, and add them up.

43. Compare the sum with the average enthalpy you measured in Part D, and calculate the percent error using the measured result (not the sum) as the accepted value.

1 Thermochemistry: Hess' Law

Name ______________________________
Section __________________Locker ____
Instructor ___________________________

Enter the data or answer the questions *according to the corresponding step in the procedure*

A. Heat Capacity of the Calorimeter

	Trial #1	Trial #2
1. Difference in thermometer readings		
2. Temperature of the cold water		
3. Temperature of the hot water		
4. Temperature of the mixture		
5. Heat lost by the hot water		
6. Heat gained by the cold water		
7. Heat gained by the calorimeter		
8. Heat capacity of the calorimeter		
	Average	

CALCULATIONS

B. Enthalpy of Neutralization – Strong Acid and Strong Base

9. Temperature of the 1.0 *M* HCl		
10. Temperature of the 1.0 *M* NaOH		
11. Average of the two		
12. Temperature of the mixture		
13. Heat gained by the mixture		
14. Heat gained by the calorimeter		
15. Total heat of reaction		
16. Enthalpy of Neutralization		
	Average	

CALCULATIONS

C. Enthalpy of solution – Solid Strong Base

	Trial #1	Trial #2
17. Mass of vial and NaOH pellets		
18. Temperature of the distilled water		
19. Final temperature of the mixture		
20. Mass of the empty vial		
21. Mass of the solid NaOH		
22. Moles of solid NaOH		
23. Heat gained by the solution		
24. Heat gained by the calorimeter		
25. Total heat of reaction		
26. Enthalpy of Solution		
	Average	

CALCULATIONS

D. Enthalpy of Neutralization – Strong Acid and Solid Base

27. Temperature of acid solution		
28. Mass of vial and NaOH		
29. Final temperature of the mixture		
30. Mass of the empty vial		
31. Mass of the solid NaOH		
32. Moles of solid NaOH		
33. Heat gained by the solution		
34. Heat gained by the calorimeter		
35. Total heat of reaction		
36. Enthalpy of Neutralization		
	Average	

CALCULATIONS

E. Enthalpy of Neutralization – Weak Acid and Strong Base

Temperature of the 1.0 *M* $HC_2H_3O_2$		
Temperature of the 1.0 *M* NaOH		
Average of the two		
Temperature of the mixture		
Heat gained by the mixture		
Heat gained by the calorimeter		
Total heat of reaction		
Enthalpy of Neutralization		
	Average	

F. Hess' Law

37. Equation Part C:	
38. Equation Part B:	
39. Equation Part D:	
40. Enthalpy Part C (after Step 26)	
41. Enthalpy Part B (after Step 16)	
42. Sum of the enthalpies	
43. Percent error (with Step 36)	

APPLICATION OF PRINCIPLES

1. Suppose this experiment was performed with hydrofluoric acid, HF *(aq)* a weak acid, instead of hydrochloric acid. Write the three molecular equations that would appear in Steps 37, 38, and 39. Then write the corresponding net ionic equation for each of these molecular equations. Why can't you just write an F everywhere there would be a Cl?

2. Mercury(II) hydroxide, $Hg(OH)_2$, is so insoluble in water that only about 2 formula units per billion dissolve. It does, however, neutralize hydrochloric acid. Explain, with appropriate net-ionic equations, how the methods in this experiment can be used to obtain the enthalpy of solution for $Hg(OH)_2$ even when direct measurements of that property is not possible.

3. The enthalpy of reaction for $HCN + OH^- \rightarrow CN^- + H_2O$ is -12.1 kJ/mol. Use this information and your experimental data from Part B to calculate the enthalpy of reaction for the ionization of HCN. ($HCN \rightarrow H^+ + CN^-$)