1 Thermochemistry: Virtual 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.

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.

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

or

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

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.

formula unit equation

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

ionic equation

$H^+ + \cancel{Cl^-} + \cancel{Na^+} + OH^- \rightarrow \cancel{Na^+} + \cancel{Cl^-} + H_2O(l)$

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

- **The enthalpy of the overall reaction is the sum of the enthalpies of the intermediate steps.**

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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. Obtain a styrofoam calorimeter from the stockroom. Place 100.0 mL of water in the calorimeter. Turn on the stirrer. Measure and record the temperature of the water.

2-5. Adjust the current on the heater to between 100 and 200 mA. Open the timer, then turn on the heater. Allow the heater to heat the water in the calorimeter for approximately 50 seconds. While the heater is on, record the current and voltage. After approximately 50 seconds, stop the heater and immediately record the temperature. The timer will automatically stop when the heater is turned off, record the time.

6. Calculate the total energy released by the heater from the following equation:

$$energy = current \times voltage \times time$$

Where energy is in *J*, current is in *A*, voltage is in *V*, and time is in *s*.

For Step 7 that follows, use $q=mC\Delta T$ to calculate the heat. Use 1.0 g/mL as the density of water and 4.18 joules/g·˚C as the specific heat of water.

7. Using the temperature change of the water in the calorimeter, calculate the amount of heat gained by the water.

8. Find the difference between the heat released by the heater and the heat gained by the water. This equals the heat gained by the calorimeter (q_{cal}).

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

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

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

10. Place 50.0 mL of 1.0 *M* HCl*(aq)* in the calorimeter and record the temperature.

11. Add 50.0 mL of 1.0 *M* NaOH*(aq)* to the calorimeter, turn on the stirrer, and monitor the temperature. Record the maximum temperature reached by the solution in the calorimeter as the temperature of the mixture.

12. 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**.

13. 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.

14. Calculate the total heat produced in the reaction by adding the heat gained by the mixture to the heat gained by the calorimeter.

15. 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

16. Obtain approximately 1 g of solid NaOH. Record the mass of the NaOH.

17. Place 25.0 mL of water in the calorimeter and record the temperature.

18. Place the solid NaOH in the calorimeter, and turn on the stirrer. Monitor the temperature and record the highest temperature as the final temperature.

19-23. Calculate the enthalpy of solution in kilojoules per mole of NaOH. The total mass of the solution will be about **26 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

24. Place 25.0 mL of 1.0 *M* HCl*(aq)* in the calorimeter, and measure the temperature.

25. Obtain approximately 1 g of NaOH and record the mass.

26. Add the NaOH to the calorimeter, and turn on the stirrer. Record the maximum temperature.

27-31. 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. Hess' Law

32-34. Write the formula unit 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.

35-37. Copy down the average enthalpies you measured from Parts B and C, and add them up.

38. 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 __________________
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. Initial water temperature		
2. Heater current		
3. Heater voltage		
4. Heating Time		
5. Water temperature after heating		
6. Energy released by heater		
7. Heat gained by the water		
8. Heat gained by calorimeter		
9. Heat capacity of the calorimeter		
	Average	

CALCULATIONS

B. Enthalpy of Neutralization – Strong Acid and Strong Base

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

CALCULATIONS

C. Enthalpy of solution – Solid Strong Base

	Trial #1	**Trial #2**
16. Mass of solid NaOH		
17. Temperature of water		
18. Final temperature of the mixture		
19. Moles of solid NaOH		
20. Heat gained by the solution		
21. Heat gained by the calorimeter		
22. Total heat of reaction		
23. Enthalpy of solution		
	Average	

CALCULATIONS

D. Enthalpy of Neutralization – Strong Acid and Solid Base

24. Temperature of acid solution		
25. Mass of NaOH		
26. Final temperature of the mixture		
27. Moles of solid NaOH		
28. Heat gained by the solution		
29. Heat gained by the calorimeter		
30. Total heat of reaction		
31. Enthalpy of Neutralization		
	Average	

CALCULATIONS

E. Hess' Law

32. Equation Part C:	
33. Equation Part B:	
34. Equation Part D:	
35. Enthalpy Part B	
36. Enthalpy Part C	
37. Sum of the enthalpies	
38. Percent error (with Step 31)	

APPLICATION OF PRINCIPLES

1. Suppose this experiment was performed with hydrofluoric acid, HF *(aq)* a weak acid, instead of hydrochloric acid. Write the three formula unit equations that would appear in Steps 32, 33, and 34. Then write the three net ionic equations that correspond to each of these equations. Why can't you just write an F everywhere there would be a Cl in the net ionic equations?

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. ($HCN \rightarrow H^+ + CN^-$)