Calorimetry: Heats of Solution

Objective: Use calorimetric measurements to determine heats of solution of two ionic compounds.

Materials: Solid ammonium nitrate (NH_4NO_3) and anhydrous calcium chloride ($CaCl_2$).

Equipment: Styrofoam cup calorimeters; thermometers; 25-mL or 50-mL Erlenmeyer flasks; 100-mL graduated cylinder; stop watch or timing device; spatula

Safety: The ammonium nitrate and calcium chloride solutions are mild irritants and should be handled with care. If these solutions make contact with skin wash the affected area immediately. Thermometers are fragile and should be handled gently. Wear safety goggles in the lab at all times.

Waste Disposal: All reagents and reaction solutions may be washed down the sink with plenty of water

INTRODUCTION

One indication of a chemical reaction is the production of heat. The amount of heat gained or lost during a reaction is due to the breaking of bonds between atoms in the reactants, and the formation of bonds between atoms to form products. The heat of reaction is also called the **enthalpy** of reaction, or ΔH. For **endothermic** reactions, ΔH is positive and heat flows into the reaction. For **exothermic** reactions ΔH is negative and heat is given off by the reaction.

Heats of reaction are measured by **calorimetry**, or the study of heat flow. For reactions that take place in solution, the total amount of heat flow in a reaction can be expresses as

$$q = S.H. \times m \times \Delta T \qquad (1)$$

where q is the heat flow (in calories), $S.H.$ stands for the **specific heat** of the reaction solution (in cal/g·°C), m is the mass of the solution (in g), and ΔT is the change in temperature (in °C). For an exothermic reaction, $q_{reaction}$ is negative. The heat released by the reaction will increase the temperature of the solution in the calorimeter, and $q_{calorimeter}$ will be positive, or

$$-q_{reaction} = q_{calorimeter} \qquad (2)$$

A **calorimeter** is a device that can be used to measure heat flow. The main requirement for a calorimeter is that it be well insulated, so that there is no heat lost to the surroundings during the measurement. If this condition is met, then all the heat produced during a reaction will be retained within the calorimeter, and the temperature in the calorimeter will increase. A simple calorimeter can be constructed using Styrofoam cups with cardboard lids. While not perfectly insulated, it works well enough to give reasonably good results.

Many endothermic and exothermic processes have practical applications. For example, one common reaction used in hand warmers involves the reaction of finely divided iron powder with oxygen:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad \Delta H_{rxn} = -198 \text{ kcal/mol}$$

Removing the seal on the hand warmer packet exposes the iron powder to oxygen in the atmosphere, and the reaction can continue to produce heat for several hours.

In this lab we will investigate two solution reactions that are used in hot and cold packs typically found in first aid kits:

1. $NH_4NO_3(s) + H_2O(l) \rightarrow NH_4NO_3(aq) \qquad \Delta H_{soln} = 6.7$ kcal/mol (3)
2. $CaCl_2(s) + H_2O(l) \rightarrow CaCl_2(aq) \qquad \Delta H_{soln} = -19.5$ kcal/mol (4)

The enthalpies associated with the dissolution of these are identified as heats of solution, ΔH_{soln}.

Pre-Lab Questions

1. Define the following terms:

a. Calorimetry -

b. Enthalpy –

c. Specific heat –

d. Exothermic –

e. Heat of Solution –

2. A piece of metal weighing 12.4 g is heated to raise its temperature from 22.5°C to 42.2°C. It is found that the metal absorbed 52.8 cal of heat in the process.

a. Calculate the specific heat of the metal. Include appropriate units.

b. Based on your results, identify the metal from the list below. Metal = _________

Element	Specific heat (cal/g·°C)
Aluminum	0.216
Copper	0.093
Iron	0.107
Silver	0.057

3. A 5.0 g sample of an ionic compound (MW = 96.5 g/mol) is placed in 50.0 g of water at 25 °C and the solution is stirred. When the salt is completely dissolved, the temperature of the solution is 32.7 °C.

   a) Is the heat of solution **endothermic** or **exothermic**?

   b) If we assume that the specific heat of the solution is 1.0 cal/g, calculate the ΔH_{soln} for this compound in kcal/g and in kcal/mol.

PROCEDURE

Students should work in pairs. Each pair of students will require a Styrofoam cup calorimeter (see Figure 1), one thermometer, and one timing device (watch with second hand).

Part A: Heat of Solution (ΔH_{soln}) for NH_4NO_3

1. Measure 50.0 mL of DI water (to the nearest 0.1 mL) in a graduated cylinder and transfer to the calorimeter.

2. Weigh out a 5.0 g sample (to the nearest 0.01 g) of NH_4NO_3 into a 50.0-mL beaker.

3. Place the thermometer in the cup containing the water and allow it to equilibrate for one minute. Record the temperature (to the nearest 0.1 ^oC) in one minute intervals for three more minutes, and record these temperatures on Data Sheet 1. At the 4 minute mark, pour the 5.0 g of NH_4NO_3 into the water in the calorimeter and mix thoroughly.

4. Replace the calorimeter cover and thermometer, and monitor the temperature. At this point, your calorimeter should resemble the example provided in Figure 1.

5. Note the solution temperature (to the nearest 0.1^oC) at the 5, 6, 7, and 8 minute marks and record these temperatures on Data Sheet 1.

6. Remove the thermometer from the calorimeter, taking care not to lose any of the solution. Take the calorimeter with the reaction solution to the analytical balance and record the mass (with solution) to the nearest 0.01 g on Data Sheet 1. Discard the solution down the sink, and rinse and dry the cup. Obtain the mass of the dry calorimeter cup, and record the mass on Data Sheet 1 to the nearest 0.01 g. By difference, calculate the mass of the reaction solution and record this value on Data Sheet 1.

Rinse and dry the other calorimeter, and perform a second determination by repeating Steps 1-4 of Part A.

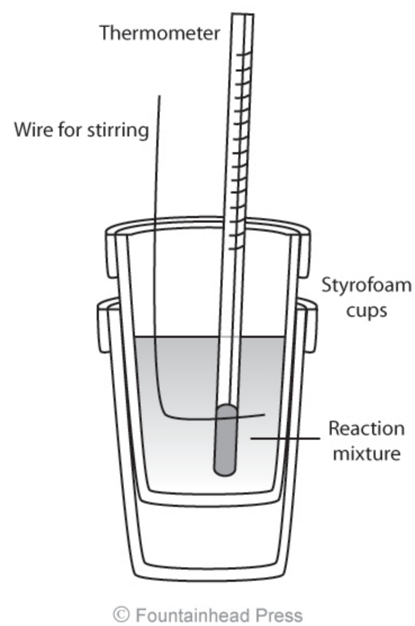

Figure 1. Styrofoam cup calorimeter assembly

Part B: Heat of Solution (ΔH_{soln}) of $CaCl_2$.

7. Measure 50.0 mL of DI water (to the nearest 0.1 mL) in a graduated cylinder and transfer to the calorimeter.

8. Weigh out a 5.0 g sample (to the nearest 0.01 g) of $CaCl_2$ into a 50.0-mL beaker. Anhydrous calcium chloride is hygroscopic—be sure to replace the cap on the reagent bottle! Otherwise it will absorb moisture from the air.

9. Place the thermometer in the cup containing the water and allow it to equilibrate for one minute. Record the temperature (to the nearest 0.1^{o}C) in one minute intervals for three more minutes, and record these temperatures on Data Sheet 1. At the 4 minute mark, pour the 5.0 g of $CaCl_2$ into the water in the calorimeter and mix thoroughly.

10. Replace the calorimeter cover and thermometer, and monitor the temperature.

11. Note the solution temperature (to the nearest 0.1^{o}C) at the 5, 6, 7, and 8 minute marks and record these temperatures on Data Sheet 2.

12. Remove the thermometer from the calorimeter taking care not to lose any of the solution. Take the calorimeter with the reaction solution to the analytical balance and record the mass (with solution) to the nearest 0.01 g on Data Sheet 1. Discard the solution down the sink, and rinse and dry the cup. Obtain the mass of the dry calorimeter cup, and record the mass on Data Sheet 1 to the nearest 0.01 g. By difference, calculate the mass of the reaction solution and record this value on Data Sheet 1.

13. Rinse and dry the other calorimeter, and perform a second determination by repeating Steps 8-12 of Part B.

CALCULATIONS

Recall from the introduction that the heat associated with a reaction (q) can be calculated from Eq. (1)

$$q(cal) = S.H.(cal/g\cdot{}^oC)\cdot m(g)\cdot \Delta T({}^oC) \qquad (1)$$

The specific heat (S.H.) of the solutions in Parts A and B can be estimated and have been provided in the Calculations sections on Data Sheets 1 and 2. Knowing the mass of the reaction solution (m) and the change in temperature (ΔT), we can calculate the heat of the reaction.

We can calculate the temperature change for the reaction in the calorimeter as the difference between the initial and final calorimeter temperatures. Typically, the initial temperature measured during the first three minutes of each trial should be constant. If it is not, use the temperature at 3 minutes as the initial temperature. During reactions, heat may be transferred quickly, so that the last temperature reading may not reflect the true temperature change. The highest or lowest temperature reached during the reaction should be recorded as the final temperature for use in the calculations.

For an exothermic process ($q_{reaction}$ = negative), the heat generated by reaction is absorbed by solution and results in a temperature increase in the calorimeter ($q_{calorimeter}$ = positive). For an endothermic process ($q_{reaction}$ = positive), the heat absorbed by the reaction is taken from the solution and results in a temperature decrease in the calorimeter ($q_{calorimeter}$ = negative). Thus,

$$q_{reaction} = - q_{calorimeter}$$

Finally, enthalpies of reactions are expressed in cal/mol. Therefore, we must calculate the moles of reactants in each trial. We can convert from grams to moles by dividing the mass of the salt used in each trial by the molar mass of the compound.

The % error in your experiment can be calculated as:

$$\% \text{ error} = \frac{\Delta H_{actual} - \Delta H_{exp}}{\Delta H_{actual}} \text{ x } 100 \qquad (5)$$

Data Sheet 1: Heat of Solution (ΔH_{soln}) for NH_4NO_3

Mass of NH_4NO_3: 1.______________ 2. ______________ (NH_4NO_3 = 80.05 g/mol)

		Trial 1	*Trial 2*
	Volume of water (mL)	____________	____________
Temperature (^oC):	1 min:	____________	____________
	2 min:	____________	____________
	3 min:	____________	____________
	4 min (MIX)		
	5 min:	____________	____________
	6 min:	____________	____________
	7 min:	____________	____________
	8 min:	____________	____________
	$\Delta T = (T_{final} - T_{initial})$:	____________	____________
	Mass of Calorimeter + Solution (g):	____________	____________
	Mass of Calorimeter empty (g):	____________	____________
	Mass of Solution (g):	____________	____________

Calculations Part A:

	Trial 1	***Trial 2***
$q_{calorimeter}$ (cal) = (0.961 cal/g ^oC)·(m)·(ΔT):	____________ (cal)	____________ (cal)
$q_{reaction} = - q_{calorimeter}$:	____________ (cal)	____________ (cal)
# moles NH_4NO_3:	____________ (mol)	____________ (mol)
$\Delta H_{soln} = (q_{reaction}$ / moles NH_4NO_3):	____________ (cal/mol)	____________ (cal/mol)
Average ΔH_{soln} (NH_4NO_3):	____________ (cal/mol)	
% error =	____________	

Data Sheet 2: Heat of Solution (ΔH_{soln}) for $CaCl_2$

Mass of $CaCl_2$: 1. ____________ 2. _____________ ($CaCl_2$ = 110.97 g/mol)

		Trial 1	*Trial 2*
	Volume of water (mL)	____________	____________
Temperature (^oC):	1 min:	____________	____________
	2 min:	____________	____________
	3 min:	____________	____________
	4 min (MIX)		
	5 min:	____________	____________
	6 min:	____________	____________
	7 min:	____________	____________
	8 min:	____________	____________
	$\Delta T = (T_{final} - T_{initial})$:	____________	____________
	Mass of Calorimeter + Solution (g)	____________	____________
	Mass of Calorimeter empty (g):	____________	____________
	Mass of Solution (g):	____________	____________

Calculations Part B:

	Trial 1	***Trial 2***
$q_{calorimeter}$ (cal) = (0.961 cal/g ^oC)·(m)·(ΔT):	___________ (cal)	___________ (cal)
$q_{reaction} = - q_{calorimeter}$:	___________ (cal)	___________ (cal)
# moles $CaCl_2$	___________ (mol)	___________ (mol)
$\Delta H_{soln} = (q_{reaction}$ / moles $CaCl_2$):	____________ (cal/mol)	___________ (cal/mol)

Average ΔH_{soln} ($CaCl_2$) : ________________ (cal/mol) % error = __________________

Post-Lab Questions

1. In the Calculations section you were asked to calculate the percent error in your ΔH_{soln} determination. Discuss at least <u>two</u> possible sources of error that could contribute to your percent error.

2. A student is performing Part B and does not completely dissolve the $CaCl_2$ pellets before acquiring the final temperature. How will this affect his value for ΔH_{soln} and his percent error calculations?

3. In a different experiment it is observed that 66.5 cal of heat is absorbed as the temperature of 48.7 g of Fe(s) is raised from 22.0 ^{o}C to 32.8^{o}C. Calculate the specific heat of Ni in cal/g·^{o}C, and the % error in your calculated value. The S.H. for Fe is 0.107 cal/g·^{o}C.

4. You wish to prepare a hot pack that will generate a temperature of 78°C (172.5°F). If your hot pack initially contains 150 mL of water at 22°C, what mass of $CaCl_2$ will you need to include in your hot pack? (Assume the specific heat of the resulting solution is 1.0 cal/(g°C))