6 Enthalpy of Formation of Ammonium Salts

Purpose

The objective of this experiment is to determine the enthalpy of formation of solid ammonium salts, NH_4NO_3 by measuring the heat of neutralization.

Theory

Enthalpy of formation is (or heat of formation) is the enthalpy change (ΔH) associated with the formation of one mole the compound from its elements in their standard states. There are direct and indirect methods used to define the enthalpy of systems. Hess's law states that if a reaction is carried out in a series of steps, the enthalpy change of a reaction will equal the sum of the enthalpy changes for the individual steps.

In the laboratories, ΔH can be found by determining the heat flow by measuring the temperature change during a chemical reaction. Calorimetry is defined as the measurement of heat flow and a device used to measure the heat flow is known as a calorimeter. There are two types of calorimeter commonly used for this purpose; "coffee-cup" (constant pressure) and "bomb" calorimeters (constant volume). In this laboratory, a coffee-cup calorimeter that provides constant pressure will be used. The coffee-cup calorimeter prevents the heat exchange between the system and surroundings. This type of system is known as adiabatic if there is no heat exchange between the system and the surroundings. Therefore the heat produced by the reaction is absorbed by the solution. The heat of the system is defined as

$$q_{system} = 0 = n\Delta H_m + C_p \Delta T$$

where n is the mole of reaction, ΔH_m is the molar enthalpy which the enthalpy of reaction for 1 mole reactant and C_p is the specific heat of the solution.

If the reaction is exothermic ($\Delta H<0$), the heat lost by the reaction must be gained by the solution. This will result in increase in temperature of solution and ΔT of the solution will be positive. The heat capacity, C_p, heat required to increase the temperature of the system by 1.0 °C, is inversely proportional to ΔT. The larger the C_p, the smaller will be the ΔT required to absorb the heat from the reaction.

$$q_{system} = 0 = n\Delta H_m + C_p \Delta T$$

$$n\Delta H_m = -C_p \Delta T$$

If the reaction is endothermic (ΔH>0), heat gained by the reaction must be given off by the solution. This will result in decrease in temperature of solution and ΔT of the solution will be negative. As we have a dilute aqueous solution, we will assume that

$$m(solution) \approx m(water) = d(water).V(solution)$$

$$n\Delta H_{reaction} = m(water) x C_p(water) x \Delta T$$

During the experiment, temperature-time data will be collected and temperature versus time graphs will be plotted to measure ΔT. The rate of temperature drift before and after the reaction will show the ΔT as shown in the figure below

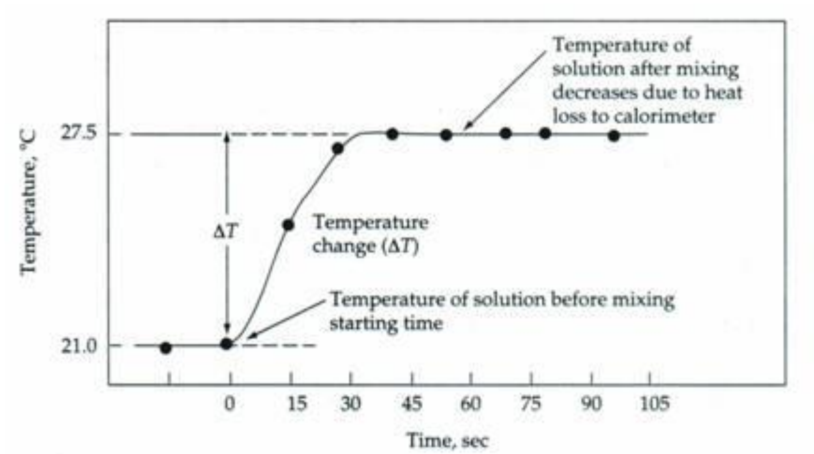

Figure 1. Temperature vs time plot for an exothermic reaction (ΔT>0)

In this laboratory, the enthalpy of formation of NH_4NO_3 will be determined measuring the enthalpy of neutralization reaction of NH_3 and HNO_3;

$1/2\ N_2(g) + 3/2H_2(g) \rightarrow NH_3(aq)$	$\Delta H_{f\ NH3(aq)} = -81.17$ kJ/mole
$1/2\ H_2(g) + 1/2\ N_2(g) + 3/2\ O_2(g) \rightarrow HNO_3(aq)$	$\Delta H_{f\ HNO3(aq)} = -206.0$ kJ/mole
$NH_3(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$	$\Delta H_{neutralization}$
$NH_4NO_3(aq) \rightarrow NH_4NO_3(s)$	$-\Delta H_{dissolution}$

$N_2(g) + 2H_2(g) + 3\ 2O_2(g) \rightarrow NH_4NO_3(s)$

$\Delta H_{f\ NH4NO3(s)} = \Delta H_{f\ NH3(aq)} + \Delta H_{f\ HNO3(aq)} + \Delta H_{neutralization} + (-\Delta H_{dissolution})$

The heat of formation of aqueous ammonia is -81.17 kJ/mole, and the heat of formation of aqueous nitric acid is -206.0 kJ/mole. You will determine the heat of neutralization and the heat of solution experimentally using an open or coffee-cup calorimeter.

- Useful info for calculations;

1. C_p per gram for the system is equal to C_p per gram for water (4.184 J/g. °C).
2. Density of the solution is equal to density of water (1.00 g/mL)

Pre-Laboratory Work

1. Calculate the volume of 1.5 M HNO_3 acid required in Part 1.
2. Calculate the mass of NH_4NO_3 salt produced from the neutralization reaction that is required in Part 2.

Experimental Procedure

Chemicals List	***Equipments***
NH_3, ammonia HNO_3, nitric acid NH_4NO_3, ammonium nitrate	Graduated cylinder Balance Styrofoam cup Thermometer

Part 1. Neutralization

1. Take the Styrofoam cup. Pour 50 mL of 1.5 M NH_3 into it.
2. Measure the temperature of ammonia solution in the Styrofoam cup.
3. Calculate the volume of an acid (1.5 M HNO_3) needed to neutralize the NH_3. Take the required volume to the graduated cylinder.
4. Pour the acid through the Styrofoam cup to start the reaction.
5. Collect temperature-time data for each 30 seconds for 5 minutes and write the data on the data report sheet.

Part 2. Dissolution

1. NH_4NO_3 salt will be produced as a product of neutralization reaction in Part 1. Calculate the mass of salt produced from the neutralization reaction and weigh and put it into a clean weighing cup.
2. Measure the final volume of solution prepared in Part 1. Place the distilled water with the same volume and pour it in to a Styrofoam cup. Collect temperature-time data for 5 minutes for each 30 seconds and write the data on the data report sheet.
3. After completing 5 minutes, immediately add the salt you weighed into Styrofoam cup containing distilled water and collect temperature-time data for 10 minutes for each 30 seconds and write the data on the data report sheet.

Part 3. Representation of Data

1. Plot temperature versus time graphs you obtained in Part-1 for neutralization reaction and Part-2 for dissolution.

2. Calculate the enthalpy of formation for NH_4NO_3(s).

Experiment 6 – Report (Page 1)

Name of the student:	Student ID:
Name and signature of the assistant:	Section & Date:

Data and Calculations

Part A. Pre-laboratory work (Show all your calculations)

1. (10 pts) Calculate the volume of 1.5 M HNO_3 acid required in Part 1.

2. (10 pts) Calculate the mass of NH_4NO_3 salt produced from the neutralization reaction that is required in Part 2.

Experiment 6 – Report (Page 2)

Name of the student:	Student ID:

Part B. Temperature-Time Data Tables

	Part 1. Neutralization		***Part 2. Dissolution***
Time (s)	**Temperature (°C)** (NH_3 solution before mixing with HNO_3)		**Temperature (°C)** (distilled water before addition of NH_4NO_3 salt)
0			
30			
60			
90			
120			
150			
180			
210			
240			
270			
300			

	Part 1. Neutralization		***Part 2. Dissolution***
Time (s)	**Temperature (°C)** (NH_3 and HNO_3 solution)		**Temperature (°C)** (NH_4NO_3 solution)
0			
30			
60			
90			
120			
150			
180			
210			
240			
270			
300			
330			
360			
390			
420			
450			
480			
510			
540			
570			
600			

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Name of the student:	Student ID:

Part C. Temperature-Time Graphs

Part 1. Neutralization

(10 pts) Draw the graphs for $\Delta H_{neutralization}$ of NH_4NO_3. (by using Excel)

Part 2. Dissolution

(10 pts) Draw the graphs for $\Delta H_{dissolution}$ of NH_4NO_3. (by using Excel)

Experiment 6 – Report (Page 4)

Name of the student:	Student ID:

Part D. Calculations

1. (10 pts) $\Delta H_{neutralization}$ of NH_4NO_3.

2. (10 pts) $\Delta H_{dissolution}$ of NH_4NO_3.

3. (20 pts) $\Delta H_{formation}$ of NH_4NO_3.

Experiment 6 – Report (Page 5)

Name of the student:	Student ID:

QUESTIONS

1. (10 pts) Suppose that you used a metal container, rather than a Styrofoam cup, as the calorimeter. How might this affect the temperature-time curve? If the mass of the container and solvent is the same in both cases, will the heat capacity values be the same for both calorimeters? Explain your answers.

2. (10 pts) Sketch the temperature vs. time graph that you would expect for endothermic and exothermic reactions carried out in a calorimeter similar to the one used in the experiment.