Experiment 8: The Heat of Neutralization

(This experiment was adapted from CC-BY Torres & González-Urbina, CUNY)

Purpose

This experiment introduces the technique of calorimetry. The enthalpy change of acid base neutralization reactions will be determined using a coffee-cup calorimeter. The heat released or consumed by the reactions will allow for the calculation of the enthalpy change, ΔH . The chemical reactions will be (1) HCl with NaOH, and (2) HCl with NH₃, and (3) NH₄Cl with NaOH.

Background

Reactants and products in a chemical reaction normally have different amounts of energy, and this difference in energy is reflected by a release or absorption of heat during the reaction. By means of a coffee-cup calorimeter and a thermometer, the temperature changes produced by a chemical reaction can be measured. When a reaction produces heat, the temperature inside the calorimeter will rise. When a reaction consumes heat, the temperature inside the calorimeter will decrease. These heat (energy) changes are related to the enthalpy change of the chemical reaction. This is a classical college chemistry experiment implemented in many lab manuals with different choices of acids and bases [1-4].

Measurement of heat

Heat (thermal energy, q) is the energy transferred as a result of a difference in temperature. Heat flows from regions of high-temperature to low-temperature. Heat is connected to the change of temperature, ΔT , by means of the specific heat C: $q = m \cdot C \cdot \Delta T$ where m is the mass of the object and ($\Delta T = T_f - T_i$). For aqueous solutions, the specific heat of water is used, 4.184 J \cdot (°C⁻¹ \cdot g⁻¹),

Enthalpy change of a chemical reaction

The energy change in a chemical reaction measured at constant pressure (in an open container) is called the enthalpy change, ΔH . All chemical reactions are accompanied by a change in energy. For example, the reaction between an acid and a base is called neutralization, and for the case of HCI and NaOH is the following reaction:

HCl + NaOH \rightarrow NaCl + H₂O Δ H = -52 kJ / mole The heat involved in this process is -52 kJ / mole (per mole means with the coefficients shown in the balanced equation). The negative sign means that the heat is being released. Reactions that release heat are called exothermic (Δ H < 0), whereas reactions that absorb heat are called endothermic (Δ H > 0).

Using a coffee-cup calorimeter

Two nested polystyrene coffee-cups make a good constant-pressure calorimeter, as polystyrene is a good heat insulator. With a coffee-cup calorimeter and a thermometer, we can measure the enthalpy change, ΔH , of a chemical reaction happening inside the calorimeter: the heat, q, consumed or released inside a calorimeter is related to the enthalpy change of the reaction by: $\Delta H_{rxn} + q = 0$ which rearranges to $\Delta H_{rxn} = -q$

Often times heat flows through the walls of calorimeter, as these devices are never perfect. To take this lose of heat into account, we can use the following formula:

 $\Delta H_{rxn} = (-1) \cdot ((m \cdot C \cdot \Delta T) + (C_{Cal} \cdot \Delta T)) \qquad \text{where } C_{Cal} \text{ is the calorimeter constant and it is calculated to be } C_{Cal} = 10.0 \text{ J} \cdot^{\circ} \text{ C}^{-1} \text{ for a standard calorimeter. It accounts for the energy absorbed by the calorimeter.}$

Example Calculation:

When 10.00 ml of 1.0 M, HNO₃, reacts with an of excess NaOH (but no additional volume): $HNO_3(aq) + NaOH(aq) \rightarrow NaNO_3(aq) + H_2O(aq)$ in a coffee-cup calorimeter with a heat capacity of 10. J $\cdot^{\circ}C^{-1}$, the temperature of the calorimeter rises by 10.0°C. Calculate the reaction enthalpy for this process assuming the density of the mixture is 1.00 g/mL.

Answer:

Answer: the heat absorbed by the calorimeter is the heat exchanged during the chemical reaction:

Mass of solution = $(d \cdot V)$ where V is the volume used of (nitric acid + NaOH) (for this example, NaOH did not add volume)

 $\Delta H_{rxn} = (-1) \left((m \cdot C \cdot \Delta T) + (C_{Cal} \cdot \Delta T) \right)$

Plugging all the values:

mass of solution = $(1.00g \cdot mL^{-1} \cdot 10.00mL) = 10.0 g$ $\Delta H_{rxn} = (-1) ((10.0g \cdot 4.184 J \cdot C^{-1} \cdot g^{-1} \cdot 10.0C^{-1}) + (10.J \cdot C^{-1} \cdot 10.0C))$

Solving for ΔH_{rxn} we have -520 J. The number of moles of HNO₃ is: n =0.01000 L× 1.0 mole/L =0.010mol. Therefore, on a per mole basis, the ΔH_{rxn} = -520 J / 0.010 mole = -52000 J/mole or -52 kJ /mole.

Hess's Law

Hess's law states that the total enthalpy change during a chemical reaction is the same whether the reaction results from one step or several steps. For example:

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\begin{array}{ccc} HCI + NaOH \rightarrow NaCI + H_2O & \Delta H_1 \\ and & \\ NH_3 + HCI \rightarrow NH_4CI & \Delta H_2 \\ or & \\ NaOH + NH_4CI \rightarrow NaCI + NH_3 + H_2O & \Delta H_{rxn} \end{array}
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You might have noted there is a relationship among these equations: if you reverse the second equation and add it to the first equation, the third equation is generated. This provided the basis for Hess's law and you will find you can predict the enthalpy change for the third reaction by combining the enthalpy change for the first and second reactions:

 $\Delta H_{rxn} = \Delta H_1 + \Delta H_2$ (after reaction 2 is reversed) You will calculate the expected ΔH_{rxn} with your experimentally determined ΔH_1 and ΔH_2 values.

Chemicals

HCI(aq), NH₃(aq), NaOH(aq), NH₄CI(aq)

(Caution: All solutions are 1 M concentration.)

(Note: When NH_3 is in solution, it is typically written as $NH_4OH_{(aq)}$. However, the $NH_{3(aq)}$ version is better for the Hess's Law work.)

Equipment

Coffee-cup calorimeter with lid (not air tight, still considered an open container) ONE Thermometer (Use <u>THE SAME</u> thermometer for all temperature measurements.) Graduated cylinders 150 mL and 250 mL beakers

Procedure (*Make sure to use the same thermometer throughout the experiment so the results are consistent.*) **Measuring** Δ **H for the HCI, NaOH Reaction**

- 1) Obtain a coffee-cup calorimeter with a thermometer and lid.
- 2) Obtain approximately 110 mL of HCl and 110 mL of NaOH, each in their own beaker.
- 3) Place 50.0 mL of HCl and 50.0 ml of NaOH in separate graduated cylinders.
- 4) Measure the temperature of each of these solutions. Make sure you clean the thermometer in between measurements as the chemicals will react. Record the mean of the two temperatures as your initial temperature, t_i.
- 5) Get the timer ready.
- 6) Add the acid to the calorimeter. Then add the base. Start the timer immediately and place the lid on the calorimeter. Use the stirrer gently to mix the solutions.
- Record the maximum temperature observed over a 4-minute time period. Do not stop the timer during the trial. Record the maximum temperature (which is the final temperature, t_f).
- 8) Calculate the change of enthalpy, ΔH, by using the following formulas: Mass of solution = (d ·V) where V is the volume of (acid + base) used. ΔH₁ = (-1) ((m ·C ·ΔT) +(C_{Cal} ·ΔT))
- 9) Repeat steps 1-8 for trial 2. Calculate the ΔH for each trial as per mole of acid. Then calculate the average ΔH (use units of kJ / mole for the average value).

Measuring ΔH for the HCl, NH₃ Reaction

- 1) Clean and dry the coffee cup used previously.
- 2) Obtain approximately 110 mL of HCl and 110 mL of NH₃, each in their own beaker.
- 3) Place 50.0 mL of HCl and 50.0 ml of NH₃ in separate graduated cylinders.
- Measure the temperature of each of these solutions. Record the mean of the two temperatures as your initial temperature t_i.
- 5) Get the timer ready.
- 6) Add the acid to the calorimeter. Then add the base. Start the timer immediately and place the lid on the calorimeter. Use the stirrer gently to mix the solutions.
- Record the maximum temperature observed over a 4-minute time period. Do not stop the timer during the trial. Record the maximum temperature (which is the final temperature, t_f).
- 8) Calculate the change of enthalpy, ΔH , by using the following formulas: Mass of solution = (d ·V) where V is the volume of (acid + base) used. $\Delta H_2 = (-1) \left((m \cdot C \cdot \Delta T) + (C_{cal} \cdot \Delta T) \right)$
- 9) Repeat steps 1-8 for trial 2. Calculate the ΔH for each trial as per mole of acid. Then calculate the average ΔH (use units of kJ / mole for the average value).

Measuring ΔH for the NH₄Cl, NaOH Reaction

- 1) Clean and dry the coffee cup used previously.
- 2) Obtain approximately 110 mL of NH₄Cl and 110 mL of NaOH, each in their own beaker.
- Place 50.0 mL of NH₄Cl and 50.0 ml of NaOH in separate graduated cylinders. Make sure the cylinders are clean and dry.
- 4) Measure the temperature of each of these solutions. Record the mean of the two temperatures as your initial temperature t_i.
- 5) Get the timer ready.
- 6) Add the acid to the calorimeter. Then add the base. Start the timer immediately and place the lid on the calorimeter. Use the stirrer to gently mix the solutions.
- Record the maximum temperature observed over a 4-minute time period. Do not stop the timer during the trial. Record the maximum temperature (which is the final temperature, t_f).
- 8) Calculate the change of enthalpy, ΔH, by using the following formulas: Mass of solution = (d ·V) where V is the volume of (acid + base) used. ΔH_{rxn} = (-1) ((m ·C ·ΔT) +(C_{Cal} ·ΔT))
- 9) Repeat steps 1-8 for trial 2. Calculate the ΔH for each trial as per mole of acid. Then calculate the average ΔH (use units of kJ / mole for the average value).