Calorimetry and Hess’s Law

Objectives

The objectives of this laboratory are as follows:

- To experimentally measure the $\Delta H$ values of two reactions using the technique of constant pressure calorimetry, and
- To apply these $\Delta H$ values in a Hess’s Law calculation to determine the enthalpy of combustion of a metal.

Background

The combustion of a metal in oxygen produces the corresponding metal oxide as the only product. Such reactions are exothermic and release heat, which is called the “enthalpy of combustion” of the metal:

\[
\text{Metal (s) } + \text{ O}_2 (g) \rightarrow \text{ Metal Oxide (s) } \quad \Delta H_{\text{rxn}} = \text{enthalpy of combustion}
\]

Since it is very difficult to measure the enthalpy of combustion of a metal directly, in this lab it will be determined indirectly by applying Hess’s Law of Heat Summation. Hess’s Law states that the enthalpy change of an overall process is equal to the sum of the enthalpy changes of its individual steps. A worked example illustrating Hess’ Law is shown on the next page.

In order to use Hess’ Law to determine the heat of combustion of a metal, it is first necessary to obtain $\Delta H$ values for reactions that can be summed together appropriately. Three reactions are required:

1. \(\text{Metal (s) } + \text{ HCl (aq) } \rightarrow \text{ Metal chloride (aq) } + \text{ H}_2 (g) \quad \Delta H_1\)
2. \(\text{Metal Oxide (s) } + \text{ HCl (aq) } \rightarrow \text{ Metal Chloride (aq) } + \text{ H}_2\text{O (l)} \quad \Delta H_2\)
3. \(2 \text{ H}_2 (g) + \text{ O}_2 (g) \rightarrow 2 \text{ H}_2\text{O (l)} \quad \Delta H_3\)

$\Delta H_1$ and $\Delta H_2$ will be experimentally determined in this lab using Constant Pressure Calorimetry. Reactions 1 and 2 are both exothermic and occur in aqueous solution, thus the heat released by the reactions (q) will be absorbed into the surrounding solution. As long as these reactions are performed in an insulated container (such as a coffee cup calorimeter) there will be negligible heat exchange with the container walls or outside air. By monitoring the temperature change of the solution when specific quantities of reactants are used, the amount of heat (in J) released by these reactions can be determined:

\[
\text{heat released by reaction } (-q_{\text{reaction}}) = \text{heat absorbed by solution } (+q_{\text{solution}})
\]

where \(q_{\text{solution}} = (m \times c \times \Delta T)_{\text{solution}}\)

Here, \(m\) is the total mass of the solution (combined mass of all the reactants) in grams, \(\Delta T\) is the maximum temperature change that occurs during the reaction in °C, and \(c\) is the specific heat capacity of the solution (in J/g°C). Since these reactions occur in an excess of hydrochloric
acid, it is reasonable to substitute the specific heat capacity of hydrochloric acid for the specific heat capacity of the solution. Note that the specific heat capacity of hydrochloric acid depends on its concentration; \( c = 4.18 \text{ J/g} \cdot ^\circ \text{C} \) for 1M HCl (since the solution is dilute it approximates that of water) and \( c = 3.05 \text{ J/g} \cdot ^\circ \text{C} \) for 6M HCl.

At constant pressure – the conditions of this experiment – the heat released by the reaction \( (q_P) \) yields the reaction enthalpy \( (\Delta H) \). Since the heat released by each reaction is proportional to the amount of metal or metal oxide used, \( \Delta H_1 \) and \( \Delta H_2 \) can be easily calculated using stoichiometric techniques.

In contrast to Reactions 1 and 2, Reaction 3 (the formation of water from its elements) will not be experimentally studied in this lab. Instead, \( \Delta H_3 \) must be obtained from tabulated thermodynamic data in the textbook – specifically, the Standard Enthalpy of Formation of water. Finally, Reactions 1, 2 and 3 and their respective \( \Delta H \) values may be summed together according to Hess’s Law to determine the enthalpy of combustion of the given metal.

**Hess’s Law Example**

Determine \( \Delta H \) for the target reaction: \( 2 \text{ NO}_2 (g) + \frac{1}{2} \text{ O}_2 (g) \rightarrow \text{ N}_2\text{O}_5 (g) \)
given the following information,

- Reaction A \( \text{ N}_2\text{O}_5 (g) \rightarrow 2 \text{ NO} (g) + \frac{3}{2} \text{ O}_2 (g) \quad \Delta H_A = +223.7 \text{ kJ} \)
- Reaction B \( \text{ NO}_2 (g) \rightarrow \text{ NO} (g) + \frac{1}{2} \text{ O}_2 (g) \quad \Delta H_B = -57.1 \text{ kJ} \)

**Solution:** Reactions A and B have to be carefully manipulated before they can be summed to produce the target reaction. Reaction A must be reversed, causing a sign change to \( \Delta H_A \). Reaction B must be multiplied by a factor of 2, causing \( \Delta H_B \) to be multiplied by 2. Only then will they yield the target equation when added together:

\[
\Delta H = -(+223.7) = -223.7 \text{ kJ} \\
\Delta H = 2 \times (-57.1) = -114.2 \text{ kJ} \\
\text{Target}
\]

Thus, \( \Delta H_{\text{Target}} = -223.7 + (-114.2) = -337.9 \text{ kJ} \)
Procedure

Chemicals

Mg (s) and MgO (s), Zn (s) and ZnO (s), 1M HCl (aq), 6M HCl (aq)

Equipment

2 nested styrofoam cups with lid (coffee cup calorimeter)*, thermometer, looped stirring rod*, slotted stopper*, 100-mL graduated cylinder, small 50-mL beaker, medium 250-mL beaker, utility clamp, ring stand, electronic balance, and wash bottle filled with distilled water

*Items with an asterisk may have to be checked out from the stockroom.

Safety

① Hydrogen gas will be generated during this experiment. As hydrogen is flammable, keep all heat and flames away from your reaction vessel.

② Hydrochloric acid is extremely caustic. If any HCl (aq) comes into contact with your skin or eyes, wash immediately under running water for at least ten minutes. The sodium bicarbonate solution by the sinks may be used to neutralize and clean up any acid spills.

Data Acquisition

Instead of a regular thermometer, some sections may use a temperature probe and data acquisition system to directly monitor temperature changes over time. Detailed instructions for setting up this system will be provided by your instructor at the beginning of the lab period. Please note that your experimental procedure will still be the same regardless of the method used to monitor temperature.

Instructions

1. You will be assigned a specific metal/metal oxide pair to investigate by your instructor. Record their identities on your report form. Note that you will perform the following procedure for a total of four times, twice with the metal, then twice with the metal oxide.

2. The table below indicates the quantities of reactants to be used for each metal/metal oxide combination. Note that the reactions involving Mg require the dilute 1M acid while the reactions involving Zn require the concentrated 6M acid.

<table>
<thead>
<tr>
<th></th>
<th>Mg / MgO</th>
<th>Zn / ZnO</th>
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<tbody>
<tr>
<td></td>
<td>0.15 g Mg, 25 mL 1M HCl</td>
<td>0.40 g Zn, 25 mL 6M HCl</td>
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<tr>
<td></td>
<td>0.25 g MgO, 25 mL 1M HCl</td>
<td>0.60 g ZnO, 25 mL 6M HCl</td>
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3. Use an electronic balance to weigh your empty, dry calorimeter (the two nested Styrofoam® cups with lid). Remove the calorimeter from the balance, then pour approximately 25-mL of HCl into it. Make sure the HCl you have obtained has the correct molarity concentration (see table above)! Now weigh the calorimeter and acid together. Record these masses on your lab report.
4. Now weigh an empty, dry 50-mL beaker. Remove the beaker from the balance, add the recommended mass of your assigned metal to it (see table above), then weigh it again. Record these masses on your lab report.

5. Assemble your equipment as shown in the figure on the next page. The thermometer and the stirring rod must be inserted through the holes in the calorimeter lid. The thermometer bulb should be immersed in the acid, but must not touch the bottom of the calorimeter. Place the calorimeter in a medium 250-mL beaker to prevent it from tipping over, then clamp the thermometer in place using the slotted stopper, utility clamp and ring stand.

6. Measure and record the temperature of the HCl (aq) in the calorimeter (while covered with the lid). Next, carefully add the metal sample to the acid. Quickly replace the lid and monitor the temperature change as the reaction occurs. Stir the solution continuously with the stirring rod using a gentle “up-down” motion. Record the maximum temperature achieved by the solution (should occur in 5-10 minutes). Note that the solution first warms up as the reaction occurs, but will then gradually cool as heat is lost to the surroundings. However, as Styrofoam is a poor conductor of heat this cooling will occur slowly. Thus it will be very easy for you to identify the maximum temperature.

7. When finished, dispose of your chemical waste as directed by your instructor. Then rinse the calorimeter, thermometer and stirring rod thoroughly with distilled water, dry, and repeat the experiment again. Once you have completed both trials with the metal, perform your two trials using the metal oxide using the identical procedure.

Note that (1) the calorimeter should be placed in a medium 250-mL beaker for extra stability, and (2) the thermometer must be clamped in place using the slotted stopper and utility clamp/stand.