Calorimetry and Thermochemistry

- Learn how to measure Heat flow.
- Learn about the Specific Heat of substances.
- Learn about Exothermic and Endothermic chemical reactions.
- Learn about the Enthalpy function.

In this laboratory exercise we will measure the Specific Heat of a metal and determine the Enthalpy of Reaction (ΔH) for two solvation processes; the solvation of Magnesium Sulfate Heptahydrate and the solvation of its Anhydrous salt. These measured Enthalpy changes will allow us to determine the amount of heat required to dehydrate the hydrated salt. Each of these three experiments will require us to measure the amount of Heat (q) produced or absorbed during the process or chemical reaction. This measurement will be performed within a Calorimeter.

Heat Flow (q) is generally thought of as the transfer of thermal energy from a "hot" object to a "cold" object. The warming of a soft drink on a hot day is a typical example of this transfer. The “hot” Air loses thermal energy and the “cold” soft drink gains it. However, nearly all chemical reactions involve the release or absorption of heat as well. The burning of Coal is a dramatic example of a chemical reaction in which a great deal of heat is released.

\[
C(s) + O_2(g) \rightarrow CO_2(g) + \text{Heat}
\]

Thermal energy stored in the bonds of the reactants is transferred to the cold surroundings as the reaction proceeds. Dissolving the salt Potassium Nitrate in water is an example of a chemical reaction in which heat is absorbed. As the salt dissolves, the solution becomes quite cold.

\[
KNO_3(s) + \text{Heat} \rightarrow K^+(aq) + NO_3^-(aq)
\]

This type of reaction is the basis for chemical cold packs used to treat minor injuries. In many instances, this transfer of Energy, measured in units of calories or Joules, can be quantified by observing the changes in temperature of the respective objects as heat flows between them.

The change in temperature (Δt) of a given substance as heat flows into or out of the substance will depend on the magnitude of the heat flow (q), the mass of the substance (m), and the "ability of the substance to absorb or release heat". The ability of a substance to absorb or release heat is simply the Specific Heat (sp) of the substance. Substances with large specific heats are "heat sponges" and can absorb a considerable amount of heat without a significant change in temperature. Water has a fairly high specific heat. Substances with small specific heats are "heat conductors." Metals are good conductors of heat and so have small specific heats. In terms of the temperature change, the heat flow is given as:
\[ q = sp \times m \times \Delta t \]  
(Eq. 1)

\[ \Delta t = \text{temp. change} \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( sp ) (cal/g°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.170</td>
</tr>
<tr>
<td>Gold</td>
<td>0.0308</td>
</tr>
<tr>
<td>Water</td>
<td>1.00</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.588</td>
</tr>
<tr>
<td>Wood</td>
<td>0.421</td>
</tr>
<tr>
<td>Cement</td>
<td>0.210</td>
</tr>
<tr>
<td>Glass</td>
<td>0.201</td>
</tr>
</tbody>
</table>

The measurement of heat flows during physical and chemical processes is called **Calorimetry**. Calorimetry involves observing the temperature change of a calorimetric substance, usually Water, as it absorbs or releases the heat by-product of said reaction or process. The system which contains the calorimetric substance and the reaction/process is called a Calorimeter. A simple Coffee-Cup Calorimeter is pictured below. The Styrofoam walls of the coffee cup make an excellent insulator for the calorimeter; i.e. there is extremely little heat flow to and from the surroundings. The calorimetric substance is Water, whose specific heat is 1.00 cal/g°C. The temperature of the Water can easily be observed. If the mass of the Water in the calorimeter is known, then the heat flow can be calculated via the equation given above. A simplifying assumption, which is fairly easily relieved, is that the calorimeter itself absorbs or releases relatively little heat during the course of the measurements. For the small heat exchanges involved in the cases examined in this experiment, this simplifying assumption is fairly good.
We will consider two different calorimetric measurements; heat flow out of a hot metal and heat flow during two different chemical reactions. The first, measuring the heat flow out of a metal, will allow us to determine the specific heat (sp) of the metal. The second set of measurements, heat flow during chemical reactions, will allow us to predict the heat requirements of a chemical reaction for which it is difficult to measure the heat flow.

Specific Heat of a Metal

To measure the specific heat of a metal, the metal is heated to a known temperature. The "hot" metal is then placed in the Water in the calorimeter. The temperature change of the Water in the calorimeter is observed. (See picture below.)

The heat flow into the Water can be calculated.

\[
q_{\text{wat}} = (1.00 \text{cal/g}^\circ \text{C}) \times (m_{\text{wat}}) \times (\Delta t_{\text{wat}})
\]

By the Law of Conservation of Energy, the heat flow out of the metal must equal the flow into the Water:

\[
q_{\text{met}} = q_{\text{wat}}
\]

(Eq. 2)
(Again, this assumes the Calorimeter absorbs very little heat; a good assumption for our experiment.) Finally, the specific heat of the metal can be determined via:

\[ s_{\text{met}} = \frac{q_{\text{met}}}{(m_{\text{met}})x(\Delta t_{\text{met}})} \]  

(Eq. 3)

**Thermochemical Measurements**

Thermochemistry is the study of the quantity of heat absorbed or produced by chemical reactions. A chemical reaction is **Exothermic** when heat is produced and **Endothermic** when heat is absorbed. To measure the heat flow during a chemical reaction, the chemical reaction is carried out inside a calorimeter and the temperature change for the calorimetric fluid is observed. This can be done in a couple of different ways. If the reaction occurs in an aqueous environment, the reaction can be carried out directly in the Water of the calorimeter. In this case, the Water is acting as both a solvent and the calorimetric substance. (This arrangement is typical for acid-base neutralization reactions and for the solvation of salts.) If not, the reaction can be carried out inside a metal encased "bomb" which is then immersed into the Water of the calorimeter. (This arrangement is typical for combustion reactions.) In either case, the heat flow into the Water can be calculated:
\[ q_{\text{wat}} = (1.00 \text{cal/g}^\circ \text{C}) \times (m_{\text{wat}}) \times (\Delta t_{\text{wat}}) \]

By the Law of Conservation of Energy, the heat flow accompanying the chemical reaction must be equal to the heat gained or lost by the water:

\[ q_{\text{rxn}} = q_{\text{wat}} \]  \hspace{1cm} \text{(Eq. 4)}

(Again, this assumes no heat is absorbed by the Calorimeter.) This is as pictured below, for a chemical reaction which is exothermic and occurs in an aqueous environment.

For reactions which occur under conditions of constant Pressure, which is the case for the reaction pictured above, and is typical of many chemical reactions, the heat flow is defined as the Change in the Enthalpy (\( \Delta H \)) for the reaction:

\[ \Delta H = q_{\text{rxn}} \text{ at const. Pressure} \]  \hspace{1cm} \text{(Eq. 5)}

\[ = H_{\text{Products}} - H_{\text{Reactants}} \]  \hspace{1cm} \text{(Eq. 6)}

The Enthalpy (H) is a type of Chemical Energy, sometimes referred to as the "Heat Content" of the reactants. Frequently, the Enthalpy is reported on a per mole basis. By convention, Endothermic reactions have a positive heat flow and hence a positive Enthalpy Change; they are gaining thermal energy. Exothermic reactions have a negative heat flow and hence a negative Enthalpy Change; they are losing thermal energy.
Tabulated enthalpy changes can be used to predict the heat content of a reaction which is difficult to carry-out or for which measuring the heat flow is difficult.

As an example, suppose we measure the Enthalpy Change for the following two reactions, which are experimentally easy to carry-out:

\[ \text{Sn(s)} + \text{Cl}_2(g) \rightarrow \text{SnCl}_2(s) \quad \Delta H = -325.1 \text{ kJoule} \]
\[ \text{SnCl}_2(s) + \text{Cl}_2(g) \rightarrow \text{SnCl}_4(l) \quad \Delta H = -186.2 \text{ kJoule} \]

This means the Enthalpy Change for the composite reaction, which is more difficult to carry-out experimentally:

\[ \text{Sn(s)} + 2 \text{Cl}_2(g) \rightarrow \text{SnCl}_4(l) \]

can be calculated as:

\[ \Delta H = -325.1 \text{ kJoule} + -186.2 \text{ kJoule} = -511.3 \text{ kJoule} \]

Pictorially, this is represented in an Enthalpy Diagram as:
In this laboratory we will measure the specific heat for a metal and the enthalpy change for the solvation of MgSO$_4$ and MgSO$_4$$\cdot$7H$_2$O. These measurements will be done in a coffee-cup calorimeter. The metal’s specific heat will be compared with the known specific heat as tabulated in reference sources in order to give us a sense of the quality of the measurement. The enthalpy changes for dissolving anhydrous Magnesium Sulfate, MgSO$_4$, and Magnesium Sulfate Heptahydrate, MgSO$_4$$\cdot$7H$_2$O in Water:

\[
\text{MgSO}_4$$\cdot$7H$_2$O(s) \rightarrow \text{MgSO}_4(aq) + 7\text{H}_2\text{O}(l) \quad \text{(Eq. 7)}
\]

\[
\text{MgSO}_4(s) \rightarrow \text{MgSO}_4(aq) \quad \text{(Eq. 8)}
\]

will be used to determine the enthalpy change for the dehydration of the Hydrate:

\[
\text{MgSO}_4$$\cdot$7H$_2$O(s) \rightarrow \text{MgSO}_4(s) + 7\text{H}_2\text{O}(g) \quad \text{(Eq. 9)}
\]
Pre-Lab Safety Questions

Some general questions this time around:

1. What is the OHSA definition of a "Flammable Liquid"?

2. What quantity of liquid chemical describes the general transition between maximum amounts to keep at workbenches and amounts to be stored?

3. What is the difference between a "Flammable Liquid Storage" and "Explosion Proof" refrigerator?

4. What precaution should be taken when transferring flammable liquids from a metal container to a metal receiver?
Procedure

Specific Heat of a Metal

1. Obtain a 50g sample of metal. Weigh this accurately. Place it in a large test tube. Heat the metal in a boiling water bath for 15 minutes. This brings the temperature of the metal to 100°C.

2. While the metal is heating, construct a coffee cup calorimeter. Place 50g of room temperature water in the calorimeter. Measure the temperature of the water in the calorimeter.

3. When the metal is done heating, quickly place the metal in the calorimeter. Stirring constantly, observe the temperature of the water. Record the maximum temperature observed.

Thermochemical Measurements

1. Weigh out 12.3g of MgSO₄•7H₂O.

2. Construct a coffee cup calorimeter. Place 50g of room temperature water in the calorimeter. Measure the temperature of the water in the calorimeter.

3. Add the 12.3g of magnesium sulfate heptahydrate to the calorimeter water and stir with a magnetic stirrer. Record the maximum temperature observed.

4. Repeat the process for 6.0g of MgSO₄.
Data Analysis

Specific Heat of a Metal

1. Calculate the heat flow into the water of the calorimeter.
2. Determine the heat flow out of the metal.
3. Calculate the specific heat of the metal.
4. Compare the measured specific heat with the accepted value listed in the CRC Handbook of Chemistry and Physics. Report the percentage error for your measurement.
5. What is the largest source of error in your experiment?

Thermochemical Measurements

1. Calculate the heat flow into/out-of the water of the calorimeter for the MgSO₄•7H₂O solvation. How many moles of the salt is used in this reaction? What is ΔH for the solvation on a per mole basis? (Be sure to use the correct sign.)

2. Calculate the heat flow into/out-of the water of the calorimeter for the MgSO₄ solvation. How many moles of salt is used in this reaction? What is ΔH for the solvation on a per mole basis? (Be sure to use the correct sign.)

3. Consider the hypothetical case of removing the magnesium sulfate from solution and reforming the anhydrous salt:

   \[
   \text{MgSO}_4(aq) \rightarrow \text{MgSO}_4(s)
   \]

   What is the molar Enthalpy Change ΔH for this reaction?

4. The Enthalpy Change for the vaporization of Water is:

   \[
   \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)
   \]

   10.5 kcal/mole. What is the Enthalpy Change for the following reaction:

   \[
   7 \text{H}_2\text{O}(l) \rightarrow 7 \text{H}_2\text{O}(g)
   \]
5. Tabulate the above Enthalpy Change values:

\[
\begin{array}{lcl}
\text{Reaction} & \Delta H (\text{kcal}) \\
\text{MgSO}_4\cdot7\text{H}_2\text{O}(s) \rightarrow \text{MgSO}_4(\text{aq}) + 7 \text{H}_2\text{O}(l) & \hn & \\
\text{MgSO}_4(\text{aq}) \rightarrow \text{MgSO}_4(\text{s}) & \hn & \\
7 \text{H}_2\text{O}(l) \rightarrow 7 \text{H}_2\text{O}(g) & \hn &
\end{array}
\]

and then determine the Enthalpy Change for the following reaction:

\[
\text{MgSO}_4\cdot7\text{H}_2\text{O}(s) \rightarrow \text{MgSO}_4(\text{s}) + 7\text{H}_2\text{O}(g)
\]

6. Sketch an Enthalpy Diagram for this series of reactions.
Post-Lab Questions

1. Suppose your thermometer were reading too high by 1.5°C. How would this affect your measurement of the specific heat of a metal using our method?

2. 35g of Gold (sp = 0.0308 cal/g°C) at 100°C is added to 40g of Water at 22°C in a Coffee-Cup Calorimeter. What is the final temperature of the system?

3. What is the Specific Heat of Gold in units of J/gK?

4. Is the Specific Heat an intensive or extensive physical property? Why does this matter?