Determining Enthalpy Change: Calorimetry

Tabulated $\Delta H_{\text{rxn}}$ values are derived from experimental data. Experiments that measure heat exchange are referred to collectively as calorimetry experiments, and the measurement device is called a calorimeter. There are two important types of calorimetry experiments, constant-pressure calorimetry (also known as coffee-cup calorimetry) and constant-volume calorimetry (also known as bomb calorimetry).

In constant-pressure calorimetry, the heat evolved or absorbed during a chemical change is measured under conditions where the pressure does not change. This typically means that the chemical change is allowed to occur in a reaction vessel that is open to the atmosphere, and thus the pressure remains essentially constant. Under these conditions, the heat evolved or absorbed, $q$, is equal to the enthalpy change for the reaction, $\Delta H$.

Heat exchange under conditions of constant pressure can be measured using a simple coffee-cup calorimeter (shown Figure 5.YY). The reaction vessel consists of two nested styrofoam coffee cups that are covered with a lid. A thermometer measures the temperature change. Most coffee-cup calorimetry experiments involve a solvent such as water and a stirring device ensures thorough mixing in the reaction vessel.

Figure 5.YY. A coffee-cup calorimeter

Chapter Goals Revisited

- Relate energy to chemical change.
- Calculate enthalpy change from calorimetry experiments.
In a constant-pressure calorimetry experiment, the system consists of the chemicals undergoing change, and the surroundings consist of the other contents of the calorimeter, the calorimeter itself, and all materials around the calorimeter. However, the calorimeter is designed to minimize energy transfer, and thus it is possible to assume that the surroundings consist only of the contents of the calorimeter. Therefore, the temperature change measured by the thermometer allows calculation of $q_{\text{surroundings}}$ for a chemical change in a coffee-cup calorimeter.

$$q_{\text{surroundings}} = (\text{mass of calorimeter contents})(\text{specific heat of solution})(\Delta T)$$

Because $0 = q_{\text{system}} + q_{\text{surroundings}}$, the enthalpy change for a chemical process taking place in a coffee-cup calorimeter is

$$\Delta H = q_{\text{system}} = -q_{\text{surroundings}}$$

In a typical experiment, enthalpy change is reported per mol of reactant (kJ/mol). Note that in constant-pressure calorimetry experiments, an increase in temperature indicates an exothermic reaction ($q_{\text{surroundings}}$ is positive, $q_{\text{system}}$ and $\Delta H$ are negative) and a decrease in temperature indicates an endothermic reaction ($q_{\text{surroundings}}$ is negative, $q_{\text{system}}$ and $\Delta H$ are positive).

**EXAMPLE PROBLEM: Constant-Pressure Calorimetry**

Ammonium chloride is very soluble in water. When 4.50 g NH₄Cl is dissolved in 53.00 g of water, the temperature of the solution decreases from 20.40 ºC to 15.20 ºC. Calculate the enthalpy of dissolution of NH₄Cl in kJ/mol. Assume that the specific heat of the solution is 4.18 J/g·ºC and that the heat absorbed by the calorimeter is negligible.

**SOLUTION:**

First calculate the energy change for the surroundings ($q_{\text{solution}}$) in the coffee-cup calorimeter.

$$c_{\text{solution}} = 4.18 \text{ J/g·ºC}$$

$$m_{\text{solution}} = 4.50 \text{ g} + 53.00 \text{ g} = 57.50 \text{ g}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 15.20 \text{ ºC} - 20.40 \text{ ºC} = -5.20 \text{ ºC}$$

$$q_{\text{solution}} = m_{\text{solution}}c_{\text{solution}}\Delta T = (57.50 \text{ g})(4.18 \text{ J/g·ºC})(-5.20 \text{ ºC}) = -1250 \text{ J}$$

Next calculate $q$ for the dissolution of NH₄Cl, $q_{\text{system}}$.

$$q_{\text{dissolution}} + q_{\text{solution}} = 0$$

$$q_{\text{solution}} = -q_{\text{dissolution}} = 1250 \text{ J}$$

Finally, calculate the amount of NH₄Cl dissolved (mol) and $\Delta H$ for the dissolution of NH₄Cl (kJ/mol).

$$\frac{4.50 \text{ g NH₄Cl}}{53.49 \text{ g}} \times \frac{1 \text{ mol NH₄Cl}}{1 \text{ mol NH₄Cl}} = 0.0841 \text{ mol NH₄Cl}$$

$$\Delta H_{\text{dissolution}} = \frac{q_{\text{dissolution}}}{\text{mol NH₄Cl}} = \frac{1250 \text{ J}}{0.0841 \text{ mol}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 14.9 \text{ kJ/mol}$$

Notice that the temperature of the solution decreased, indicating an endothermic process and a positive value for $\Delta H_{\text{dissolution}}$.
The chemical reaction studied in a bomb calorimeter takes place inside a sealed steel vessel (the bomb) that is completely surrounded by a water bath, and an insulated jacket surrounds the water bath. The temperature change of the chemical reaction is determined by measuring the temperature change of the water surrounding the bomb.

Because the reaction studied in a bomb calorimetry experiment takes place in a sealed bomb, this is a constant-volume calorimetry experiment, not a constant-pressure experiment. Under constant volume conditions the heat evolved or absorbed by a chemical change, \( q \), is equal to the change in energy, \( \Delta E \), not the change in enthalpy, \( \Delta H \). However, the difference between \( \Delta E \) and \( \Delta H \) is quite small for most chemical reactions.

The heat evolved in a bomb calorimeter combustion reaction (\( q_{\text{reaction}} \)) is absorbed by the steel bomb (\( q_{\text{bomb}} \)) and the water in the water bath (\( q_{\text{water}} \)).

\[ 0 = q_{\text{reaction}} + q_{\text{bomb}} + q_{\text{water}} \]

The heat absorbed by the steel bomb is calculated from the temperature change of the water bath (\( \Delta T \)) and the bomb heat capacity (\( c_{\text{bomb}}, \text{J/}^\circ\text{C} \)). The heat absorbed by the water bath is calculated from the mass of water, the specific heat of water, and the water bath temperature change.
**EXAMPLE PROBLEM: Constant-Volume Calorimetry**

A 0.444-g sample of sucrose (C\text{12}H\text{22}O\text{11}) is burned in a bomb calorimeter and the temperature increases from 20.00 °C to 22.06 °C. The calorimeter contains 748 g of water and the bomb has a heat capacity of 420. J/°C. Calculate \( \Delta E \) for the combustion reaction per mole of sucrose burned (kJ/mol).

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + 12 \text{O}_2(g) \rightarrow 12 \text{CO}_2(g) + 11 \text{H}_2\text{O}(l)
\]

**SOLUTION:**

First, calculate the energy absorbed by the water bath and the bomb.

**Water bath:**
\[
c_{\text{water}} = 4.184 \text{ J/g·°C} \\
m_{\text{water}} = 748 \text{ g} \\
\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.06 \text{ °C} - 20.00 \text{ °C} = 2.06 \text{ °C} \\
q_{\text{water}} = m\cdot c_{\text{water}} \cdot \Delta T = (748 \text{ g})(4.184 \text{ J/g·°C})(20.6 \text{ °C}) = 6450 \text{ J}
\]

**Bomb:**
\[
c_{\text{bomb}} = 420. \text{ J/°C} \\
\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.06 \text{ °C} - 20.00 \text{ °C} = 2.06 \text{ °C} \\
q_{\text{bomb}} = c_{\text{bomb}} \cdot \Delta T = (420 \text{ J/g·°C})(2.06 \text{ °C}) = 865 \text{ J}
\]

Next, calculate the energy released by the combustion reaction.

\[
0 = q_{\text{reaction}} + q_{\text{bomb}} + q_{\text{water}} \\
q_{\text{reaction}} = -(q_{\text{bomb}} + q_{\text{water}}) = -(6450 \text{ J} + 865 \text{ J}) = -7320 \text{ J}
\]

Finally, calculate the amount (mol) of sucrose burned in the combustion reaction and the energy change for the reaction.

\[
0.444 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.3 \text{ g}} = 0.00130 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}
\]

\[
\Delta E = \frac{q_{\text{reaction}}}{\text{mol C}_{12}\text{H}_{22}\text{O}_{11}} = \frac{-7320 \text{ J}}{0.00130 \text{ mol}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = -5640 \text{ kJ/mol}
\]

This is an exothermic reaction. Temperature increased and \( q_{\text{reaction}} \) and \( \Delta E \) are negative. In addition, because the difference between \( \Delta E \) and \( \Delta H \) is quite small, this energy change can be taken as the enthalpy of combustion (\( \Delta H_{\text{comb}} \)) for sucrose.