Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data
- To use calorimetric data to calculate enthalpy changes.

Measuring Heat Flow

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process.

![Figure \(\PageIndex{1}\): In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system. Image used with permission (CC-BY; OpenStax).](image)

The thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat \( (q_{\text{rxn}} < 0) \), then heat is absorbed by the calorimeter \( (q_{\text{calorimeter}} > 0) \) and its temperature increases. Conversely, if the reaction absorbs heat \( (q_{\text{rxn}} > 0) \), then heat is transferred from the calorimeter to the system \( (q_{\text{calorimeter}} < 0) \) and the temperature of the calorimeter decreases. In both cases, the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

Note
The amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction.

**Constant-Pressure Calorimetry**

Because $\Delta H$ is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give $\Delta H$ values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a coffee-cup calorimeter (Figure 2), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree ($10^{-6}^\circ C$).

![Coffee-Cup Calorimeter Diagram](image)

**Figure 2**: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Before we practice calorimetry problems involving chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same...
temperature—that is, when they reach thermal equilibrium (Figure 5.3.4). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter’s surroundings. Under these ideal circumstances, the net heat change is zero:

\[ q_{\text{substance M}} + q_{\text{substance W}} = 0 \] \( \label{7.3.1} \)

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

\[ q_{\text{substance M}} = -q_{\text{substance W}} \] \( \label{7.3.2} \)

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that \( q_{\text{substance M}} \) and \( q_{\text{substance W}} \) are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either \( q \) value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, \( q_{\text{substance M}} \) is a negative value and \( q_{\text{substance W}} \) is positive, since heat is transferred from M to W.

![Figure 5.3.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.](image)

**Example \((\PageIndex{1})\): Heat Transfer between Substances at Different Temperatures**

A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

**Solution**

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the
water, with no heat “lost” to the surroundings, then heat given off by rebar = −heat taken in by water, or:

\[ q_{\text{rebar}} = -q_{\text{water}} \quad \text{(5.3.3)} \]

Since we know how heat is related to other measurable quantities, we have:

\[(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}} \quad \text{(5.3.4)} \]

Letting \( f \) = final and \( i \) = initial, in expanded form, this becomes:

\[ c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}}) \quad \text{(5.3.5)} \]

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

\[ (0.449 \text{ J/g \degree C})(360 \text{ g})(42.7 \degree C - T_{\text{i,rebar}}) = -(4.184 \text{ J/g \degree C})(425 \text{ g})(42.7 \degree C - 24.0 \degree C) \quad \text{(5.3.6a)} \]

\[ T_{\text{i,rebar}} = \frac{(4.184 \text{ J/g \degree C})(425 \text{ g})(42.7 \degree C - 24.0 \degree C)}{(0.449 \text{ J/g \degree C})(360 \text{ g})} + 42.7 \degree C \quad \text{(5.3.6b)} \]

Solving this gives \( T_{\text{i,rebar}} = 248 \degree C \), so the initial temperature of the rebar was 248 °C.

Exercise \( \PageIndex{1A} \):

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

**Answer:**

The initial temperature of the copper was 335.6 °C.

Exercise \( \PageIndex{1B} \):

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

**Answer:**

The final temperature (reached by both copper and water) is 38.8 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Example \( \PageIndex{2} \): Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

**Solution**
Assuming perfect heat transfer, heat given off by metal = −heat taken in by water, or:

\[ q_{\text{metal}} = -q_{\text{water}} \] \( \text{label}{5.3.7} \)

In expanded form, this is:

\[ c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}}) \] \( \text{label}{5.3.8} \)

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

\[ c_{\text{metal}} \times (59.7 \text{ g}) \times (28.5°C - 100.0°C) = -c_{\text{water}} \times (60.0 \text{ g}) \times (28.5°C - 22.0°C) \] \( \text{label}{5.3.9} \)

Solving this:

\[ c_{\text{metal}} = \frac{-c_{\text{water}} \times (60.0 \text{ g}) \times 6.5°C}{(59.7 \text{ g}) \times (-71.5°C)} = 0.38 \text{ J/g °C} \]

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise \( \PageIndex{2} \)

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

\[ c_{\text{metal}} = 0.13 \text{ J/g °C} \]

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), \( q_{\text{reaction}} \), plus the heat absorbed or lost by the solution (the "surroundings"), \( q_{\text{solution}} \), must add up to zero:

\[ q_{\text{reaction}} + q_{\text{solution}} = 0 \] \( \text{label}{ \PageIndex{3}} \)

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

\[ q_{\text{reaction}} = -q_{\text{solution}} \] \( \text{label}{ \PageIndex{4}} \)

This concept lies at the heart of all calorimetry problems and calculations. Because the heat released or absorbed at constant pressure is equal to \( \Delta H \), the relationship between heat and \( \Delta H_{\text{rxn}} \) is
\[
\Delta H_{\text{rxn}} = q_{\text{rxn}} = -q_{\text{calorimeter}} = -mC_{s}\Delta T
\]

The use of a constant-pressure calorimeter is illustrated in Example \(\PageIndex{3}\).

Example \(\PageIndex{3}\)

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm\(^3\). What is \(\Delta H_{\text{soln}}\) (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

**Given:** mass of substance, volume of solvent, and initial and final temperatures

**Asked for:** \(\Delta H_{\text{soln}}\)

**Strategy:**

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.

B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation \(\PageIndex{1}\).

C. Use the molar mass of KOH to calculate \(\Delta H_{\text{soln}}\).

**Solution:**

A To calculate \(\Delta H_{\text{soln}}\), we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

\[
\left(100.0 \; \text{mL}\right) \left(0.9969 \; \text{g/mL}\right) + 5.03 \; \text{g} \; \text{KOH} = 104.72 \; \text{g}
\]

The temperature change is (34.7°C − 23.0°C) = +11.7°C.

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

\[
q_{\text{calorimeter}} = mC_{s}\Delta T = \left(104.72 \; \text{g}\right) \left(\frac{4.184 \; \text{J}}{\text{g}\cdot^\circ\text{C}}\right) \left(11.7 \; ^\circ\text{C}\right) = 5130 \; \text{J} = 5.13 \; \text{kJ}
\]

The temperature of the solution increased because heat was absorbed by the solution \(q > 0\). Where did this heat come from? It was released by KOH dissolving in water. From Equation \(\PageIndex{1}\), we see that

\[
\Delta H_{\text{rxn}} = -q_{\text{calorimeter}} = -5.13 \; \text{kJ}
\]

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the release of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate \(\Delta H_{\text{soln}}\)—the heat released when dissolving 1 mol of KOH:
Exercise \(\PageIndex{3}\)

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example \(\PageIndex{3}\), find \(\Delta H_{\text{soln}}\) for \(\text{NH}_4\text{Br}\) (in kilojoules per mole).

**Answer:** 16.6 kJ/mol

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**Constant-Volume Calorimetry**

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter (A device used to measure energy changes in chemical processes. shown schematically in Figure \(\PageIndex{3}\)). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the “bomb”). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.
a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.

Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in internal energy ($\Delta U$) rather than the enthalpy change ($\Delta H$); $\Delta U$ is related to $\Delta H$ by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta U < \Delta H$, the relationship between the measured temperature change and $\Delta H_{\text{comb}}$ is given in Equation \ref{7.3.6}, where $C_{\text{bomb}}$ is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{\text{comb}} < q_{\text{comb}} = q_{\text{calorimeter}} = C_{\text{bomb}} \Delta T \ \label{7.3.6}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its $\Delta H_{\text{comb}} = -26.38$ kJ/g). This value and the measured increase in temperature of the calorimeter can be used in Equation \ref{5.42} to determine $C_{\text{bomb}}$. The use of a bomb calorimeter to measure the $\Delta H_{\text{comb}}$ of a substance is illustrated in Example \ref{PageIndex{4}}.

**Video \ref{PageIndex{1}}**: Video of view how a bomb calorimeter is prepared for action.

**Example \ref{PageIndex{4}}**: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the
calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the $\Delta H_{\text{comb}}$ of glucose?

**Given:** mass and $\Delta T$ for combustion of standard and sample

**Asked for:** $\Delta H_{\text{comb}}$ of glucose

**Strategy:**

A. Calculate the value of $q_{\text{rxn}}$ for benzoic acid by multiplying the mass of benzoic acid by its $\Delta H_{\text{comb}}$. Then use Equation (\PageIndex{2}) to determine the heat capacity of the calorimeter ($C_{\text{bomb}}$) from $q_{\text{comb}}$ and $\Delta T$.

B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the $\Delta H_{\text{comb}}$ of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

**Solution:**

The first step is to use Equation (\PageIndex{2}) and the information obtained from the combustion of benzoic acid to calculate $C_{\text{bomb}}$. We are given $\Delta T$, and we can calculate $q_{\text{comb}}$ from the mass of benzoic acid:

\[
q_{\text{comb}} = (0.579 \; \text{g}) \times (-26.38 \; \text{kJ/g}) = -15.3 \; \text{kJ}
\]

From Equation (\PageIndex{2}),

\[
-C_{\text{bomb}} = \frac{q_{\text{comb}}}{\Delta T} = \frac{-15.3 \; \text{kJ}}{2.08 \; ^\circ C} = -7.34 \; \text{kJ/}^\circ \text{C}
\]

According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

\[
q_{\text{comb}} = -C_{\text{bomb}} \times \Delta T = (7.34 \; \text{kJ/}^\circ \text{C}) \times (3.64 \; ^\circ \text{C}) = 26.7 \; \text{kJ}
\]

Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the $\Delta H_{\text{comb}}$ of glucose is

\[
\Delta H_{\text{comb}} = \frac{-26.7 \; \text{kJ}}{1.732 \; \text{g}} \times \frac{180.16 \; \text{g/mol}}{\text{mol}} = \text{(mol)}
\]
This result is in good agreement (< 1% error) with the value of $\Delta H_{\text{comb}} = -2803 \text{ kJ/mol}$ that calculated using enthalpies of formation.

Exercise (PageIndex{4}): Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine ($\text{CH}_3\text{NNHNH}_2$) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the $\Delta H_{\text{comb}}$ of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.

Answer: $-1.30 \times 10^3 \text{ kJ/mol}$

Summary

- Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system.

Calorimetry is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called calorimeters, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The heat capacity ($C$) of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The specific heat ($C_s$) of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the molar heat capacity ($C_p$) is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a constant-pressure calorimeter, which gives $\Delta H$ values directly, or a bomb calorimeter, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called calorimeters. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects
the temperature of an object.

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