

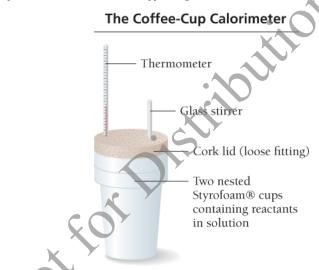
9.7: Measuring ΔH for Chemical Reactions: Constant-Pressure Calorimetry

For many aqueous reactions, we can measure $\Delta H_{\rm rxn}$ fairly simply using a <u>coffee-cup calorimeter</u> shown in Figure 9.8. The calorimeter consists of two Styrofoam® coffee cups, one inserted into the other, to provide insulation from the laboratory environment. The calorimeter is equipped with a thermometer and a stirrer. The reaction occurs in a specifically measured quantity of solution within the calorimeter, so that the mass of the solution is known. During the reaction, the heat evolved (or absorbed) causes a temperature change in the solution, which the thermometer measures. If we know the specific heat capacity of the solution, normally assumed to be that of water, we can calculate $q_{\rm soln}$, the heat absorbed by or lost from the solution (which is acting as the surroundings) using the equation:

$$q_{
m soln} = m_{
m soln} imes C_{
m s, \, soln} imes \Delta T$$

Figure 9.8 The Coffee-Cup Calorimeter

A coffee-cup calorimeter measures enthalpy changes for chemical reactions in solution.



The insulated calorimeter prevents heat from escaping, so we assume that the heat gained by the solution equals that lost by the reaction (or vice versa):

$$q_{
m rxn} = -q_{
m soln}$$

The equation, $q_{
m rxn}=-q_{
m soln}$, assumes that no heat is lost to the calorimeter itself. If heat absorbed by the calorimeter is accounted for, the equation is $q_{
m rxn}=-(q_{
m soln}+q_{
m cal})$.

Because the reaction happens under conditions of constant pressure (open to the atmosphere), $q_{\rm rxn}=q_{\rm p}=\Delta H_{\rm rxn}$ (Equation 9.13.). This measured quantity is the heat of reaction for the specific amount (which is measured ahead of time) of reactants that reacted. To get $\Delta H_{\rm rxn}$ per mole of a particular reactant—a more general quantity—we divide by the number of moles that actually reacted, as demonstrated in Example 9.8.

Summarizing Calorimetry:

- Bomb calorimetry occurs at constant volume and measures $\Delta \textit{E}$ for a reaction.
- Coffee-cup calorimetry occurs at constant *pressure* and measures ΔH for a reaction.

Example 9.8 Measuring ΔH_{rxn} in a Coffee-Cup Calorimeter

Magnesium metal reacts with hydrochloric acid according to the balanced equation:

$$\mathrm{Mg}\left(s
ight) + 2\ \mathrm{HCl}\left(aq
ight)
ightarrow \mathrm{MgCl}_{2}\left(aq
ight) + \mathrm{H}_{2}\left(g
ight)$$

In an experiment to determine the enthalpy change for this reaction, you combine 0.158 g of Mg metal with enough HCl to make 100.0 mL of solution in a coffee-cup calorimeter. The HCl is sufficiently concentrated so that the Mg completely reacts. The temperature of the solution rises from 25.6 $^{\circ}$ C to 32.8 °C as a result of the reaction. Find $\Delta H_{
m rxn}$ for the reaction as written. Use 1.00 g/mL as the density of the solution and $C_{\rm s,\,soln}=4.18~{
m J/g}\cdot{
m ^{\circ}C}$ as the specific heat capacity of the solution.

SORT You are given the mass of magnesium, the volume of solution, the initial and final temperatures, the density of the solution, and the heat capacity of the solution. You are asked to find the change in enthalpy for the reaction.

GIVEN:

 $0.158 \; \mathrm{g \; Mg}$ $100.0 \mathrm{\ mL\ soln}$ $T_{
m i} = 25.6\,{
m ^{\circ}C}$ $T_{
m f} = 32.8\,{
m ^{\circ}C}$ $d_{\mathrm{soln}} = 1.00 \; \mathrm{g/mL} \quad C_{\mathrm{s, soln}} = 4.18 \; \mathrm{J/g} \cdot \mathrm{^{\circ}C}$

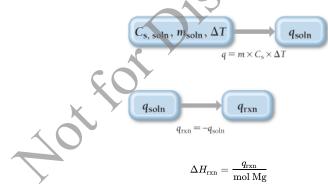
FIND: $\Delta H_{\rm rxn}$

STRATEGIZE The conceptual plan has three parts. In the first part, use the temperature change and the other given quantities, together with the equation $q=m imes C_{
m s} imes \Delta T$, to find $q_{
m soln}$.

In the second part, use $q_{
m soln}$ to get $q_{
m rxn}$ (which simply involves changing the sign). Because the pressure is constant, $q_{
m rxn}$ is equivalent to $\Delta H_{
m rxn}$ for the amount of magnesium that reacts.

In the third part, divide $q_{
m rxn}$ by the number of moles of magnesium to get $\Delta H_{
m rxn}$ per mole of magnesium.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$$q = m imes C_{
m s} imes \Delta T$$
 $q_{
m rxn} = -q_{
m soln}$

SOLVE Gather the necessary quantities in the correct units for the equation $q=m imes C_{
m s} imes \Delta T$ and substitute into the equation to calculate $q_{
m soln}$. Notice that the sign of $q_{
m soln}$ is positive, meaning that the solution absorbed heat from the reaction.

Find $q_{\rm rxn}$ by taking the negative of $q_{\rm soln}$. Notice that $q_{\rm rxn}$ is negative, as expected for an exothermic reaction.

Finally, find ΔH_{rxn} per mole of magnesium by dividing q_{rxn} by the number of moles of magnesium that reacts. Find the number of moles of magnesium from the given mass of magnesium and its molar mass.

Because the stoichiometric coefficient for magnesium in the balanced chemical equation is 1, the calculated value represents $\Delta H_{\rm rxn}$ for the reaction as written.

SOLUTION

$$\begin{split} C_{\text{s, soln}} &= 4.18 \text{ J/g} \cdot {^{\circ}\text{C}} \\ m_{\text{soln}} &= 100.0 \text{ mL soln} \times \frac{1.00 \text{ g}}{1 \text{ mL soln}} = 1.00 \times 10^2 \text{ g} \\ \Delta T &= T_{\text{f}} - T_{\text{i}} \\ &= 32.8 \text{ °C} - 25.6 \text{ °C} = 7.2 \text{ °C} \\ q_{\text{soln}} &= m_{\text{soln}} \times C_{\text{s, soln}} \times \Delta T \\ &= 1.00 \times 10^2 \text{ g/s} \times 4.18 \frac{\text{J}}{\text{g/s}^{\circ} \text{ g/s}} \times 7.2 \text{ °g/s} = 3.0 \times 10^3 \text{ J} \\ q_{\text{rxn}} &= -q_{\text{soln}} = -3.0 \times 10^3 \text{ J} \\ \Delta H_{\text{rxn}} &= \frac{q_{\text{rxn}}}{\text{mol Mg}} \\ &= \frac{-3.0 \times 10^3 \text{ J}}{0.158 \text{ g Mg/s}} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \\ &= -4.6 \times 10^5 \text{ J/mol Mg} \\ \text{Mg} \, (s) + 2 \, \text{HCl} \, (aq) \rightarrow \text{MgCl}_2 \, (aq) + \text{H}_2 \, (g) \, \Delta H_{\text{rxn}} = -4.6 \times 10^5 \text{ J} \end{split}$$

CHECK The units of the answer (J) are correct for the change in enthalpy of a reaction. The sign is negative, as you would expect for an exothermic reaction.

FOR PRACTICE 9.8 The addition of hydrochloric acid to a silver nitrate solution precipitates silver chloride according to the reaction:

$$\mathrm{AgNO}_{3}\left(aq\right)+\mathrm{HCl}\left(aq\right)\Rightarrow\mathrm{AgCl}\left(s\right)+\mathrm{HNO}_{3}\left(aq\right)$$

When you combine 50.0 mL of 0.100 M AgNO $_3$ with 50.0 mL of 0.100 M HCl in a coffee-cup calorimeter, the temperature changes from 23.40 °C to 24 21 °C. Calculate $\Delta H_{\rm rxn}$ for the reaction as written. Use 1.00 g/mL as the density of the solution and $C=4.18~{\rm J/g}\cdot{\rm ^{\circ}C}$ as the specific heat capacity.

Interactive Worked Example 9.8 Measuring ΔH_{rxn} in a Coffee-Cup Calorimeter

Conceptual Connection 9.7 Constant-Pressure versus Constant-Volume Calorimetry

Aot for Distribution