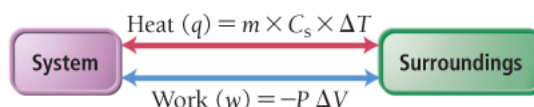


9.5: Measuring ΔE for Chemical Reactions: Constant-Volume Calorimetry

We now have a complete picture of how a system exchanges energy with its surroundings via heat and pressure–volume work:



Recall from [Section 9.3](#) that the change in internal energy that occurs during a chemical reaction (ΔE) is a measure of *all of the energy* (heat and work) exchanged with the surroundings ($\Delta E = q + w$). Therefore, we can measure the changes in temperature (to calculate heat) and the changes in volume (to calculate work) that occur during a chemical reaction, and sum them together to calculate ΔE . However, an easier way to obtain the value of ΔE for a chemical reaction is to force all of the energy change associated with a reaction to manifest itself as heat rather than work. We can then measure the temperature change caused by the heat flow.

Recall that $\Delta E = q + w$ and that $w = -P\Delta V$. If a reaction is carried out at constant volume, then $\Delta V = 0$ and $w = 0$. The heat evolved (given off), called the *heat at constant volume* (q_v), is then equal to ΔE_{rxn} .

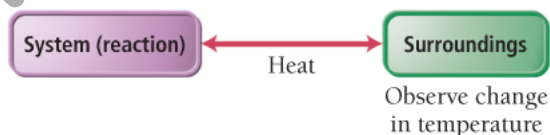
[9.8]

$$\Delta E_{\text{rxn}} = q_v + w$$

↙ Equals zero at constant volume

$$\Delta E_{\text{rxn}} = q_v$$

We measure the heat evolved in a chemical reaction using *calorimetry*. In **calorimetry**, we measure the thermal energy the reaction (defined as the system) and the surroundings exchange by observing the change in temperature of the surroundings.



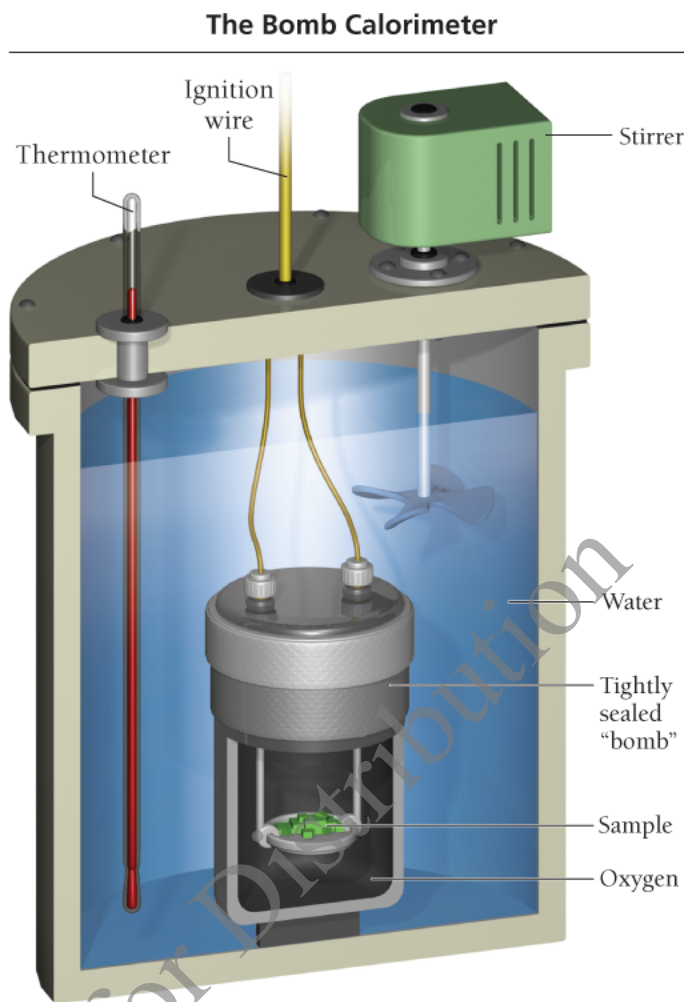
The magnitude of the temperature change in the surroundings depends on the magnitude of ΔE for the reaction and on the heat capacity of the surroundings.

[Figure 9.7](#) shows a **bomb calorimeter**, a piece of equipment designed to measure ΔE for combustion reactions. In a bomb calorimeter, the reaction occurs in a sealed container called a *bomb*. This ensures that the reaction occurs at constant volume. To use a bomb calorimeter, we put the sample to be burned (of known mass) into a cup equipped with an ignition wire. We then seal the cup into the bomb, which is filled with oxygen gas, and place the bomb in a water-filled, insulated container. The container is equipped with a stirrer and a thermometer. Finally, we ignite the sample with a wire coil, and monitor the temperature with the thermometer. The temperature change (ΔT) is related to the heat absorbed by the entire calorimeter assembly (q_{cal}) by the equation:

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta T$$

Figure 9.7 The Bomb Calorimeter

A bomb calorimeter measures changes in internal energy for combustion reactions.



where C_{cal} is the heat capacity of the entire calorimeter assembly (which is usually determined in a separate measurement involving the burning of a substance that gives off a known amount of heat). If no heat escapes from the calorimeter, the amount of heat *gained* by the calorimeter exactly equals that *released* by the reaction (the two are equal in magnitude but opposite in sign):

[9.10]

$$q_{\text{cal}} = -q_{\text{rxn}}$$

The heat capacity of the calorimeter, C_{cal} , has units of energy over temperature; its value accounts for all of the heat absorbed by all of the components within the calorimeter (including the water).

Because the reaction occurs under conditions of constant volume, $q_{\text{rxn}} = q_v = \Delta E_{\text{rxn}}$. This measured quantity is the change in the internal energy of the reaction for the specific amount of reactant burned. To determine ΔE_{rxn} per mole of a particular reactant—a more general quantity—we divide by the number of moles that actually react, as demonstrated in [Example 9.5](#).

Example 9.5 Measuring ΔE_{rxn} in a Bomb Calorimeter

When 1.010 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) undergoes combustion in a bomb calorimeter, the temperature rises from 24.92 °C to 28.33 °C. Find ΔE_{rxn} for the combustion of sucrose in kJ/mol sucrose. The heat capacity of the bomb calorimeter, determined in a separate experiment, is 4.90 kJ/°C. (You can ignore the heat capacity of the small sample of sucrose because it is negligible compared to the heat capacity of the calorimeter.)

SORT You are given the mass of sucrose, the heat capacity of the calorimeter, and the initial and final temperatures. You are asked to find the change in internal energy for the reaction.

GIVEN:

1.010 g $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, $T_i = 24.92$ °C,
 $T_f = 28.33$ °C, $C_{\text{cal}} = 4.90$ kJ/°C

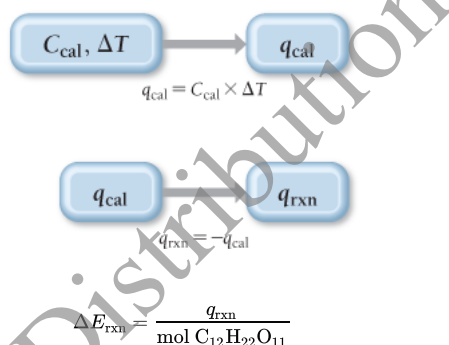
FIND: ΔE_{rxn}

STRATEGIZE The conceptual plan has three parts. In the first part, use the temperature change and the heat capacity of the calorimeter to find q_{cal} .

In the second part, use q_{cal} to determine q_{rxn} (which just involves changing the sign). Because the bomb calorimeter ensures constant volume, q_{rxn} is equivalent to ΔE_{rxn} for the amount of sucrose burned.

In the third part, divide q_{rxn} by the number of moles of sucrose to find ΔE_{rxn} per mole of sucrose.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta T = -q_{\text{rxn}}$$

$$\text{molar mass C}_{12}\text{H}_{22}\text{O}_{11} = 342.3 \text{ g/mol}$$

SOLVE Gather the necessary quantities in the correct units and substitute these into the equation to calculate q_{cal} .

Find q_{rxn} by taking the negative of q_{cal} .

Find ΔE_{rxn} per mole of sucrose by dividing q_{rxn} by the number of moles of sucrose (calculated from the given mass of sucrose and its molar mass).

SOLUTION

$$\begin{aligned} \Delta T &= T_f - T_i \\ &= 28.33 \text{ °C} - 24.92 \text{ °C} = 3.41 \text{ °C} \\ q_{\text{cal}} &= C_{\text{cal}} \times \Delta T \\ q_{\text{cal}} &= 4.90 \frac{\text{kJ}}{\text{°C}} \times 3.41 \text{ °C} = 16.7 \text{ kJ} \\ q_{\text{rxn}} &= -q_{\text{cal}} = -16.7 \text{ kJ} \\ \Delta E_{\text{rxn}} &= \frac{q_{\text{rxn}}}{\text{mol C}_{12}\text{H}_{22}\text{O}_{11}} \\ &= \frac{-16.7 \text{ kJ}}{1.010 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.3 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}} \\ &= -5.66 \times 10^3 \text{ kJ/mol C}_{12}\text{H}_{22}\text{O}_{11} \end{aligned}$$

$$= -3.91 \times 10^3 \text{ kJ/mol C}_7\text{H}_8$$

CHECK The units of the answer (kJ) are correct for a change in internal energy. The sign of ΔE_{rxn} is negative, as it should be for a combustion reaction that gives off energy.

FOR PRACTICE 9.5 When 1.550 g of liquid hexane (C_6H_{14}) undergoes combustion in a bomb calorimeter, the temperature rises from 25.87 °C to 38.13 °C. Find ΔE_{rxn} for the reaction in kJ/mol hexane. The heat capacity of the bomb calorimeter, determined in a separate experiment, is 5.73 kJ/°C.

FOR MORE PRACTICE 9.5 The combustion of toluene has a ΔE_{rxn} of -3.91×10^3 kJ/mol. When 1.55 g of toluene (C_7H_8) undergoes combustion in a bomb calorimeter, the temperature rises from 23.12 °C to 37.57 °C. Find the heat capacity of the bomb calorimeter.

Interactive Worked Example 9.5 Measuring ΔE_{rxn} in a Bomb Calorimeter

Not for Distribution

Not for Distribution