**Pearson**

# 9.6: Enthalpy: The Heat Evolved in a Chemical Reaction at Constant Pressure

**Key Concept Video   The Change in Enthalpy for a Chemical Reaction**

In Section 9.5, we saw that when a chemical reaction occurs in a sealed container under conditions of constant volume, the energy evolves only as heat. However, when a chemical reaction occurs open to the atmosphere under conditions of constant pressure—for example, a reaction occurring in an open beaker or the burning of natural gas on a stove—the energy can evolve as both heat and work. As we have also seen, $\Delta E_{rxn}$ is a measure of the *total energy change* (both heat and work) that occurs during a reaction. However, in many cases, we are interested only in the heat exchanged, not the work done. For example, when we burn natural gas on a stove to cook food, we do not really care how much work the combustion reaction does on the atmosphere by expanding against it—we just want to know how much heat is given off to cook the food. Under conditions of constant pressure, a thermodynamic quantity called *enthalpy* represents exactly this.

We define the **enthalpy ($H$)** of a system as the sum of its internal energy and the product of its pressure and volume:

[9.11]

$$H = E + PV$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function. The *change in enthalpy* ($\Delta H$) for any process occurring under constant pressure is given by the expression:

[9.12]

$$\Delta H = \Delta E + P\Delta V$$

To better understand this expression, we can interpret the two terms on the right with the help of relationships already familiar to us. We saw previously that $\Delta E = q + w$. If we represent the heat at constant pressure as $q_p$, then the change in internal energy at constant pressure is $\Delta E = q_p + w$. In addition, from our definition of pressure–volume work, we know that $P\Delta V = -w$. Substituting these expressions into the expression for $\Delta H$ gives us:

[9.13]

$$\begin{aligned} \Delta H &= \quad \Delta E + P\Delta V \\ &= \quad \left(q_p + w\right) + P\Delta V \\ &= \quad q_p + w - w \\ \Delta H &= \quad q_p \end{aligned}$$

We can see that $\Delta H$ is equal to $q_p$, the heat at constant pressure.

Conceptually (and often numerically), $\Delta H$ and $\Delta E$ are similar: They both represent changes in a state function for the system. However, $\Delta E$ is a measure of *all of the energy* (heat and work) exchanged with the surroundings, while $\Delta H$ is a measure of only the heat exchanged under conditions of constant pressure. For chemical reactions that do not exchange much work with the surroundings—that is, those that do not cause a large change in reaction volume as they occur—$\Delta H$ and $\Delta E$ are nearly identical in value. For chemical reactions that produce or consume large amounts of gas, and therefore result in large volume changes, $\Delta H$ and $\Delta E$ will be slightly different in value.

Conceptual Connection 9.5   **The Difference between ΔH and ΔE**

The signs of $\Delta H$ and $\Delta E$ follow the same conventions. A positive $\Delta H$ indicates that heat flows into the system as the reaction occurs. A chemical reaction with a positive $\Delta H$, called an **endothermic reaction**⊕, absorbs heat from its surroundings. (We first discussed endothermic processes in Section E.6.) A chemical cold pack used to ice athletic injuries is a good example of an endothermic reaction. When a barrier separating the reactants in a chemical cold pack is broken, the substances mix, react, and absorb heat from the surroundings. The surroundings—including, say, your bruised wrist—become *colder* because they *lose* energy as the cold pack absorbs it.

A chemical reaction with a negative $\Delta H$, called an **exothermic reaction**⊕, gives off heat to its surroundings. The reaction that occurs when ethanol burns (discussed in Section 9.1⊡) is a good example of an exothermic reaction. As the reaction occurs, heat is given off into the surroundings making them warmer. The burning of natural gas is another example of an exothermic reaction. As the gas burns, it gives off energy, raising the temperature of its surroundings.



Endothermic

Exothermic

The reaction that occurs in a chemical cold pack is endothermic—it absorbs energy from the surroundings. The combustion of natural gas is an exothermic reaction—it releases energy to the surroundings.

**Summarizing Enthalpy:**

- The value of $\Delta H$ for a chemical reaction is the amount of heat absorbed or evolved in the reaction under conditions of constant pressure.
- An endothermic reaction has a *positive* $\Delta H$ and absorbs heat from the surroundings. An endothermic reaction feels cold to the touch (if it is occurring near room temperature).
- An exothermic reaction has a *negative* $\Delta H$ and gives off heat to the surroundings. An exothermic reaction feels warm to the touch (if it is occurring near room temperature).

**Example 9.6** Exothermic and Endothermic Processes

Identify each process as endothermic or exothermic and indicate the sign of $\Delta H$.

**a.** sweat evaporating from skin
**b.** water freezing in a freezer
**c.** wood burning in a fire

**SOLUTION**

**a.** Sweat evaporating from skin cools the skin and is therefore endothermic, with a positive $\Delta H$: The skin must supply heat to the perspiration in order for it to continue to evaporate.
**b.** Water freezing in a freezer releases heat and is therefore exothermic, with a negative $\Delta H$: The refrigeration system in the freezer must remove this heat for the water to continue to freeze.
**c.** Wood burning in a fire releases heat and is therefore exothermic, with a negative $\Delta H$.

**FOR PRACTICE 9.6**   Identify each process as endothermic or exothermic and indicate the sign of $\Delta H$.

**a.** an ice cube melting

**b.** nail polish remover quickly evaporating after it is accidentally spilled on the skin

**c.** gasoline burning within the cylinder of an automobile engine

# Exothermic and Endothermic Processes: A Particulate View

When a chemical system undergoes a change in enthalpy, where does the energy come from or go to? For example, we just saw that an exothermic chemical reaction gives off *thermal energy*—what is the source of that energy?

First, we know that the emitted thermal energy *does not* come from the original thermal energy of the system. Recall from Section 9.2 that the thermal energy of a system is the total kinetic energy of the atoms and molecules that compose the system. This kinetic energy *cannot* be the source of the energy given off in an exothermic reaction because, if the atoms and molecules that compose the system were to lose kinetic energy, their temperature would necessarily fall—the system would get colder. Yet, we know that in exothermic reactions, the temperature of the system and the surroundings rises. So there must be some other source of energy.

Recall from Section 9.3 that the internal energy of a chemical system is the sum of its kinetic energy and its *potential energy*. This potential energy is the source in an exothermic chemical reaction. Under normal circumstances, chemical potential energy (or simply chemical energy) arises primarily from the electrostatic forces among the protons and electrons that compose the atoms and molecules within the system. In an exothermic reaction, some bonds break and new ones form, and the nuclei and electrons reorganize into an arrangement with lower potential energy. As the molecules rearrange, their potential energy converts into thermal energy, the heat emitted in the reaction. In an endothermic reaction, the opposite happens: As some bonds break and others form, the nuclei and electrons reorganize into an arrangement with higher potential energy, absorbing thermal energy in the process.

> **Conceptual Connection 9.6   Exothermic and Endothermic Reactions**

# Stoichiometry Involving $\Delta H$: Thermochemical Equations

The enthalpy change for a chemical reaction, abbreviated $\Delta H_{rxn}$, is also called the **enthalpy of reaction** or **heat of reaction** and is an extensive property, one that depends on the amount of material undergoing the reaction. In other words, the amount of heat generated or absorbed when a chemical reaction occurs depends on the *amounts* of reactants that actually react. We usually specify $\Delta H_{rxn}$ in combination with the balanced chemical equation for the reaction. *The magnitude of $\Delta H_{rxn}$ is for the stoichiometric amounts of reactants and products for the reaction as written*.

For example, the balanced equation and $\Delta H_{rxn}$ for the combustion of propane (the main component of LP gas) are as follows:

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(g)   \Delta H_{rxn} = -2044\,\text{kJ}$$
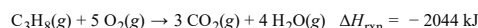
> Throughout this book, combustion reactions such as this one are written using *gaseous* water as the product because, when we actually burn a hydrocarbon such as propane, water is formed in the gaseous state. Some books use *liquid* water as the product, which gives a moderately different

the gaseous state. Some books use *liquid* water as the product, which gives a moderately different value for $\Delta H_{\text{rxn}}$.

This means that when 1 mol of $C_3H_8$ reacts with 5 mol of $O_2$ to form 3 mol of $CO_2$ and 4 mol of $H_2O$, 2044 kJ of heat is emitted. We can write these relationships in the same way that we expressed stoichiometric relationships in Chapter 7 as ratios between two quantities. For example, for the reactants, we write:

$$1 \text{ mol } C_3H_8 : -2044 \text{ kJ} \quad \text{or} \quad 5 \text{ mol } O_2 : -2044 \text{ kJ}$$
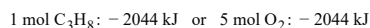
These ratios indicate that 2044 kJ of heat evolves when 1 mol of $C_3H_8$ and 5 mol of $O_2$ completely react. We can use these ratios to construct conversion factors between amounts of reactants or products and the quantity of heat emitted (for exothermic reactions) or absorbed (for endothermic reactions).

To find out how much heat is emitted upon the combustion of a certain mass in grams of $C_3H_8$, we use the following conceptual plan:
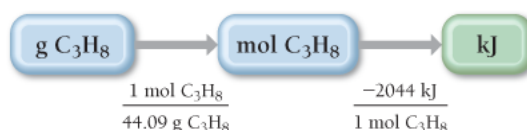


We use the molar mass to convert between grams and moles and the stoichiometric relationship between moles of $C_3H_8$ and the heat of reaction to convert between moles and kilojoules, as demonstrated in Example 9.7.

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## Example 9.7 Stoichiometry Involving $\Delta H$

An LP gas tank in a home barbeque contains 13.2 kg of propane, $C_3H_8$. Calculate the heat (in kJ) associated with the complete combustion of all of the propane in the tank.

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(g) \quad \Delta H_{\text{rxn}} = -2044 \text{ kJ}$$
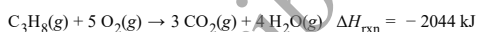
**SORT**    You are given the mass of propane and asked to find the heat evolved in its combustion.

**GIVEN:**    13.2 kg $C_3H_8$

**FIND:**    $q$

**STRATEGIZE**    Starting with kg $C_3H_8$, convert to g $C_3H_8$ and then use the molar mass of $C_3H_8$ to find the number of moles. Next, use the stoichiometric relationship between mol $C_3H_8$ and kJ to determine the heat evolved.

**CONCEPTUAL PLAN**
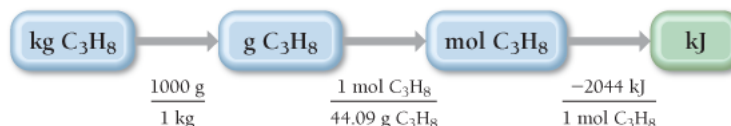


**RELATIONSHIPS USED**

1000 g = 1 kg

molar mass $C_3H_8 = 44.09$ g/mol

1 mol $C_3H_8 : -2044$ kJ (from balanced equation)

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**SOLVE**    Follow the conceptual plan to solve the problem. Begin with 13.2 kg $C_3H_8$ and multiply by the appropriate conversion factors to arrive at kJ.

**SOLUTION**

$$13.2 \text{ kg C}_3\text{H}_8 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol C}_3\text{H}_8}{44.09 \text{ g C}_3\text{H}_8} \times \frac{-2044 \text{ kJ}}{1 \text{ mol C}_3\text{H}_8} = -6.12 \times 10^5 \text{ kJ}$$
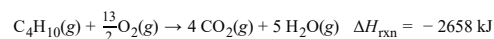
**CHECK**    The units of the answer (kJ) are correct for energy. The answer is negative, as it should be for heat evolved by the reaction.

**FOR PRACTICE 9.7**    Ammonia reacts with oxygen according to the equation:

$$4 \text{ NH}_3(g) + 5 \text{ O}_2(g) \rightarrow 4 \text{ NO}(g) + 6 \text{ H}_2\text{O}(g) \quad \Delta H_{\text{rxn}} = -906 \text{ kJ}$$
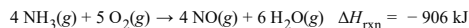
Calculate the heat (in kJ) associated with the complete reaction of 155 g of $NH_3$.

**FOR MORE PRACTICE 9.7**    What mass of butane in grams is necessary to produce $1.5 \times 10^3$ kJ of heat? What mass of $CO_2$ is produced?

$$\text{C}_4\text{H}_{10}(g) + \frac{13}{2}\text{O}_2(g) \rightarrow 4 \text{ CO}_2(g) + 5 \text{ H}_2\text{O}(g) \quad \Delta H_{\text{rxn}} = -2658 \text{ kJ}$$

**Interactive Worked Example 9.7   Stoichiometry Involving Δ*H***