Pearson

9.8: Relationships Involving ΔH_{rxn}

The change in enthalpy for a reaction is always associated with a *particular* reaction. If we change the reaction, then ΔH_{rxn} also changes. We now turn our attention to three quantitative relationships between a chemical equation and ΔH_{rxn}.

1. **If a chemical equation is multiplied by some factor, then ΔH_{rxn} is also multiplied by the same factor.**

Recall from Section 9.6 that ΔH_{rxn} is an extensive property; it depends on the quantity of reactants undergoing reaction. Recall also that ΔH_{rxn} is usually reported for a reaction involving stoichiometric amounts of reactants. For example, for a reaction $\text{A} + 2\ \text{B} \rightarrow \text{C}$, we typically report ΔH_{rxn} as the amount of heat emitted or absorbed when 1 mol A reacts with 2 mol B to form 1 mol C. Therefore, if a chemical equation is multiplied by a factor, then ΔH_{rxn} is also multiplied by the same factor. For example,

$$\begin{array}{ll} \text{A} + 2\ \text{B} \rightarrow \text{C} & \Delta H_1 \\ 2\ \text{A} + 4\ \text{B} \rightarrow 2\ \text{C} & \Delta H_2 = 2 \times \Delta H_1 \end{array}$$

2. **If a chemical equation is reversed, then ΔH_{rxn} changes sign.**

Recall from Section 9.6 that ΔH_{rxn} is a state function, which means that its value depends only on the initial and final states of the system.

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

When a reaction is reversed, the final state becomes the initial state and vice versa. Consequently, ΔH_{rxn} changes sign. For example,

$$\begin{array}{rcll} \text{A} + 2\ \text{B} & \rightarrow & \text{C} & \Delta H_1 \\ \text{C} & \rightarrow & \text{A} + 2\ \text{B} & \Delta H_2 = -\Delta H_1 \end{array}$$

3. **If a chemical equation can be expressed as the sum of a series of steps, then ΔH_{rxn} for the overall equation is the sum of the heats of reactions for each step.**

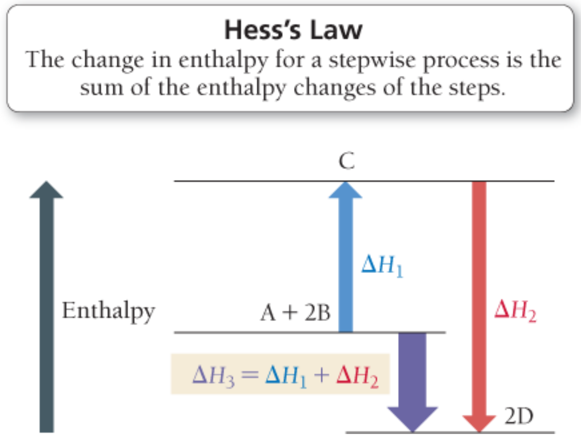
This last relationship, known as **Hess's law**, follows from the enthalpy of reaction being a state function. Because ΔH_{rxn} is dependent only on the initial and final states, and not on the pathway the reaction follows, ΔH obtained from summing the individual steps that lead to an overall reaction must be the same as ΔH for that overall reaction. For example,

$$\begin{array}{rcll} \text{A} + 2\ \text{B} & \longrightarrow & \cancel{\text{C}} & \Delta H_1 \\ \cancel{\text{C}} & \longrightarrow & 2\ \text{D} & \Delta H_2 \\ \hline \text{A} + 2\ \text{B} & \longrightarrow & 2\ \text{D} & \Delta H_3 = \Delta H_1 + \Delta H_2 \end{array}$$

We illustrate Hess's law with the energy-level diagram shown in Figure 9.9.

Figure 9.9 Hess's Law

The change in enthalpy for a stepwise process is the sum of the enthalpy changes of the steps.



These three quantitative relationships make it possible to determine ΔH for a reaction without directly measuring it in the laboratory. (For some reactions, direct measurement can be difficult.) If we can find related reactions (with known ΔH values) that sum to the reaction of interest, we can find ΔH for the reaction of interest.

For example, the reaction between C(s) and $H_2O\,(g)$ is an industrially important method of generating hydrogen gas:

$$\mathrm{C}\,(s) + \mathrm{H_2O}\,(g) \rightarrow \mathrm{CO}\,(g) + \mathrm{H_2}\,(g) \quad \Delta H_{\mathrm{rxn}} = ?$$

We can find ΔH_{rxn} from the following reactions with known ΔH values:

$$\begin{array}{ll} \mathrm{C}\,(s) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) & \Delta H = -393.5\ \mathrm{kJ} \\ 2\ \mathrm{CO}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\ \mathrm{CO_2}\,(g) & \Delta H = -566.0\ \mathrm{kJ} \\ 2\ \mathrm{H_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\ \mathrm{H_2O}\,(g) & \Delta H = -483.6\ \mathrm{kJ} \end{array}$$

We just have to determine how to sum these reactions to get the overall reaction of interest. We do this by manipulating the reactions with known ΔH values in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

Because the first reaction has C(*s*) as a reactant, and the reaction of interest also has *C*(*s*) as a reactant, we write the first reaction unchanged.	$\mathrm{C}\,(s) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) \quad \Delta H = -393.5\ \mathrm{kJ}$
The second reaction has 2 mol of CO(*g*) as a reactant. However, the reaction of interest has 1 mol of CO(*g*) as a product. Therefore, we reverse the second reaction, change the sign of Δ*H*, and multiply the reaction and Δ*H* by $\frac{1}{2}$.	$\frac{1}{2} \times [2\ \mathrm{CO_2}\,(g) \rightarrow 2\ \mathrm{CO}\,(g) + \mathrm{O_2}\,(g)] \quad \Delta H = \frac{1}{2} \times (+566.0\ \mathrm{kJ})$

The third reaction has $H_2(g)$ as a reactant. In the reaction of interest, however, $H_2(g)$ is a product. Therefore, we reverse the equation and change the sign of ΔH. In addition, to obtain coefficients that match the reaction of interest, and to cancel O_2, we must multiply the reaction and ΔH by $\frac{1}{2}$.	$\frac{1}{2} \times [2\ H_2O\,(g) \rightarrow 2\ H_2\,(g) + O_2\,(g)] \quad \Delta H = \frac{1}{2} \times (+483.6\ \mathrm{kJ})$
Lastly, we rewrite the three reactions after multiplying through by the indicated factors and show how they sum to the reaction of interest. ΔH for the reaction of interest is the sum of the ΔH values for the steps.	$C(s) + \cancel{O_2(g)} \longrightarrow \cancel{CO_2(g)} \quad \Delta H = -393.5\ \mathrm{kJ}$ $\cancel{CO_2(g)} \longrightarrow CO(g) + \cancel{\frac{1}{2}O_2(g)} \quad \Delta H = +283.0\ \mathrm{kJ}$ $H_2O(g) \longrightarrow H_2(g) + \cancel{\frac{1}{2}O_2(g)} \quad \Delta H = +241.8\ \mathrm{kJ}$ $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) \quad \Delta H_{rxn} = +131.3\ \mathrm{kJ}$

Example 9.9 Hess's Law

Find ΔH_{rxn} for the reaction:

$$3\ C\,(s) + 4\ H_2\,(g) \rightarrow C_3H_8\,(g)$$

Use these reactions with known ΔH values:

$$C_3H_8\,(g) + 5\ O_2\,(g) \rightarrow 3\ CO_2\,(g) + 4\ H_2O\,(g) \qquad \Delta H = -2043\ \mathrm{kJ}$$
$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H = -393.5\ \mathrm{kJ}$$
$$2\ H_2\,(g) + O_2\,(g) \rightarrow 2\ H_2O\,(g) \qquad \Delta H = -483.6\ \mathrm{kJ}$$

SOLUTION

To solve this and other Hess's law problems, you manipulate the reactions with known ΔH values in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

The first reaction has C_3H_8 as a reactant, and the reaction of interest has C_3H_8 as a product, so you can reverse the first reaction and change the sign of ΔH.

$3\ CO_2\,(g) + 4\ H_2O\,(g) \rightarrow C_3H_8\,(g) + 5\ O_2\,(g) \quad \Delta H = +2043\ \mathrm{kJ}$

The second reaction has carbon as a reactant and CO_2 as a product, as required in the reaction of interest. However, the coefficient for C is 1, and in the reaction of interest, the coefficient for C is 3. You need to multiply this equation and its ΔH by 3.

$3 \times [C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)] \quad \Delta H = 3 \times (-393.5\ \mathrm{kJ})$

The third reaction has $H_2\,(g)$ as a reactant, as required. However, the coefficient for H_2 is 2, and in

The third reaction has $H_2\,(g)$ as a reactant, as required. However, the coefficient for H_2 is 2, and in the reaction of interest, the coefficient for H_2 is 4. Multiply this reaction and its ΔH by 2.

$$2 \times [2\ \mathrm{H_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\ \mathrm{H_2O}\,(g)] \quad \Delta H = 2 \times (-483.6\ \mathrm{kJ})$$

Lastly, rewrite the three reactions after multiplying by the indicated factors and show how they sum to the reaction of interest. ΔH for the reaction of interest is the sum of the ΔH values for the steps.

$$\begin{array}{rcll}
\cancel{3\,\mathrm{CO_2}(g)} + \cancel{4\,\mathrm{H_2O}(g)} & \longrightarrow & \mathrm{C_3H_8}(g) + \cancel{5\,\mathrm{O_2}(g)} & \Delta H = +2043\ \mathrm{kJ} \\
3\,\mathrm{C}(s) + \cancel{3\,\mathrm{O_2}(g)} & \longrightarrow & \cancel{3\,\mathrm{CO_2}(g)} & \Delta H = -1181\ \mathrm{kJ} \\
4\,\mathrm{H_2}(g) + \cancel{2\,\mathrm{O_2}(g)} & \longrightarrow & \cancel{4\,\mathrm{H_2O}(g)} & \Delta H = -967.2\ \mathrm{kJ} \\
\hline
3\,\mathrm{C}(s) + 4\,\mathrm{H_2}(g) & \longrightarrow & \mathrm{C_3H_8}(g) & \Delta H_{\mathrm{rxn}} = -105\ \mathrm{kJ}
\end{array}$$

FOR PRACTICE 9.9 Find ΔH_{rxn} for the reaction:

$$\mathrm{N_2O}\,(g) + \mathrm{NO_2}\,(g) \rightarrow 3\ \mathrm{NO}\,(g)$$

Use these reactions with known ΔH values:

$$\begin{array}{ll}
2\ \mathrm{NO}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\ \mathrm{NO_2}\,(g) & \Delta H = -113.1\ \mathrm{kJ} \\
\mathrm{N_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\ \mathrm{NO}\,(g) & \Delta H = +182.6\ \mathrm{kJ} \\
2\ \mathrm{N_2O}\,(g) \rightarrow 2\ \mathrm{N_2}\,(g) + \mathrm{O_2}\,(g) & \Delta H = -163.2\ \mathrm{kJ}
\end{array}$$

FOR MORE PRACTICE 9.9 Find ΔH_{rxn} for the reaction:

$$3\ \mathrm{H_2}\,(g) + \mathrm{O_3}\,(g) \rightarrow 3\ \mathrm{H_2O}\,(g)$$

Use these reactions with known ΔH values:

$$\begin{array}{ll}
2\ \mathrm{H_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\ \mathrm{H_2O}\,(g) & \Delta H = -483.6\ \mathrm{kJ} \\
3\ \mathrm{O_2}\,(g) \rightarrow 2\ \mathrm{O_3}\,(g) & \Delta H = +285.4\ \mathrm{kJ}
\end{array}$$