5.4 Hess's Law

Imagine you and some friends are hiking up a mountain trail. You come to a fork in the trail and decide to break into two groups. One group follows a short, steep path while the other takes a set of stairs with a gradual slope. Eventually, both groups reach the top of the trail and are rewarded by a beautiful view. Although the two groups took different routes, everyone reached the same place. We can think of the process of a chemical reaction as behaving in a similar way to these mountain climbers. There is more than one possible route to get from reactants to products.

Enthalpy Change and Hess's Law

From experimental evidence, chemists have found that the change in enthalpy in a chemical process is independent of the path taken. This means that in going from an initial set of reactants to a final set of products, the change in enthalpy is the same regardless of whether the conversion happens in one step or in a series of steps. To illustrate this concept, consider the analogy of going from the bottom floor to the top floor of a building. The net vertical distance you travel is the same regardless of whether you take the stairs or the elevator. Similarly, the change in enthalpy of converting one chemical to another is the same whether the conversion happens in one reaction or in more than one.

Germain Henri Hess, a professor at the University of St. Petersburg, Russia, (**Figure 1**) was interested in whether the number of steps involved in a chemical process affected the enthalpy change of a reaction. At a time when most chemists were identifying new chemical substances, Hess was interested in why atoms are attracted to one another. He determined that the change in enthalpy would always be the same no matter how many steps it took to get the desired product.

Consider the reaction in which gaseous nitrogen and oxygen combine to form nitrogen dioxide gas. There are at least two ways we might get from reactants to products. The overall reaction could occur in a single step. The thermochemical equation for this single-step reaction is

$$N_2(g) + 2 O_2(g) \rightarrow 2 NO_2(g) \quad \Delta H = 68 \text{ kJ}$$

However, nitrogen dioxide can also be made using a two-step process. The thermochemical equations for the two steps are

$$N_2(g) + O_2(g) \rightarrow 2 NO(g) \quad \Delta H = 180 \text{ kJ}$$

$$2 NO(g) + O_2(g) \rightarrow 2 NO_2(g) \quad \Delta H = -112 \text{ kJ}$$

If you add these two equations, you get the equation for the overall (net) reaction for the formation of nitrogen dioxide gas. Similarly, the sum of the enthalpy changes of the reactions represented by these equations is equal to the enthalpy change for the net reaction for the formation of nitrogen dioxide gas.

$$N_2(g) + O_2(g) \rightarrow 2 \cancel{NO}(g) \quad \Delta H = 180 \text{ kJ}$$
$$\underline{2 \cancel{NO}(g) + O_2(g) \rightarrow 2 NO_2(g) \quad \Delta H = -112 \text{ kJ}}$$
$$N_2(g) + 2 O_2(g) \rightarrow 2 NO_2(g) \quad \Delta H = 68 \text{ kJ}$$

This example illustrates that when a reaction proceeds from reactants to products, the change in enthalpy is the same whether the reaction occurs in one step or several. This generalization is now called Hess's law.

Figure 1 Hess's work is one of the earliest examples of the field of theoretical chemistry.

> **Hess's law**
> The enthalpy change for the conversion of reactants to products is the same whether the conversion occurs in one step or several steps.

Hess's law is very useful for studying energy changes in chemical reactions that cannot be analyzed using calorimetry. Some reactions, such as the reaction of glycerine, $C_3H_5(OH)_3(l)$, with potassium permanganate, $KMnO_4(s)$, are too fast or dangerous (**Figure 2**). Other reactions, such as the synthesis of nitrogen dioxide from its elements, occur too slowly. **Figure 3** illustrates the application of Hess's law to this chemical reaction. The two-step process is shown in blue. The first step involves a large positive enthalpy change ($\Delta H = 180$ kJ), but the second step involves a negative enthalpy change ($\Delta H = -112$ kJ). The sum of these two enthalpy changes is equal to the enthalpy change of the one-step process (shown in red).

Figure 2 The reaction of potassium permanganate with glycerine. Potassium permanganate reacts so vigorously with most organic compounds, it must be stored separately.
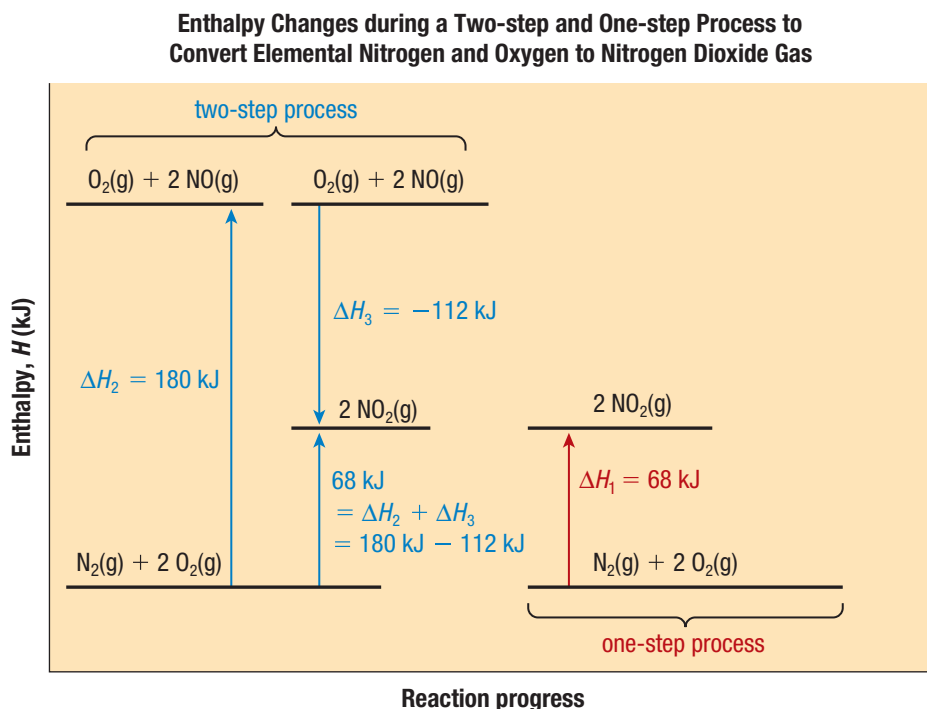
Figure 3 Enthalpy change diagram for the formation of nitrogen dioxide gas from gaseous nitrogen and oxygen. The net enthalpy change is the same whether the process occurs in one step or two.

Rules for Enthalpy Changes

To use Hess's law to calculate enthalpy changes for chemical reactions, you must apply the following two rules:

1. If you reverse a chemical reaction, you must also reverse the sign of ΔH.
2. The magnitude of ΔH is directly proportional to the number of moles of reactants and products in a reaction. If the coefficients in a balanced equation are multiplied by a factor, the value of ΔH is multiplied by the same factor.

To understand the first rule, recall that the sign of ΔH indicates the direction of the thermal energy flow. If the direction of the reaction is reversed, the direction of the thermal energy flow will also be reversed. Consider the preparation of xenon tetrafluoride, $XeF_4(s)$. The thermochemical equation for this reaction is

$$Xe(g) + 2\,F_2(g) \rightarrow XeF_4(s) \quad \Delta H = -251 \text{ kJ}$$

The forward reaction is exothermic, so 251 kJ of thermal energy flows from the chemical system to the surroundings. In the reverse reaction, solid xenon tetrafluoride decomposes to gaseous xenon, $Xe(g)$, and fluorine, $F_2(g)$, and thermal energy flows from the surroundings to the chemical system.

$$XeF_4(s) \rightarrow Xe(g) + 2\,F_2(g) \quad \Delta H = 251 \text{ kJ}$$
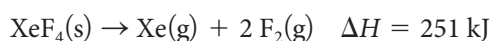
In the reverse reaction, the sign of ΔH is positive. Therefore, the reverse reaction is endothermic.

The second rule tells you that the value of ΔH depends on the amounts of the substances reacting. For example, 251 kJ of thermal energy is released during the reaction of 1 mol of xenon gas and 2 mol of fluorine gas. However, when the amounts of these reactants are doubled, twice as much thermal energy is released 502 kJ.
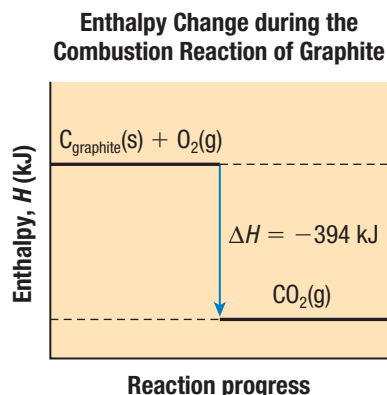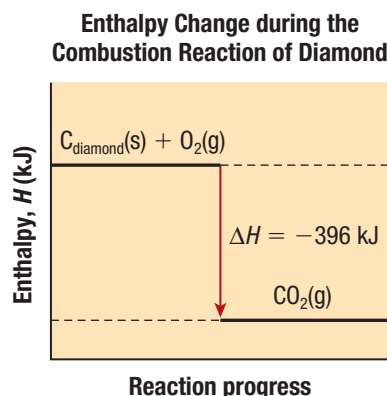
Tutorial **1** Calculating ΔH Using Hess's Law

In this tutorial, you will use Hess's law to calculate the enthalpy change of a reaction by algebraically manipulating two or more other reaction equations.
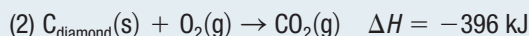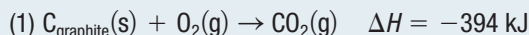
Sample Problem 1: Calculate ΔH Using Enthalpy Change Diagrams

Graphite and diamond are two forms of solid carbon. Graphite is a soft, black, slippery material that is the substance in pencils that makes marks. Diamond is a hard, crystalline substance used in making jewellery. Use the data in **Figure 4** and **Figure 5** to calculate the enthalpy change for the conversion of graphite to diamond.

$$C_{graphite}(s) \rightarrow C_{diamond}(s)$$
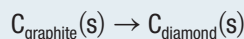
Solution

Step 1. Use the data in Figure 4 and Figure 5 to write balanced thermochemical equations for the combustion reactions.

(1) $C_{graphite}(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H = -394$ kJ

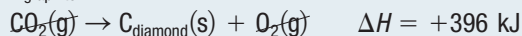(2) $C_{diamond}(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H = -396$ kJ

Step 2. Rearrange the equations as needed to get the required reactants and products.

In the conversion reaction, graphite is a reactant and diamond is a product. Therefore, reverse the second equation and change the sign of its ΔH.

(3) $CO_2(g) \rightarrow C_{diamond}(s) + O_2(g)$ $\quad \Delta H = +396$ kJ
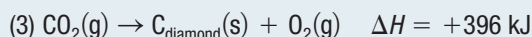
Step 3. Add equations (1) and (3) and their respective enthalpy values to obtain the conversion reaction equation and ΔH value.

$$C_{graphite}(s) + \cancel{O_2(g)} \rightarrow \cancel{CO_2(g)} \qquad \Delta H = -394 \text{ kJ}$$
$$\cancel{CO_2(g)} \rightarrow C_{diamond}(s) + \cancel{O_2(g)} \qquad \Delta H = +396 \text{ kJ}$$
$$\overline{C_{graphite}(s) \rightarrow C_{diamond}(s) \qquad \qquad \Delta H = \quad +2 \text{ kJ}}$$
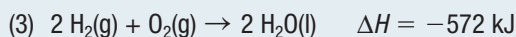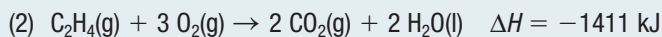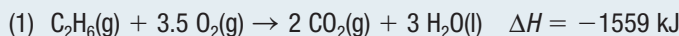
Statement: The enthalpy change during the conversion of graphite to diamond is 2 kJ/mol.

Sample Problem 2: Calculate ΔH for the Production of Ethene Using Hess's Law

Ethene gas, $C_2H_4(g)$, is the raw material for the synthesis of the plastic polyethylene. Engineers designing a process to make ethene from ethane gas, $C_2H_6(g)$, need to know the change in enthalpy of the desired reaction represented by the following balanced chemical equation:

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$
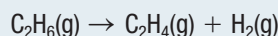
The engineers have the following thermochemical equations:

(1) $C_2H_6(g) + 3.5 O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(l)$ $\quad \Delta H = -1559$ kJ

(2) $C_2H_4(g) + 3 O_2(g) \rightarrow 2 CO_2(g) + 2 H_2O(l)$ $\quad \Delta H = -1411$ kJ

(3) $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$ $\quad \Delta H = -572$ kJ

Enthalpy Change during the Combustion Reaction of Graphite

Figure 4 Enthalpy change diagram for the combustion of graphite

Enthalpy Change during the Combustion Reaction of Diamond

Figure 5 Enthalpy change diagram for the combustion of diamond
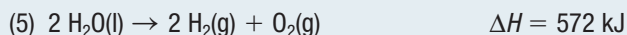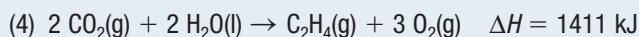
Solution

Step 1. Identify the equations that have reactants or products on the same side of the arrow as in the desired equation.

Equation (1) contains 1 mol of $C_2H_6(g)$, so use it as written:

(1) $C_2H_6(g) + 3.5 O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(l)$ $\Delta H = -1559$ kJ
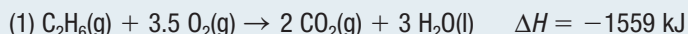
Step 2. Reverse (2) and (3) so that reactants and products are on the same side as in the desired equation. Reverse the sign of ΔH. This gives you equations (4) and (5), in which ethene gas and hydrogen gas are on the products side.

(4) $2 CO_2(g) + 2 H_2O(l) \rightarrow C_2H_4(g) + 3 O_2(g)$ $\Delta H = 1411$ kJ

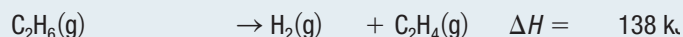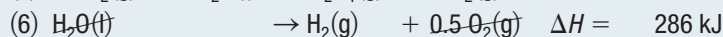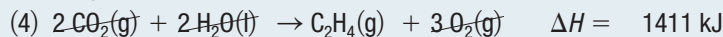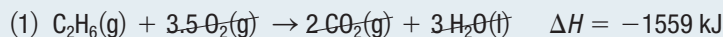(5) $2 H_2O(l) \rightarrow 2 H_2(g) + O_2(g)$ $\Delta H = 572$ kJ

Step 3. Check the coefficients of all entities in the equations to see if any must be adjusted by a factor so as to be equal to the coefficients in the desired equation. If so, then multiply each ΔH by the same factor.

Equation (5) has 2 mol of hydrogen gas on the product side, while the desired equation has only 1 mol. Multiply equation (5) and its ΔH by the factor 0.5:

(6) $H_2O(l) \rightarrow H_2(g) + 0.5 O_2(g)$ $\Delta H = 286$ kJ
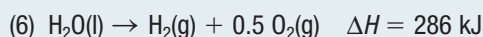
The coefficient of oxygen is now 0.5, which represents 0.5 mol of oxygen gas (not 0.5 molecules).

**Step 4.** Add equations (1), (4), and (6), and their changes in enthalpies.

(1) $C_2H_6(g) + 3.5\,O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(l)$ $\Delta H = -1559$ kJ
(4) $2\,CO_2(g) + 2\,H_2O(l) \rightarrow C_2H_4(g) + 3\,O_2(g)$ $\Delta H = 1411$ kJ
(6) $H_2O(l) \rightarrow H_2(g) + 0.5\,O_2(g)$ $\Delta H = 286$ kJ
_____

$C_2H_6(g) \rightarrow H_2(g) + C_2H_4(g)$ $\Delta H = 138$ k.

Statement: The enthalpy change for the production of ethene gas from ethane gas is 138 kJ per mole of ethane.

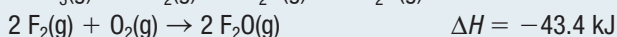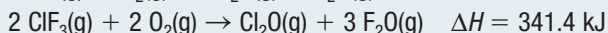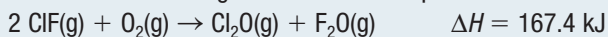## Practice

1. Consider the following thermochemical equations:
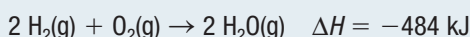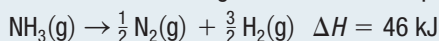
   $NH_3(g) \rightarrow \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$ $\Delta H = 46$ kJ
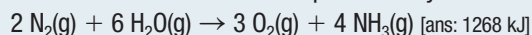
   $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$ $\Delta H = -484$ kJ
   (a) Calculate ΔH for the reaction represented by the following equation:
      $2 N_2(g) + 6 H_2O(g) \rightarrow 3 O_2(g) + 4 NH_3(g)$ [ans: 1268 kJ]
   (b) Draw an enthalpy diagram of the reaction. T/I C

2. Consider the following thermochemical equations:
   $2 ClF(g) + O_2(g) \rightarrow Cl_2O(g) + F_2O(g)$ $\Delta H = 167.4$ kJ
   $2 ClF_3(g) + 2 O_2(g) \rightarrow Cl_2O(g) + 3 F_2O(g)$ $\Delta H = 341.4$ kJ
   $2 F_2(g) + O_2(g) \rightarrow 2 F_2O(g)$ $\Delta H = -43.4$ kJ
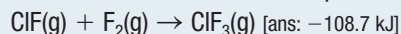   (a) Calculate ΔH for the reaction represented by the following equation:
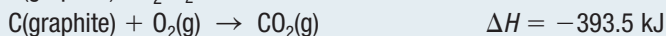 $ClF(g) + F_2(g) \rightarrow ClF_3(g)$ [ans: -108.7 kJ]
   (b) Draw an enthalpy diagram of the reaction. T/I C

3. If iron(III) oxide is heated with carbon monoxide, carbon dioxide and metallic iron are produced according to the equation
   $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$
   Determine the enthalpy of this reaction given the reactions
   $C(graphite) + \frac{1}{2} O_2 \rightarrow CO$ $\Delta H = -110.5$ kJ
   $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ
   $2Fe(s) + 3/2\,O_2(g) \rightarrow Fe_2O_3(s)$ $\Delta H = -824.2$ kJ T/I
   [ans: $\Delta H = -24.8$ kJ]
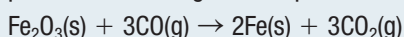
5.4 Review

Summary

- Hess's law states that the enthalpy change of a process is the same whether the process takes place in one step or in a series of steps.
- By applying Hess's law, we can manipulate and combine different chemical equations to determine the enthalpy change of a reaction of interest.

Questions

1. (a) State Hess's law in your own words.
   (b) In a correct equation for a reverse reaction, what happens to the sign and magnitude of ΔH?
   (c) When you multiply the coefficients of a balanced equation by a constant, what changes must you make to the sign and magnitude of ΔH? K/U

2. Explain how Hess's law is consistent with the law of conservation of energy. K/U

3. What characteristic of enthalpy change is the basis of Hess's law? K/U

4. Phosphorus burns spontaneously in air to produce tetraphosphorus decaoxide, $P_4O_{10}(s)$:

   $4\,P(s) + 5\,O_2(g) \rightarrow P_4O_{10}(s)$

   Using the following thermochemical equations, determine:
   (a) the enthalpy of combustion for phosphorus
   (b) the molar enthalpy of combustion for phosphorus, expressed in kJ/mol K/U T/I

   $4\,P(s) + 3\,O_2(g) \rightarrow P_4O_6(s) \quad \Delta H = -1640\ \text{kJ}$
   $P_4O_6(s) + 2\,O_2(g) \rightarrow P_4O_{10}(s) \quad \Delta H = -1344\ \text{kJ}$

5. Nitric oxide gas, $NO(g)$, can be oxidized in air to produce nitrogen dioxide gas, $NO_2(g)$:

   $2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$

   Determine the enthalpy change for this reaction using any of these thermochemical equations: K/U T/I

   $O_2(g) \rightarrow 2\,O(g) \qquad\qquad \Delta H = +495\ \text{kJ}$
   $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \quad \Delta H = -199\ \text{kJ}$
   $2\,O_3(g) \rightarrow 3\,O_2(g) \qquad\qquad \Delta H = -427\text{kJ}$

6. Liquid hydrazine, $N_2H_4(l)$, is a rocket fuel. It combusts in oxygen gas to form nitrogen gas and liquid water:

   $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\,H_2O(l)$

   Use the following thermochemical equations to calculate the enthalpy change for the combustion of liquid hydrazine: K/U T/I

   $2\,NH_3(g) + 3\,N_2O(g) \rightarrow 4\,N_2(g) + 3\,H_2O(l)$
   $\Delta H = -1010\ \text{kJ}$
   $N_2O(g) + 3\,H_2(g) \rightarrow N_2H_4(l) + H_2O(l)$
   $\Delta H = -317\ \text{kJ}$
   $2\,NH_3(g) + \frac{1}{2}O_2(g) \rightarrow N_2H_4(l) + H_2O(l)$
   $\Delta H = -143\ \text{kJ}$
   $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -286\ \text{kJ}$

7. Solid calcium carbide, $CaC_2(s)$, reacts with liquid water to produce ethyne, $C_2H_2(g)$ (acetylene):

   $CaC_2(s) + 2\,H_2O(l) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$

   Using the following thermochemical equations, calculate the enthalpy change for this reaction: K/U T/I

   $Ca(s) + 2\,C_{graphite}(s) \rightarrow CaC_2(s) \quad \Delta H = -62.8\text{kJ}$
   $Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s) \qquad \Delta H = -635.5\ \text{kJ}$
   $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$
   $\Delta H = -653.1\ \text{kJ}$
   $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2\,CO_2(g) + H_2O(l)$
   $\Delta H = -1300.\ \text{kJ}$
   $C_{graphite}(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5\ \text{kJ}$

8. The neutralization reaction between lithium hydroxide solution, $LiOH(aq)$, and hydrochloric acid, $HCl(aq)$, will produce water and aqueous lithium chloride, $LiCl(aq)$. Using the following thermochemical equations, determine the enthalpy of neutralization for 1 mol of aqueous lithium hydroxide: K/U T/I

   $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g) \qquad \Delta H = -92.3\ \text{kJ}$
   $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad\quad \Delta H = -285.8\ \text{kJ}$
   $Li(s) + \frac{1}{2}Cl_2(g) \rightarrow LiCl(s) \qquad\quad \Delta H = -815.0\ \text{kJ}$
   $Li(s) + \frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) \rightarrow LiOH(s)$
   $\Delta H = -487.0\ \text{kJ}$
   $LiOH(s) \rightarrow LiOH(aq) \qquad\qquad \Delta H = -19.2\ \text{kJ}$
   $HCl(g) \rightarrow HCl(aq) \qquad\qquad \Delta H = -77.0\ \text{kJ}$
   $LiCl(s) \rightarrow LiCl(aq) \qquad\qquad \Delta H = -36.0\ \text{kJ}$