

## 5.3: Hess's Law

### Learning Objectives

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

### Hess's Law

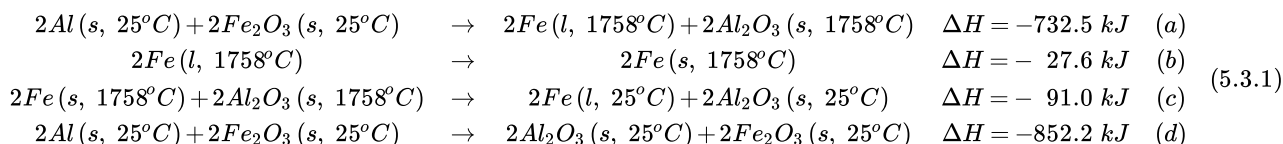
Because enthalpy is a state function, the enthalpy change for a reaction depends on *only* two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does *not* depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation,  $\Delta H$  for the net reaction is the sum of the  $\Delta H$  values for the individual reactions. This principle is called Hess's law. The enthalpy change  $\Delta H$  for an overall reaction is the sum of the  $\Delta H$  values for the individual reactions., after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate  $\Delta H$  values for reactions that are difficult to carry out directly by adding together the known  $\Delta H$  values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 9.3.1 can be viewed as occurring in three distinct steps with known  $\Delta H$  values. As shown in Figure 5.3.1, the first reaction produces 1 mol of solid aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and 2 mol of liquid iron at its melting point of  $1758^\circ\text{C}$  (part (a) in Equation 5.3.1); the enthalpy change for this reaction is  $-732.5 \text{ kJ/mol}$  of  $\text{Fe}_2\text{O}_3$ .

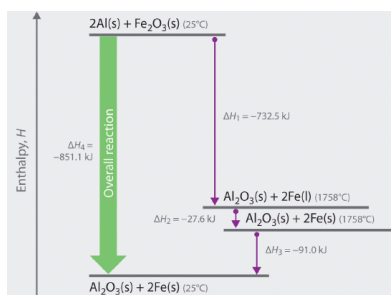
The second reaction is the conversion of 2 mol of liquid iron at  $1758^\circ\text{C}$  to 2 mol of solid iron at  $1758^\circ\text{C}$  (part (b) in Equation 9.3.1); the enthalpy change for this reaction is  $-13.8 \text{ kJ/mol}$  of  $\text{Fe}$  ( $-27.6 \text{ kJ}$  per 2 mol  $\text{Fe}$ ).

In the third reaction, 2 mol of solid iron at  $1758^\circ\text{C}$  is converted to 2 mol of solid iron at  $25^\circ\text{C}$  (part (c) in Equation 5.3.1); the enthalpy change for this reaction is  $-45.5 \text{ kJ/mol}$  of  $\text{Fe}$  ( $-91.0 \text{ kJ}$  per 2 mol  $\text{Fe}$ ).

As you can see in Figure 5.3.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation 5.3.1 gives the overall reaction, shown in part (d):



The net reaction in part (d) in Equation 5.3.1 is identical to Equation 5.3.1 the sum of parts (a) + (b) + (c). By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 5.3.1.



**Figure 5.3.1 Energy Changes Accompanying the Thermite Reaction** Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of  $\text{Al}(s)$  with 1 mol of  $\text{Fe}_2\text{O}_3(s)$  is  $-851.1 \text{ kJ}$ , whether the reaction occurs in a single step ( $\Delta H_4$ , shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid  $\text{Al}_2\text{O}_3$  and liquid iron ( $\Delta H_1$ ), solid iron at  $1758^\circ\text{C}$  ( $\Delta H_2$ ), and solid iron at  $25^\circ\text{C}$  ( $\Delta H_3$ ). Thus  $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$ , as stated by Hess's law.

Comparing parts (a) and (d) in Equation 5.3.1 also illustrates an important point: *The magnitude of  $\Delta H$  for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution).* When the product is liquid iron at its melting point (part (a) in Equation 5.3.1), only  $732.5 \text{ kJ}$  of heat are released to the surroundings compared with  $852 \text{ kJ}$  when the product is solid iron at  $25^\circ\text{C}$  (part (d) in Equation 9.3.1). The difference,  $120 \text{ kJ}$ , is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to  $25^\circ\text{C}$ . It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

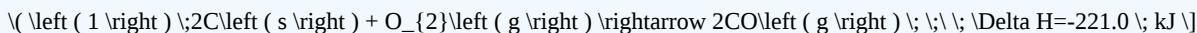
When using Hess's law to calculate the value of  $\Delta H$  for a reaction, follow this procedure:

1. Identify the equation whose  $\Delta H$  value is unknown and write individual reactions with known  $\Delta H$  values that, when added together, will give the desired equation.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of  $\Delta H$  for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its  $\Delta H$  value by that same factor.
4. Add together the individual reactions and their corresponding  $\Delta H$  values to obtain the reaction of interest and the unknown  $\Delta H$ .

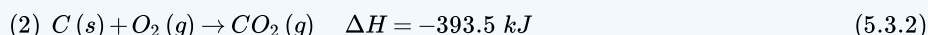
We illustrate how to use this procedure in Example 5.3.1

### ✓ Example 5.3.1

When carbon is burned with limited amounts of oxygen gas ( $O_2$ ), carbon monoxide (CO) is the main product:



When carbon is burned in excess  $O_2$ , carbon dioxide ( $CO_2$ ) is produced:



Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with  $O_2$  to give  $CO_2$ .

**Given:** two balanced chemical equations and their  $\Delta H$  values

**Asked for:** enthalpy change for a third reaction

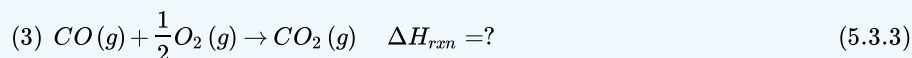
**Strategy:**

**A** After balancing the chemical equation for the overall reaction, write two equations whose  $\Delta H$  values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of  $\Delta H$ .)

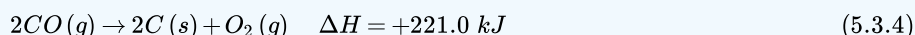
**B** Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

**Solution:**

**A** We begin by writing the balanced chemical equation for the reaction of interest:



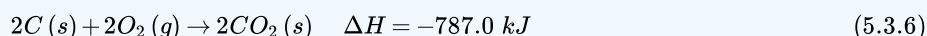
There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give



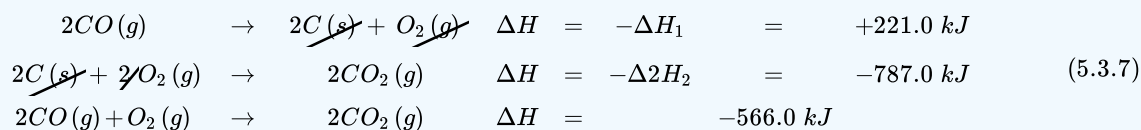
Because we have reversed the direction of the reaction, the sign of  $\Delta H$  is changed. We can use Equation 2 as written because its product,  $CO_2$ , is the product we want in Equation 3:



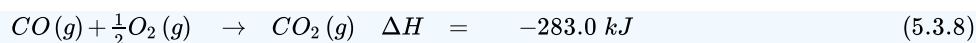
**B** Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:



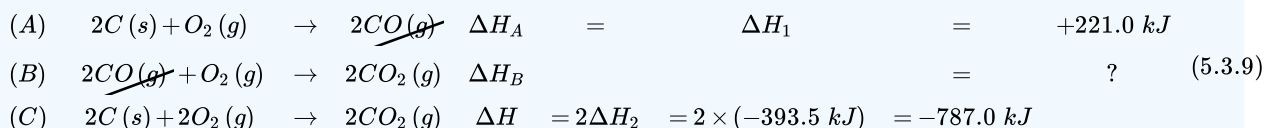
Writing the resulting equations as a sum, along with the enthalpy change for each, gives



Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with  $O_2$ , and the problem asks for the amount *per mole of CO*. Consequently, we must divide both sides of the final equation *and the magnitude of  $\Delta H$*  by 2:



An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:



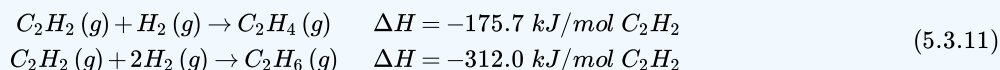
The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give  $CO_2$ . From Hess's law,  $\Delta H_A + \Delta H_B = \Delta H_C$ , and we are given  $\Delta H$  for reactions A and C. Substituting the appropriate values gives

$$\begin{aligned} -221.0 \text{ kJ} + \Delta H_B &= -787.0 \text{ kJ} \\ \Delta H_B &= -566.0 \end{aligned} \quad (5.3.10)$$

This is again the enthalpy change for the conversion of 2 mol of CO to  $CO_2$ . The enthalpy change for the conversion of 1 mol of CO to  $CO_2$  is therefore  $-566.0 \div 2 = -283.0 \text{ kJ/mol}$  of CO, which is the same result we obtained earlier. As you can see, *there may be more than one correct way to solve a problem.*

### ? Exercise 5.3.1

The reaction of acetylene ( $C_2H_2$ ) with hydrogen ( $H_2$ ) can produce either ethylene ( $C_2H_4$ ) or ethane ( $C_2H_6$ ):



What is  $\Delta H$  for the reaction of  $C_2H_4$  with  $H_2$  to form  $C_2H_6$ ?

**Answer**

-136.3 kJ/mol of  $C_2H_4$

## Enthalpies of Reaction

Chapter 7 and Chapter 8 presented a wide variety of chemical reactions, and you learned how to write balanced chemical equations that include all the reactants and the products except heat. One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- **Enthalpy of combustion ( $\Delta H_{\text{comb}}$ )** The change in enthalpy that occurs during a combustion reaction.: Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- **Enthalpy of fusion ( $\Delta H_{\text{fus}}$ )** The enthalpy change that accompanies the melting (fusion) of 1 mol of a substance.: The enthalpy change that accompanies the melting, or *fusion*, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- **Enthalpy of vaporization ( $\Delta H_{\text{vap}}$ )** The enthalpy change that accompanies the vaporization of 1 mol of a substance.: The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- **Enthalpy of solution ( $\Delta H_{\text{soln}}$ )** The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent.: The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

**Table 5.3.1 Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points**

Substance	$\Delta H_{\text{vap}}$ (kJ/mol)	$\Delta H_{\text{fus}}$ (kJ/mol)
argon (Ar)	6.3	1.3
methane ( $CH_4$ )	9.2	0.84
ethanol ( $CH_3CH_2OH$ )	39.3	7.6
benzene ( $C_6H_6$ )	31.0	10.9

Substance	$\Delta H_{\text{vap}}$ (kJ/mol)	$\Delta H_{\text{fus}}$ (kJ/mol)
water (H <sub>2</sub> O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

### Note the Pattern

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

### Summary

For a chemical reaction, the **enthalpy of reaction** ( $\Delta H_{\text{rxn}}$ ) is the difference in enthalpy between products and reactants; the units of  $\Delta H_{\text{rxn}}$  are kilojoules per mole. Reversing a chemical reaction reverses the sign of  $\Delta H_{\text{rxn}}$ . The magnitude of  $\Delta H_{\text{rxn}}$  also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion** ( $\Delta H_{\text{fus}}$ ) and the **enthalpy of vaporization** ( $\Delta H_{\text{vap}}$ ), respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion** ( $\Delta H_{\text{comb}}$ ) is the enthalpy change that occurs when a substance is burned in excess oxygen.

### Key Takeaway

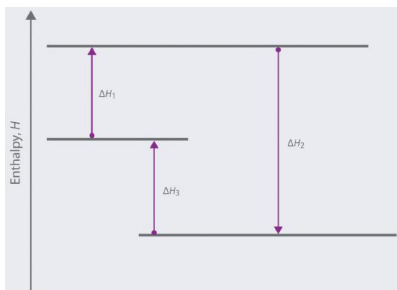
- Hess's law: The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions:

### Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9 ) before proceeding to the Conceptual Problems.

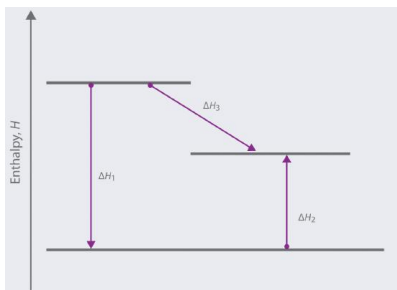
1. Based on the following energy diagram,

- write an equation showing how the value of  $\Delta H_2$  could be determined if the values of  $\Delta H_1$  and  $\Delta H_3$  are known.
- identify each step as being exothermic or endothermic.



2. Based on the following energy diagram,

- write an equation showing how the value of  $\Delta H_3$  could be determined if the values of  $\Delta H_1$  and  $\Delta H_2$  are known.
- identify each step as being exothermic or endothermic.



- Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
- When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
  - the melting of a solid

- the conversion of a gas to a liquid
  - the solidification of a liquid
  - the dissolution of a solid into water
5. In their elemental form,  $A_2$  and  $B_2$  exist as diatomic molecules. Given the following reactions, each with an associated  $\Delta H^\circ$ , describe how you would calculate  $\Delta H_f^\circ$  for the compound  $AB_2$ .



### Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.

1. Methanol is used as a fuel in Indianapolis 500 race cars. Use the following table to determine whether methanol or 2,2,4-trimethylpentane (isooctane) releases more energy per liter during combustion.

Fuel	$\Delta H^\circ_{\text{combustion}}$ (kJ/mol)	Density (g/mL)
methanol	-726.1	0.791
2,2,4-trimethylpentane	-5461.4	0.692

2. a. Use the enthalpies of combustion given in the following table to determine which organic compound releases the greatest amount of energy per gram during combustion.

Fuel	$\Delta H^\circ_{\text{combustion}}$ (kJ/mol)
methanol	-726.1
1-ethyl-2-methylbenzene	-5210.2
<i>n</i> -octane	-5470.5

- b. Calculate the standard enthalpy of formation of 1-ethyl-2-methylbenzene.
3. Given the enthalpies of combustion, which organic compound is the best fuel per gram?

Fuel	$\Delta H_f^\circ$ (kJ/mol)
ethanol	-1366.8
benzene	-3267.6
cyclooctane	-5434.7

### Answers

- 1.
  2.
    - To one decimal place  
 methanol:  $\Delta H/g = -22.6$  kJ  
 $C_9H_{12}$ :  $\Delta H/g = -43.3$  kJ  
 octane:  $\Delta H/g = -47.9$  kJ  
 Octane provides the largest amount of heat per gram upon combustion.
- b,  $\Delta H_f(C_9H_{17}) = -46.1$  kJ/mol

### Contributors

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