Thermochemistry

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CHAPTER

Thermochemistry

CHAPTER OUTLINE

- 1.1 Heat Flow
- 1.2 Enthalpy
- 1.3 Hess's Law
- 1.4 References



Energy is an integral component of chemical reactions. Some reactions require an input of energy, whereas others release energy as they proceed. When we burn propane, we are oxidizing small hydrocarbons by reacting them with oxygen. This reaction produces heat, which can be used to heat a barbeque for cooking or fill a balloon with hot air so it can soar over the countryside. In this chapter, we will focus primarily on the transfer of heat and energetic changes that occur during chemical reactions.

Adrian Pingstone. commons.wikimedia.org/wiki/File:Flame.inflates.balloon.bath.arp.jpg. Public Domain.

1.1 Heat Flow

Lesson Objectives

- Define thermochemistry.
- Define and give examples of exothermic reactions.
- Define and give examples of endothermic reactions.
- Draw a diagram of a constant-pressure calorimeter.
- Define and perform calculations related to specific heat and heat capacity.

Lesson Vocabulary

- thermochemistry: The study of energy relationships in chemical reactions.
- thermodynamics: The study of how heat, work, and various forms of energy are related to one another.
- system: The chemical reaction being observed, generally within a container.
- surroundings: Include everything that is not part of the system.
- **open system**: A system in which both matter and heat can be freely exchanged between the reaction container (the system) and the surroundings.
- **closed system**: A system in which matter cannot enter or leave, but heat can flow between the system and surroundings.
- **isolated system**: An idealized system in which neither matter nor heat can be exchanged between system and surroundings.
- **heat**: A form of thermal energy transferred between two bodies (such as a system and its surroundings) that are at different temperatures.
- exothermic: A process in which heat is released to the surroundings.
- endothermic: A process in which heat is absorbed from the surroundings.
- **calorimetry**: The measurement of heat transfers, usually through monitoring changes in the temperature of an isolated system.
- calorimeter: A device used to measure temperature changes during chemical processes.
- specific heat: The amount of energy needed to raise the temperature of one gram of a substance by 1°C.
- heat capacity: The amount of heat need to raise the temperature of a specified amount (usually mass) of a material by 1°C.

Check Your Understanding

Recalling Prior Knowledge

- What are the basic types of chemical reactions?
- What is energy?
- What is the law of conservation of energy?

Introduction

Just as the burning of wood releases energy in the form of heat, many other chemical reactions also release heat. There are also chemical reactions, such as photosynthesis in plants, which absorb energy in the form of heat. The study of energy changes in chemical reactions is called **thermochemistry**. The broader term **thermodynamics** also looks at how heat, work, and various forms of energy are related to one another. In this lesson, we will study the difference between reactions that absorb versus release heat as well as how to measure this change in energy.

Chemical Energy and Heat

There are two basic types of energy in the universe: potential energy and kinetic energy. Potential energy is stored energy that is available to do work, but it has not yet been released. The wood in a fireplace possesses potential energy. It is available for producing heat, but has not yet been ignited, so it is not releasing heat into the surrounding environment. Kinetic energy is the energy of motion. A waterfall is an example of kinetic energy. The moving water can erode the rocks in the stream, wearing them down into smaller particles. This same water motion can turn a turbine to generate electricity. In both cases, the movement of the material (water) causes work to be done.

Chemical energy, the energy stored in molecules and atoms, is one type of potential energy. Certain reactions can cause this energy to be released as heat. Other reactions require an input of energy, in which case the products will store more potential energy than the reactants. When we studied phase changes, we saw a relationship between energy and the state of matter. To melt a solid or boil a liquid, energy needs to be added in order to break up the intermolecular forces holding particles together in more ordered states. The reverse processes, condensation and freezing, release energy, because more favorable intermolecular interactions are formed.

When we consider a chemical reaction, we need to take into account both the system and the surroundings. The **system** includes the components involved in the chemical reaction itself. These will often take place in a flask, a beaker, a test tube, or some other container. The **surroundings** include everything that is not part of the system. When potassium reacts with water, part of the heat energy generated in the reaction is released into the surroundings. The boundary between system and surroundings is arbitrary, and it is generally chosen in a way that makes observations and calculations easier.

Depending on the specific setup, a few different types of systems can be described. In an **open system**, both matter and heat can be freely exchanged between the reaction container (the system) and the surroundings. An example would be an open beaker, where any gaseous materials or vaporized molecules are free to leave the system and float off into the atmosphere. In a **closed system**, matter cannot enter or leave, but heat can flow between the system and surroundings. A stoppered reaction flask would be an example of a closed system. Finally, a situation in which neither matter nor heat can be exchanged between system and surroundings is referred to as an **isolated system**. Although truly isolated systems are not really possible, a sealed, vacuum-insulated reaction flask would come very close.





FIGURE 1.2



Closed system. Heat can be exchanged between the system and the surrounding environment, but matter cannot move from one part of the system to another.

Exothermic and Endothermic Processes

Heat involves the transfer of thermal energy between two bodies that are at different temperatures. If you held a flask containing a reaction that releases energy, you would be able to feel the heat being transferred from the reaction into your hand. A process in which heat is released is referred to as **exothermic**. Conversely, reactions that absorb energy will remove energy from the surroundings, causing the container to feel cold. For example, dissolving ammonium nitrate in water will significantly lower the water temperature. Processes that absorb energy from their surroundings are called **endothermic**.

For example, the reaction between potassium and water is very exothermic:

 $2K + 2H_2O \rightarrow 2KOH + H_2 + heat$

Another exothermic reaction involves combining elemental sodium with chlorine:

 $2Na + Cl_2 \rightarrow 2NaCl + heat$

Endothermic reactions are also quite common. An example would be the splitting of water by electrolysis:

 $2H_2O + heat \rightarrow 2H_2 + O_2$

We will explore the details of the energy changes that take place during exothermic and endothermic reactions later in this chapter.

Calorimetry

The subfield of thermochemistry studies the energy changes that occur over the course of various chemical reactions. We will first look at how these changes are measured and then go into quantitative descriptions of heat transfer. **Calorimetry** is a term used to describe the measurement of heat transfers, usually by monitoring changes in the temperature of an isolated system. A **calorimeter** is a device used to measure temperature changes during chemical processes. The simplest type of calorimeter is the constant-pressure device illustrated in **Figure 1.3**.



A basic calorimeter includes the following components:

- 1. a thermometer to measure temperature changes.
- 2. a stirring rod to mix materials thoroughly
- 3. an insulated lid
- 4. an inner container
- 5. an outer container

6. spacers to separate the inner and outer containers

To use a calorimeter, the components of a reaction are placed in the inner container and mixed. As the reaction proceeds, the temperature change can be measured with the thermometer. The space between the inner and outer containers provides insulation to minimize heat loss.

Units of Heat

The SI unit for heat, and for any form of energy, is the joule. Officially, one joule is the amount of energy needed to move an object by one meter while exerting a force of one newton. Although this definition is based on the concept of work, we can also talk about the amount of heat (in joules) required to change the temperature of a given material by a specific amount.

A related unit is the calorie. This term arose prior to the establishment of the SI system and is now replaced by the joule in most situations. One calorie is defined as the amount of energy needed to increase the temperature of one gram of water by 1°C. One calorie equals 4.184 joules. Note that this calorie is not exactly the same as the calories listed on food products. One food Calorie (usually written with a capital C) is equal to 1000 "regular" calories. Thus, a 140-Calorie snack can be fully digested to produce 140,000 calories of energy. We will use the SI unit joules in our discussions of heat energy.

Heat Capacity and Specific Heat

We mentioned earlier that 4.184 joules (1 calorie) is the amount of energy needed to raise the temperature of one gram of liquid water by 1°C. This value is known as the **specific heat** of liquid water, and it has units of J/g° °C. Other materials have different specific heat values. The **Table 1.1** lists the specific heats of several substances:

Material	Specific Heat (J/g•°C)
aluminum	0.900
gold	0.129
graphite	0.720
diamond	0.502
copper	0.385
iron	0.139
water (liquid)	4.184

TABLE 1.1:

Note that the heat capacity of a substance depends on its state of matter. Except for water, all of the values in the **Table 1.1** refer to the specific heat for the solid form of that substance. Also note that water has an unusually high heat capacity. Much more heat is needed to raise the temperature of water by a given amount than to cause the same temperature increase in an equal mass of graphite, diamonds, or various metals.

A related term is **heat capacity**, which is defined as the amount of heat need to raise the temperature of a specified amount of material by 1°C. Heat capacity can be calculated using the following formula:

Heat capacity = mc

where *m* is the mass of the material and *c* is the specific heat of the material. Heat capacity has units of $J/^{\circ}C$.

We can calculate the amount of heat required to cause a specific temperature change by using the following equation:

 $q = m \times c \times \Delta T$

where q is the amount of heat added to the system, m is the mass of the substance, c is the specific heat of the

substance, and ΔT is the change in temperature.

Example 17.1

How much heat is required to increase the temperature of a 150-gram block of aluminum by 42°C? *Answer:*

$$q = m \times c \times \Delta T$$

$$q = 150 \text{ g} \times 0.900 \text{ J/g} \cdot^{\circ} \text{C} \times 42^{\circ} \text{C}$$

$$q = 5670 \text{ J}$$

Lesson Summary

- Chemical reactions essentially always involve a transfer of heat energy.
- Exothermic reactions release heat into their surroundings.
- Endothermic reactions absorb heat from their surroundings.
- Specific heat and heat capacity measure the amount of heat energy needed to change the temperature of a material by a given amount.

Lesson Review Questions

- 1. What is true of all chemical processes?
- 2. How can you distinguish a system and its surroundings?
- 3. What are the required characteristics of an isolated system?
- 4. Explain the difference between exothermic and endothermic processes.
- 5. Indicate which of the following processes are exothermic and which are endothermic:
 - a. ice melting
 - b. burning a candle
 - c. cooking an egg
 - d. the evaporation of sweat
- 6. Calculate the amount of heat needed to increase the temperature of 125 g of water from 22°C to 59°C.
- 7. Calculate the specific heat of copper, given that 204.75 J of energy raises the temperature of 15 g of copper from 35°C to 70°C.
- 8. 432 J of energy is required to raise the temperature of a block of aluminum from 20°C to 60°C. Calculate the mass of aluminum present.
- 9. 300 g of liquid ethanol at 22°C is supplied with 6480 J of heat. What is the final temperature of the ethanol? (The specific heat of ethanol is 2.44 J/g•°C).

Further Reading / Supplemental Links

- Exothermic and endothermic reactions: http://www.docbrown.info/page03/3_51energy.htm
- Interactive practice with specific heat: http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/spht.html
- Heat, work, and energy: http://www.engineeringtoolbox.com/heat-work-energy-d_292.html

Points to Consider

- How can we determine if a specific reaction is exothermic or endothermic?
- How is enthalpy related to heat?

1.2 Enthalpy

Lesson Objectives

- State the first law of thermodynamics.
- Define enthalpy.
- Explain how enthalpy changes relate to exothermic and endothermic reactions.
- Perform calculations using enthalpy values for various reactions.

Lesson Vocabulary

- **first law of thermodynamics**: States that energy can be converted from one form to another, but cannot be created or destroyed.
- **enthalpy**: A thermodynamic function of a system that is the internal heat content of a substance or system that is at a constant pressure.
- **enthalpy of reaction**: The change in enthalpy resulting from a mole of matter altered by a chemical reaction under standard conditions.
- **standard enthalpy of formation**: The enthalpy change that would be necessary to form a compound from its elements in their standard states at 25°C; has a value of zero for any element in its most stable form.

Check Your Understanding

Recalling Prior Knowledge

- What are endothermic and exothermic reactions?
- How is heat transfer measured?

Introduction

One of the most fundamental scientific laws is that the total amount of energy in the universe is constant. The **first law of thermodynamics** says that energy can be converted from one form to another, but it cannot be created or destroyed. This law is very difficult to prove, since we cannot measure the energy of the entire universe. However, we can measure energy changes as various physical and chemical processes occur, and this allows us to show that the total amount of energy in an isolated system remains constant. Our discussion in this lesson will focus on differences in energy between one state and another.

Enthalpy

In the previous lesson, we looked at how heat transfers are measured. In practice, only changes in energy and heat can be measured; we cannot measure the "energy" of a substance or system by itself. For practical reasons, most reactions are run at a constant pressure, with the reaction vessel open to the external atmosphere. **Enthalpy** is an energetic concept that can be thought of as the internal heat content of a substance or system that is at a constant pressure. Technically, it is defined as follows:

$$H = E + PV$$

where H is the enthalpy of the system, E is the internal energy, P is the pressure, and V is the volume. It can be difficult to distinguish "heat" and "enthalpy." Heat measures the transfer of thermal energy between two objects, and enthalpy measures the flow of heat. When heat flows out of a system, the change in enthalpy is negative; when heat flows into a system, the change in enthalpy is positive. Enthalpy is a useful tool for characterizing chemical reactions.

Enthalpy of Reaction

Any chemical reaction can be written in the form reactants \rightarrow products. Although the enthalpy of an isolated component cannot be directly measured, the enthalpy change over the course of a chemical reaction can be measured. We can define the **enthalpy of reaction** as follows:

$$\Delta H_{reaction} = H_{products} - H_{reactants}$$

The enthalpy of reaction allows us to determine if a given reaction is exothermic or endothermic. An exothermic reaction, in which heat is released by the reaction to the surroundings, has a negative ΔH value.

A plot of enthalpy vs. reaction progress would take the following form for an exothermic reaction:



The enthalpy of the reactants is greater than the enthalpy of the products. During the course of the reaction, heat is released to the surroundings.

If a net input of heat is required for the reaction to proceed, then ΔH is positive, and the reaction is endothermic. In an endothermic reaction, the reactants are lower in enthalpy than the products, which is why heat must be added to the system in order for the reaction to proceed. An enthalpy vs. reaction progress plot for an endothermic reaction would have the following form:



Standard Enthalpy of Formation

Although we cannot directly measure the enthalpy content of a single substance, we can determine the enthalpy change that would be necessary to form a compound from its elements in their standard states at 25°C. This value is referred to as the **standard enthalpy of formation** (ΔH_f). The term standard heat of formation can be used interchangeably; although, heat and enthalpy are technically not the same quantity. These values are tabulated for a large number of substances, and knowledge of the ΔH_f values for each component in a reaction allows you to predict the total enthalpy change for that reaction, as we will see in the following section.

The standard states for most elements can be determined just by finding out what state of matter they are in at 25°C, such as Ag(s), Hg(l), or Xe(g). However, some nonmetals have more complicated standard states. In particular, seven elements exist as diatomic substances in their standard states. H₂(g), N₂(g), O₂(g), F₂(g), Cl₂(g), Br₂(l), and I₂(s) each represent the standard forms of these elements.

Because standard enthalpy of formation values represent the change from elements in their standard state to a final substance, any element that is already in its standard state has a ΔH_f value of 0.

Calculations Using Thermochemical Equations

The total enthalpy change for a reaction can be predicted using the following equation:

 $\Delta H_{rxn} = \Sigma n \Delta H_f(products) - \Sigma n \Delta H_f(reactants)$

Essentially, if we add together the standard enthalpy of formation values for each product (multiplied by its coefficient in the balanced equation) and then subtract the ΔH_f for each reactant (again, multiplied by their coefficients), we are left with ΔH for the overall reaction.

When performing enthalpy calculations, a few points need to be remembered:

- ΔH_f values are generally given in kJ/mol, so we need to multiply each value by the total number of moles of each component in the reaction.
- The standard enthalpy of formation for any element in its most stable form at 25°C is zero.
- The state of the compound must be noted so the correct enthalpy value can be used. For example, ΔH_f is -285.8 kJ/mol for liquid water and -241.8 kJ/mol for water vapor.
- Keep close track of the signs of each value, since many ΔH_f values are negative.

The easiest way to explain this process is through an example problem. Let's consider the energy changes that occur during the combustion of methane gas:

Example 17.2

Calculate the enthalpy of reaction for the following process:

 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

You will need to make use of the following data:

- ΔH_f for $CH_4(g) = -74.87$ kJ/mol
- ΔH_f for CO₂(g) = -393.5 kJ/mol
- ΔH_f for H₂O(l) = -285.8 kJ/mol

Answer:

We are given ΔH_f values for every reaction component except for O₂(g). Because O₂(g) is the standard form of elemental oxygen, it has a ΔH_f value of zero. Now use the following equation:

$$\begin{aligned} \Delta H_{rxn} &= \Sigma n \Delta H_f(products) - \Sigma n \Delta H_f(reactants) \\ &= (-393.5 \text{ kJ/mol} + 2(-285.8 \text{ kJ/mol})) - (-74.87 \text{ kJ/mol} + 0 \text{ kJ/mol}) \\ &= -965.1 \text{ kJ/mol} - (-74.87 \text{ kJ/mol}) \\ &= -965.1 \text{ kJ/mol} + 74.87 \text{ kJ/mol} \\ &= -890.3 \text{ kJ/mol} \end{aligned}$$

The enthalpy change that takes course during this reaction is highly negative, indicating a strongly exothermic reaction. This is consistent with what we know about the combustion of methane, the primary component in natural gas.

Lesson Summary

- The first law of thermodynamics tells us that energy can be converted from one form to another but cannot be created or destroyed.
- When discussing energy changes for reactions that are run at a constant pressure, it is generally simpler to measure and tabulate changes in enthalpy (H), which can be thought of as the heat content of a system at constant pressure.
- The standard enthalpy of formation (ΔH_f) for a substance is the enthalpy change that would be necessary to form that substance from its elements in their standard states at 25°C.
- The enthalpy of a reaction can be calculated from ΔH_f values for its various components using the following equation: $\Delta H_{reaction} = \Sigma n \Delta H_{products} \Sigma n \Delta H_{reactants}$.

Lesson Review Questions

Reviewing Concepts

- 1. Which of the following situations would violate of the first law of thermodynamics? Explain your answer in each case.
 - a. Car brakes heat up when you slow down at a stop sign.
 - b. In a warm room, a glass of water spontaneously freezes.
 - c. A car parked on a hill rolls upward when the brake is released.
 - d. As sun shines on a swimming pool, more water evaporates.
- 2. How does enthalpy help us determine whether a reaction is exothermic or endothermic?

Problems

- 1. Use standard enthalpies of formation from the supplemental link below to calculate ΔH_{rxn} for the reaction: 2CO(g) + O₂(g) \rightarrow 2CO₂(g).
- 2. Use standard enthalpies of formation from the supplemental link below to calculate ΔH_{rxn} for the reaction: $4NH_3(g) + 5O_2(g) \rightarrow 6H_2O(g) + 4NO(g)$.
- 3. Complete combustion of 1.00 mol of acetone (C₃H₆O) liberates 1790 kJ of heat: C₃H₆O(l) + 4 O₂(g) \rightarrow 3 CO₂(g) + 3 H₂O(l); Δ H = -1790 kJ. Using this information and Δ H_f data for CO₂ and H₂O, calculate the standard enthalpy of formation for acetone.
- 4. Determine ΔH_f for IF, given the following information:

$$\begin{split} \mathrm{IF}_7 + \mathrm{I}_2(\mathrm{s}) &\rightarrow \mathrm{IF}_5 + 2\mathrm{IF}; \ \Delta\mathrm{H}_f = -89 \ \mathrm{kJ} \\ \Delta\mathrm{H}_f \ \mathrm{for} \ \mathrm{IF}_7 = -941 \ \mathrm{kJ} \\ \Delta\mathrm{H}_f \ \mathrm{for} \ \mathrm{IF}_5 = -840 \ \mathrm{kJ} \end{split}$$

5. Write the balanced equation for the complete combustion of C_2H_6 , and calculate the heat of combustion per mole of <u>gaseous</u> water formed using standard enthalpies of formation.

Further Reading / Supplemental Links

- Standard enthalpy of formation values: http://chemistry.about.com/od/thermodynamics/a/Heats-Of-Formatio n.htm
- Video: calculating the heat of reaction: http://www.youtube.com/watch?v=iQuy2mgbV9o

Points to Consider

• How does the state of a material affect enthalpy changes?

1.3 Hess's Law

Lesson Objectives

- State Hess's law.
- Use Hess's law to calculate standard enthalpy of formation values.

Lesson Vocabulary

• Hess's law: States that the enthalpy change between a set of reactants and a set of products will be the same, regardless of the number of reactions or steps that take place in between the two states.

Check Your Understanding

Recalling Prior Knowledge

The enthalpy of a reaction can be calculated from standard heat of formation values by using the following equation: $\Delta H_{rxn} = \Sigma n \Delta H_f(products) - \Sigma n \Delta H_f(reactants)$

Introduction

If you wished to travel from Memphis, Tennessee (home of the blues) to Nashville, Tennessee (home of country music), there are several available routes. You could take Interstate 40 east to Nashville, which would be a very direct route. You might want to head north on Interstate 55 to visit Cape Girardeau, Missouri before you turn onto U.S 61, and then Interstate 24 would take you to Nashville. Or you may decide to go south to Birmingham, Alabama on Interstate 22 before turning left on Interstate 65 to head back north to Nashville. Whatever the route chosen, all the different alternatives still take you to Nashville. The amount that you have driven depends on your route, but the overall distance between your starting point and your destination is independent of the path that you took. In this lesson, you will see that the energetics of a chemical reaction can be thought of in a similar way.

Hess's Law

In the 19th century, the Swiss-born Russian chemist Germain Hess (1802-1850) developed a law of heat summation, often referred to as **Hess's Law**. This law states that the enthalpy change between a set of reactants and a set of products will be the same, regardless of the number of reactions or steps that take place in between the two states.

In other words, the overall enthalpy change does not depend on how you got from start to finish.



FIGURE 1.6

The specific path leading to the formation of the different B products from A reactants does not influence the overall enthalpy change. $\Delta H_1 = \Delta H_2 + \Delta H_3 = \Delta H_4 + \Delta H_5 + \Delta H_6$

Indirect Method for Determining the Standard Heat of Formation

In the previous lesson, we made use of standard heat of formation values. Although the energy changes can sometimes be measured directly when a compound is generated from its constituent elements in their standard forms, many such reactions are difficult or unfeasible. An alternative way to measure the standard heat of formation is to measure the enthalpy changes for a series of reactions that result in the same net change. The general rules for manipulating thermochemical equations are as follows:

- 1. When adding two (or more) equations together, their ΔH_{rxn} values should also be added together.
- 2. Reversing the direction of a chemical equation reverses the sign of the enthalpy change but does not affect its magnitude.
- 3. If we multiply all components of a chemical reaction by some number, the enthalpy change should be multiplied by the same number.

In general, we are given a set of equations with known ΔH_{rxn} values, and by reversing or multiplying each equation by some factor, we can add them all together to give us the desired transformation. This can be shown most easily through an example.

Example 17.7

We want to determine ΔH_f for NO₂(g), but the formation reaction shown below is difficult to measure directly:

 $\frac{1}{2}$ N₂(g) + O₂(g) \rightarrow NO₂(g) $\Delta H_f^{\circ} = ?$ kJ/mol

However, we can measure the enthalpy changes for the following two reactions:

$$\begin{split} &\frac{1}{2}\mathrm{N}_2(g) + \frac{1}{2}\mathrm{O}_2(g) \to \mathrm{NO}(g) & \Delta H_f^\circ = 90 \text{ kJ/mol} \\ &\mathrm{NO}_2(g) \to \mathrm{NO}(g) + \frac{1}{2}\mathrm{O}_2(g) & \Delta H^\circ = 56 \text{ kJ/mol} \end{split}$$

Use these values to determine the standard heat of formation for $NO_2(g)$.

Answer:

We would like to manipulate the two known reactions so that when they are added together and we cancel the common terms (the compounds that appear on both the reactant and product sides), the net result is our desired transformation. In the desired reaction, nitrogen and oxygen gases are reactants, and $NO_2(g)$ is a product. If we

reverse the second known equation, $NO_2(g)$ will be a product. When reversing the direction of a chemical reaction, the magnitude of the enthalpy change stays the same, but the sign is reversed.

$$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) \quad \Delta H^\circ = -56 \text{ kJ/mol}$$

Now we can add the two reactions:

$$\frac{\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)}{NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)} \Delta H_f^\circ = 90 \text{ kJ/mol}$$

$$\frac{\Delta H^\circ = -56 \text{ kJ/mol}}{\frac{1}{2}N_2(g) + O_2(g) + NO(g) \rightarrow NO(g) + NO_2(g)} \Delta H^\circ = 34 \text{ kJ/mol}$$

The ΔH value for this transformation is the sum of the two simpler reactions. The final equation can also be simplified. The NO cancels out, because it is on both sides of the equation, leaving only the desired transformation:

 $\frac{1}{2}$ N₂(g) + O₂(g) \rightarrow NO₂(g) $\Delta H_f^{\circ} = 34$ kJ/mol

Note that the enthalpy change for any transformation can be determined in this way; this method can be used for more than just finding heat of formation values.

Example 17.8

What is ΔH_{rxn} for the following reaction?

 $CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$

The following formation reactions have known ΔH values:

$C(s) + 2S(s) \rightarrow CS_2(l)$	$\Delta H_f = 87.9 \text{ kJ/mol}$
$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H_f = -393.5 \text{ kJ/mol}$
$S(s) + O_2(g) \rightarrow SO_2(g)$	$\Delta H_f = -296.8 \text{ kJ/mol}$

Answer:

Which components of the first known equation are part of the desired reaction? Carbon and sulfur are not involved in the desired transformation, but one molecule of CS_2 is present as a reactant. If we reverse the first equation, we get the following:

$$CS_2(l) \rightarrow C(s) + 2S(s)$$
 $\Delta H = -87.9 \text{ kJ/mol}$

Now, look at the second equation. A single molecule of CO_2 is present as a product, which is what we want for our final equation. Since CO_2 does not show up in any of the other equations, we can assume that this equation will be used as is:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ/mol}$$

Finally, look at the third known equation. It has a single molecule of SO_2 as a product. However, we need two molecules of SO_2 on the product side, so we multiply the entire equation, including its ΔH value, by a factor of two:

$$2S(s) + 2O_2(g) \rightarrow 2SO_2(g) \quad \Delta H = -593.6 \text{ kJ/mol}$$

Now, add these three equations together:

$\mathbf{CS}_2(l) \to \mathbf{C}(s) + 2\mathbf{S}(s)$	$\Delta H = -87.9 \text{ kJ/mol}$
$\mathbf{C}(s) + \mathbf{O}_2(g) \to \mathbf{CO}_2(g)$	$\Delta H = -393.5 \text{ kJ/mol}$
$2\mathbf{S}(s) + 2\mathbf{O}_2(g) \to 2\mathbf{SO}_2(g)$	$\Delta H = -593.6 \text{ kJ/mol}$
$CS_2(l) + 3O_2(g) + C(s) + 2S(s) \rightarrow CO_2(g) + 2SO_2(g) + C(s) + 2S(s)$	$\Delta H = -1075.0 \text{ kJ/mol}$

One mole of carbon and two moles of sulfur appear on both sides of the equation. Cancelling out these terms, we are left with the desired reaction:

$$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g) \Delta H = -1075.0 \text{ kJ/mol}$$

Lesson Summary

- Hess's law states that the enthalpy change for a given transformation depends only on the initial and final states, and not on how many stages or steps are taken in between.
- Standard enthalpies of formation can be calculated indirectly using the ΔH_{rxn} values for reactions that are easier to measure directly.

Lesson Review Questions

Reviewing Concepts

- 1. State Hess's law.
- 2. Why is this law important?

Problems

1. Calculate the heat released by the burning of sulfur in oxygen: $2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$. ΔH values are known for the following reactions:

$$\begin{split} \mathbf{S}(s) + \mathbf{O}_2(g) & \Delta H = -296 \text{ kJ} \\ 2\mathbf{SO}_2(g) + \mathbf{O}_2(g) & \Delta H = -198 \text{ kJ} \end{split}$$

2. Calculate ΔH for the following reaction, which describes the production of syn-gas from carbon: $H_2O(g) + C(s) \rightarrow CO(g) + H_2(g)$. The following enthalpy changes are known:

$$\begin{aligned} \mathrm{H}_{2}(g) + \frac{1}{2}\mathrm{O}_{2}(g) \to \mathrm{H}_{2}\mathrm{O}(g) \\ 2\mathrm{CO}(g) \to 2\mathrm{C}(s) + \mathrm{O}_{2}(g) \end{aligned} \qquad \Delta H = -242.0 \ \mathrm{kJ} \\ \Delta H = +221.0 \ \mathrm{kJ} \end{aligned}$$

3. Calculate the heat of reaction for the following equation: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$. The following formation reactions have known ΔH values:

$3\mathbf{C}(s) + 4\mathbf{H}_2(g) \rightarrow \mathbf{C}_3\mathbf{H}_8(g)$	$\Delta H = -103.8 \text{ kJ}$
$2\mathrm{H}_2(g) + \mathrm{O}_2(g) \to 2\mathrm{H}_2\mathrm{O}(g)$	$\Delta H = -484 \text{ kJ}$
$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H = -393 \text{ kJ}$

Further Reading / Supplemental Link

- Hess's Law: http://www.science.uwaterloo.ca/~cchieh/cact/c120/hess.html
- Hess's Law worked example: http://www.utc.edu/Faculty/Gretchen-Potts/chemistryhelp/hess.htm
- Hess's Law video: http://www.khanacademy.org/science/physics/thermodynamics/v/hess-s-law-and-reactionenthalpy-change

Points to Consider

- How do chemical reactions occur?
- What affects the rate of a chemical reaction?

1.4 References

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