

# CHAPTER 3 – THE FIRST LAW OF THERMODYNAMICS

## Introduction

In this chapter, we discuss the First Law of Thermodynamics (energy cannot be created or destroyed). In our discussion, we will define some important terms and demonstrate some valuable tools that are required to treat the energy flow in a chemical reaction.

## 3.1 Some Definitions and Conventions

### Introduction

Determining the magnitude and direction of the energy flow is a common goal of thermodynamics. However, both the sign and magnitude depend upon the exact definition of the problem. In this section, we introduce some terms that will help us in this task.

#### Objectives

- Distinguish between a system, its surroundings, and the universe for a thermodynamic process.

#### 3.1-1. Energy Flow

We first define three important terms:

- **thermodynamic system:** That portion of the universe under investigation. It can be a volume in space or a carefully defined set of materials. It is the reference point for the direction of energy flow.
- **thermodynamic surroundings:** That portion of the universe that interacts with the system. Energy flows between the system and its surroundings.
- **thermodynamic universe:** A system and its surroundings.

The subscripts “univ” and “sur” are used to denote the universe and surroundings, but no subscripts are used for the system.

- $\Delta E$  = energy change of the system
- $\Delta E_{\text{sur}}$  = energy change in the surroundings
- $\Delta E_{\text{univ}}$  = energy change in the universe

Since the universe is simply the sum of the system and its surroundings, we can write

$$\Delta E_{\text{univ}} = \Delta E + \Delta E_{\text{sur}}$$

The sign or direction of energy flow is given by

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Therefore,  $\Delta E > 0$  means that  $E_{\text{final}} > E_{\text{initial}}$ , so the energy of the system increases, which requires energy to flow from the surroundings into the system, but  $\Delta E < 0$  implies that  $E_{\text{final}} < E_{\text{initial}}$ , so there is a loss of energy in the system as energy flows out of the system and into the surroundings. Indeed, a negative sign is usually read as “lost” or “released.” For example,  $\Delta E = -50$  J is usually read “50 J is released by the system,” while  $\Delta E = +50$  J is read “50 J is absorbed by the system.”

#### 3.1-2. Cash Flow Analogy

We now apply the definitions of system, surroundings, and sign to a cash flow problem where you write a check for \$50 to a friend. The first step in “setting up the books” is to define the system, which we will define as your account. In this problem, only your friend’s account interacts with (exchanges money with) the system, so it can be thought

of as the surroundings. We define  $\Delta B$  as the change in the balance of your account (the system); then  $\Delta B = -\$50$  because money transferred out of the system, which caused your balance to decrease by \$50. Similarly,  $\Delta B_{\text{sur}} = +\$50$  because money transferred into the surroundings, which increased the balance in your friend's account by \$50. Money was conserved in the process because money was neither created nor destroyed, it was simply transferred from the system to the surroundings. Thus,  $\Delta B_{\text{univ}} = \Delta B + \Delta B_{\text{sur}} = -50 + 50 = 0$ . If both accounts are held by the same bank, then the bank would be the universe for the problem as no money was transferred into or out of the bank. However, it is important to realize that the value of  $\Delta B$  depends upon our definitions. Consider the following possibilities:

- your account is the system:  $\Delta B = -\$50$
- your friend's account is the system:  $\Delta B = +\$50$
- the bank is the system:  $\Delta B = 0$

Consequently, it is very important to clearly define the system.

## 3.2 Work, Heat, and Energy

### Introduction

Heat and work are forms of energy transfer, and they represent the most common way for systems to exchange energy with their surroundings.

#### Objectives

- Calculate the heat absorbed by a system given its heat capacity and temperature change.
- Distinguish between heat capacity and specific heat.
- State the difference between the effects of work done *on* and work done *by* a system.

#### 3.2-1. Work

Consider Figure 3.1, in which a larger mass  $M$  is attached to a smaller mass  $m$  through a pulley. Upon release, the larger mass would drop and its potential energy would decrease, but as it falls, it exerts a force on the other mass causing it to move up. **Work**,  $w$ , is defined as a force through a distance, so the larger mass does work on the smaller one. For this discussion, we assume that 50 J of work is done. By convention,  $w$  is defined as the work done **on** the system.

So we would deduce that  $w = -50$  J if the larger mass is the system, but  $w = +50$  J if the smaller mass is the system.

The sign of  $w$  is given conversationally by using “on” or “by” as follows:

- $w > 0$ : the work is done **on** the system
- $w < 0$ : the work is done **by** the system

Thus, we would say that 50 J of work was done by the larger mass ( $w < 0$ ) or that 50 J of work was done on the smaller mass ( $w > 0$ ).

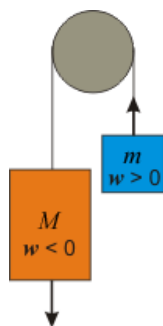


Figure 3.1: Work and the Sign of  $w$

### 3.2-2. Sign of $w$ Exercise

#### **EXERCISE 3.1:**

A person lifts a 70 kg mass to a height of 2.0 m, which changes the potential energy of the mass by 1.4 kJ.

1.4 kJ of work was done \_\_\_\_\_ the person, and 1.4 kJ of work was done \_\_\_\_\_ the mass.

First answer blank:

on

by

Second answer blank:

on

by

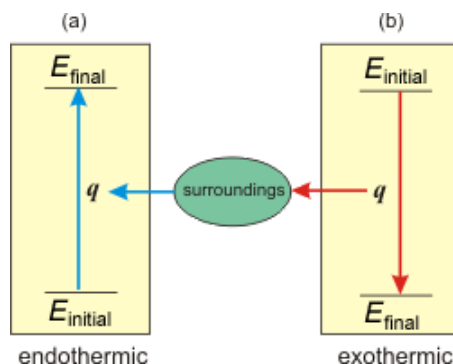
If the person is the system  $w =$  \_\_\_\_\_ kJ

If the mass is the system  $w =$  \_\_\_\_\_ kJ

### 3.2-3. Heat

Heat and work are the most common ways for energy to be transferred between a system and its surroundings.

**Heat**,  $q$ , is energy that is transferred as a result of a temperature difference.  $q$  is defined as the heat **absorbed** by the system. In Figure 3.2a, heat is absorbed by the system, so  $q > 0$ , which means that energy is transferred from the surroundings to the system increasing the energy of the system. In processes that absorb heat, heat enters the system, so they are said to be **endothermic**. In Figure 3.2b, heat is given off, so  $q < 0$  and energy is transferred from the system to the surroundings. In processes that give off heat, heat exits the system, so they are said to be **exothermic**.



**Figure 3.2: Heat and the Sign of  $q$**  (a) Endothermic process:  $q > 0$  and heat flows from the surroundings into the system. (b) Exothermic process:  $q < 0$  and heat flows from the system into the surroundings.

### 3.2-4. Sign of $q$ Exercise

#### **EXERCISE 3.2:**

A piece of metal is placed into hot water and 120 J of heat is transferred from the water to the metal.

If the *metal* is the system,  $q =$  \_\_\_\_\_ J and the process is said to be \_\_\_\_\_.

exothermic

endothermic

If the *water* is the system,  $q =$  \_\_\_\_\_ J and the process is said to be \_\_\_\_\_.

exothermic

endothermic

120 J of heat were \_\_\_\_\_ by the metal and 120 J of heat were \_\_\_\_\_ by the water.

First answer blank:

absorbed  
given off

Second answer blank:

absorbed  
given off

### 3.2-5. Heat Capacity and Specific Heat

The heat capacity of a substance depends upon its mass, but the specific heat does not.

Adding heat to a substance increases either its thermal energy (temperature) or its potential energy (phase change). Thus, adding heat to ice at  $-10\text{ }^{\circ}\text{C}$  increases the temperature of the ice, while adding it at  $0\text{ }^{\circ}\text{C}$  causes the ice to melt but does not change the temperature. The temperature change that results is proportional to the heat added, and the proportionality constant is called the **heat capacity**,  $C$ . The heat capacity is the amount of heat required to raise the temperature of the substance by  $1\text{ }^{\circ}\text{C}$ . It depends upon both the identity and the amount of substance. For example, the heat capacity of 4 g of water is four times that of 1 g.

$$q = C\Delta T \quad \text{Heat, Heat Capacity, and Temperature Change} \quad (3.1)$$

Tabulated values of heat capacities are not possible because they depend upon the mass, so we define the **specific heat**,  $s$ , as the heat capacity of one gram of material; i.e., the specific heat is the amount of heat required to raise the temperature of one gram of substance by  $1\text{ }^{\circ}\text{C}$ . Thus, the heat capacity equals the specific heat times the mass.

$$C = ms \quad \text{Specific Heat and Heat Capacity} \quad (3.2)$$

Combining Equation 3.1 and Equation 3.2, we obtain the following expression for heat in terms of the specific heat and mass of the substance.

$$q = ms\Delta T \quad \text{Heat, Specific Heat, and Temperature Change} \quad (3.3)$$

Note that if the temperature increases,  $\Delta T > 0$ , so  $q > 0$ , which means that  $q$  joules must be absorbed when the temperature of a substance with mass  $m$  and specific heat  $s$  increases by  $\Delta T$  degrees. If the temperature decreases,  $\Delta T < 0$ , so  $q < 0$ , and  $q$  joules would be given off when a substance with mass  $m$  and specific heat  $s$  cools by  $\Delta T$  degrees.

The accompanying table gives the specific heats of some selected substances.

Substance	Specific Heat ( $\text{J} \cdot \text{g}^{-1} \cdot \text{C}^{-1}$ )
Al( $s$ )	0.90
Cu( $s$ )	0.38
Fe( $s$ )	0.44
Hg( $l$ )	0.14
Kr( $g$ )	0.25
N <sub>2</sub> ( $g$ )	1.04
CCl <sub>4</sub> ( $g$ )	0.86
C <sub>2</sub> H <sub>5</sub> OH( $l$ )	2.46
H <sub>2</sub> O( $l$ )	4.18
H <sub>2</sub> O( $s$ )	2.00
H <sub>2</sub> O( $g$ )	2.00

Table 3.1: Specific Heats of Selected Substances

### 3.2-6. Specific Heat Exercise

#### **EXERCISE 3.3:**

How many kilojoules of heat are required to heat 17 g of ice from  $-22\text{ }^{\circ}\text{C}$  to  $-10\text{ }^{\circ}\text{C}$ ?

The specific heat of ice is  $2.0\text{ J}\cdot\text{g}^{-1}\cdot^{\circ}\text{C}^{-1}$ .

The heat capacity of 17 g of ice is \_\_\_\_\_  $\text{J}\cdot^{\circ}\text{C}^{-1}$

The temperature change is  $\Delta T =$  \_\_\_\_\_  $^{\circ}\text{C}$

The amount of heat required is  $q =$  \_\_\_\_\_ kJ

### 3.2-7. Kinetic and Potential Energy

Energy can be kinetic or potential.

**Energy** is the capacity to do work or to transfer heat. It can be in the form of kinetic energy or potential energy.

- **Kinetic energy** is energy of motion. Any particle in motion has the capacity to do work and to transfer heat. For example, a moving truck can move another object (do work on it) by colliding with it. It can transfer its energy as heat through the brake drums and tires when the brakes are applied.
- **Potential energy** is energy of position. A stopped truck at the top of a hill has no kinetic energy, but its potential energy can be converted into kinetic energy by releasing the brake. The atoms in molecules have potential energy because of their positions relative to other atoms.

## 3.3 The First Law of Thermodynamics

### Introduction

“Energy cannot be created or destroyed” is one of many statements of the First Law of Thermodynamics. In this section, we discuss how this law impacts the energy of a system.

### Prerequisites

- (CAMS) 9.1 First Law of Thermodynamics

### Objectives

- Use the expression,  $\Delta E = q + w$ , to determine how much of an energy flow is in the form of heat and how much is in the form of work.
- Define a state function.
- Calculate the amount of work associated with a change in the number of moles of gas in a reaction carried out at constant temperature and pressure.

### 3.3-1. First Law of Thermodynamics

Energy is conserved in all processes.

The **First Law of Thermodynamics** states that energy is conserved in all processes.

$$\Delta E_{\text{univ}} = 0 \quad \text{Conservation of Energy} \quad (3.4)$$

However, the universe is the sum of the system and its surroundings, so we can write  $\Delta E_{\text{univ}} = \Delta E + \Delta E_{\text{sur}} = 0$ , which leads to the following statement of the first law:

$$\Delta E = -\Delta E_{\text{sur}} \quad \text{Energy can only be transferred.} \quad (3.5)$$

The above shows that, although it cannot be created or destroyed, energy can be transferred between a system and its surroundings. Heat and work are the two most common ways of transferring energy. Thus, the energy of a system is increased when the surroundings transfers heat into the system and/or does work on it. The energy of the system decreases when it transfers heat to the surroundings or does work on them. This relationship is expressed mathematically in the following, which is **another statement of the First Law of Thermodynamics**:

$$\Delta E = q + w \quad \text{Energy is transferred by heat and work.} \quad (3.6)$$

### 3.3-2. First Law Exercise

#### **EXERCISE 3.4:**

What energy change is experienced by a system that absorbs 358 J of heat and does 412 J of work?

$$\Delta E = \text{_____ J}$$

### 3.3-3. Partitioning Energy Changes

Energy change can be partitioned into heat and work.

The potential energy of a system (blue block in the following animation) decreases when it drops from a height, but the energy of the universe must be conserved in the process. The energy loss, which is transferred to the surroundings, is partitioned into heat and work ( $\Delta E = q + w$ ) in the following animation by transferring the energy to the thermal and mechanical surroundings:

- The **mechanical surroundings** is that portion of the surroundings that exchanges energy with the system in the form of work. In the following, the system can lift another block. In doing so, the system does work on the lifted block, so some of the energy change of the system is transferred as work.
- The **thermal surroundings** is that portion of the surroundings that exchanges energy with the system in the form of heat. In the following, the falling system is stopped by friction, which converts the kinetic energy of the system into heat that is transferred to the thermal surroundings.

As the energy transferred to the mechanical surroundings increases, the amount transferred to the thermal surroundings decreases. Consequently, the speed with which the system drops decreases with the mass of the lifted block.

A video or simulation is available online.

### 3.3-4. State Functions

In the experiments described in the previous animation, we examined the transition between the same initial and final states by three different thermodynamic paths that differed in their distributions of  $q$  and  $w$ .  $\Delta E$  was the same for each path because  $\Delta E$  depends only upon the initial and final states—not on how they were achieved:  $\Delta E = E_{\text{final}} - E_{\text{initial}}$ . Properties, like energy, that depend only upon the state of the system are called **state functions**. The fact that energy is a state function means that  $\Delta E$  for a chemical process depends only upon the states of the reactants and products, not on the manner in which they react! This is an important property because it allows us to determine  $\Delta E$  for a reaction using any path—even one that is unreasonable—as long as the reactants and products remain the same. Both  $q$  and  $w$  are path dependent, so they are not state functions.  $q$  and  $w$  for a reaction depend not only on the reactants and products; they also depend on how the reaction is carried out.

### 3.3-5. Changing the Number of Moles of Gas in a Reaction

$\Delta n_{\text{g}}$  is the change in the number of moles of gas.

Most reactions carried out in a chemistry laboratory start and end at the same temperature and pressure, so  $\Delta T = 0$  and  $\Delta P = 0$ . These conditions are very common and they simplify the thermodynamics, so we limit our discussions to processes run at constant temperature and pressure.

Almost all reactions exchange energy with the thermal surroundings, but those involving gases can also exchange energy with the mechanical surroundings, and we now show how to partition the energy change of a reaction involving gases into heat and work. We begin by expressing the ideal gas law for a mixture as the following:

$$PV = n_g RT$$

$n_g$  is the total number of moles of gas in the mixture, but  $n_g$  can change during a reaction as gases are consumed or created. Under conditions of constant temperature and pressure,  $P$ ,  $R$ , and  $T$  are all constant, so the volume of the container must also change if  $n_g$  changes. The relationship is expressed as follows:

$$P\Delta V = \Delta n_g RT \quad \text{Volume Change in Chemical Reactions} \quad (3.7)$$

$\Delta V$  is the volume change, and  $\Delta n_g$  is the change in the total number of moles of gas. The change in the number of moles of gas in a reaction would be determined as follows:

$$\Delta n_g = \text{moles of gas phase products} - \text{moles of gas phase reactants} \quad (3.8)$$

**EXAMPLE:**

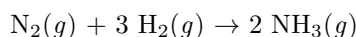
$\Delta n_g$  would be determined from the chemical equation  $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$  as  $\Delta n_g = 2$  moles gaseous product  $- 3$  moles gaseous reactants  $= -1$  mole gas, but that is  $-1$  mole of gas for every two moles of  $\text{H}_2\text{O}$  that are produced. However, if the reaction actually produced  $0.5$  mol  $\text{H}_2\text{O}$ , then  $\Delta n_g$  would be determined as follows:

$$\Delta n_g = 0.5 \text{ mol H}_2\text{O} \times \frac{-1 \text{ mol gas}}{2 \text{ mol H}_2\text{O}} = -0.25 \text{ mol gas}$$

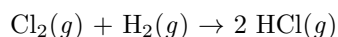
### 3.3-6. Change in Moles Exercise

**EXERCISE 3.5:**

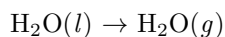
Determine the value of  $\Delta n_g$  for each of the following processes.



$$\Delta n_g = \text{_____ mol}$$



$$\Delta n_g = \text{_____ mol}$$



$$\Delta n_g = \text{_____ mol}$$

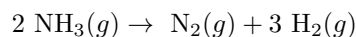


$$\Delta n_g = \text{_____ mol}$$

### 3.3-7. Volume Change Example

Work is done whenever gases are produced or consumed in a reaction.

Consider the following reaction carried out at constant  $T$  and  $P$ .



$$\Delta n_g = 4 \text{ mol} - 2 \text{ mol} = 2 \text{ moles of gas}$$

The number of moles of gas in the container increases by 2 mol for every 2 mol of  $\text{NH}_3$  that react. However, the reaction takes place at constant  $T$  and  $P$ , so the volume of the container must change. We can use the ideal gas equation to relate the volume change to  $\Delta n_g$  as follows.

$$P\Delta V = \Delta n_g RT$$

The volume change is demonstrated by the animation.

A video or simulation is available online.

### 3.3-8. $PV$ Work

The piston moves as the volume changes in the animation above, so work was done when the number of moles of gas changed. We now determine how much work was done. The work done **by** an object is the force exerted by the object times the distance moved,  $Fd$ . However,  $w$  is defined as the work done **on** the object, so  $w = -Fd$ . A force is exerted by the expanding gas because it must push back the atmosphere, which is exerting a pressure on the cylinder. We will call this pressure the opposing pressure,  $P_{\text{op}}$ . The force that must be overcome by the expanding gas is then  $P_{\text{op}}A$ , where  $A$  is the cross-sectional area of the piston. Consequently, we can write that  $w = -P_{\text{op}}Ad$ , but the product of the cross-sectional area of the piston times the distance that it moves is the volume change that the gas undergoes ( $Ad = \Delta V$ ), so we can express the work done on the gas as

$$w = -P_{\text{op}}\Delta V \quad PV \text{ Work} \quad (3.9)$$

Recall that  $P\Delta V = \Delta n_g RT$  for processes at constant temperature and pressure, so we can also express the work done on the gases in a reaction as

$$w = -\Delta n_g RT \quad \text{Work Due to a Change in the Number of Moles of Gas} \quad (3.10)$$

A video or simulation is available online.

### 3.3-9. Expansion Work Exercise

#### **EXERCISE 3.6:**

How much work is done when 12 g of water evaporates at 25 °C?

$$\Delta n_g = \text{_____ mol H}_2\text{O} \quad RT = \text{_____ J/mol}$$

$$w = \text{_____ J}$$

Is the work done “on” or “by” the water?

on

by

### 3.3-10. $PV$ Work Exercise

#### **EXERCISE 3.7:**

What is the energy change of a gas that absorbs 432 J of heat and expands from 0.932 L to 1.684 L against an opposing pressure of 4.46 atm?

First determine the amount of energy exchanged with the thermal surroundings.

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



Next, use Equation 3.9 to determine the amount exchanged with the mechanical surroundings.

$$\Delta V = \text{_____ L} \qquad w = -P\Delta V = \text{_____ L}\cdot\text{atm}$$

Use the fact that 1 L·atm = 101.3 J to convert  $w$  from L·atm to J.

$$w = \text{_____ J}$$

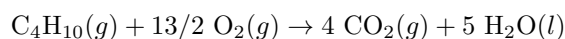
Use  $q$  and  $w$  to determine the energy change.

$$\Delta E = \text{_____ J}$$

### 3.3-11. Work in Combustion Exercise

#### **EXERCISE 3.8:**

How much work is done by the gases when 5.000 g of butane is combusted at 25 °C and 1 atm?



$\Delta n_g$  for the reaction shown above = \_\_\_\_\_ mol

This results in work being done \_\_\_\_\_ the system.  
on  
by

The number of moles of butane that react is \_\_\_\_\_ mol

$\Delta n_g$  for the combustion of 5.000 g of butane = \_\_\_\_\_ mol

$w$  for the combustion of 5.000 g of butane = \_\_\_\_\_ J

## 3.4 Enthalpy

### Introduction

In the last section, we saw that some of the energy change ( $\Delta n_g RT$ ) of a reaction carried out at constant pressure is in the form of work as escaping gases push back the atmosphere. This portion of the energy is lost and not available to do other work. Thus, it is only the heat that is absorbed or given off by a reaction that is important in processes carried out at constant pressure. Thus,  $\Delta E$  does not represent the energy that is important in constant pressure processes. In this section, we define a new thermodynamic function that is more appropriate for these processes.

### Prerequisites

- (CAMS) 9.2 Enthalpy
- (CAMS) 9.3 Enthalpies of Combustion

### Objectives

- Define the enthalpy of reaction and distinguish between it and the energy change of a reaction in terms of the heat absorbed at constant pressure or volume.
- Calculate the enthalpy of reaction from the energy change of the reaction and vice versa.

### 3.4-1. $\Delta H$ vs. $\Delta E$

$\Delta H$  is the heat absorbed at constant pressure, while  $\Delta E$  is the heat absorbed at constant volume.

We have seen that the First Law of Thermodynamics can be expressed in the following manner:

$$\Delta E = q + w$$

For chemical processes,  $w$  is the work done by gases as they react or are produced. We now examine this statement under two different conditions: constant volume and temperature and constant pressure and temperature.

**Constant Volume Processes:** Nothing moves if the volume does not change, so no work is done ( $w = 0$ ) and the first law expression can be written as the following:

$$\Delta E = q_V + w = q_V + 0 = q_V$$

where  $q_V$  is the heat absorbed at constant volume. Based on the above, we conclude that  **$\Delta E$  is the heat absorbed in a process carried out at constant volume and temperature.**

**Constant Pressure Processes:** The volume changes to maintain a constant pressure as gases are produced or consumed, so work can be done and the first law expression is

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

where  $q_P$  is the heat absorbed at constant pressure and  $P\Delta V$  is the work done by the gases. Solving this expression for the heat absorbed at constant pressure we obtain

$$q_P = \Delta E - P\Delta V$$

$q_P$  is the difference between two state functions, so it too must be a state function, which is called the **enthalpy of reaction** and given the symbol  $\Delta H$ . Thus,  **$\Delta H$  is the heat absorbed by the reaction carried out at constant pressure and temperature.** Substitution of  $\Delta H$  for  $q_P$  and  $\Delta n_g RT$  for the work into the first law expression for a constant pressure process yields the following:

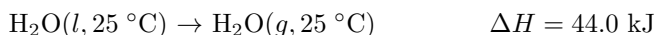
$$\Delta E = \Delta H - \Delta n_g RT \quad \Delta H \text{ and } \Delta E \text{ Related} \quad (3.11)$$

which can be read ***the heat absorbed by a process carried out at constant volume ( $\Delta E$ ) equals the heat absorbed by the process when carried out at constant pressure ( $\Delta H$ ) plus the work done by changing the number of moles of gas.***

### 3.4-2. Enthalpy-Energy Exercise

#### **EXERCISE 3.9:**

The enthalpy of vaporization of water at 25 °C is 44.0 kJ·mol<sup>-1</sup>. What is  $\Delta E$  for the vaporization of a mole of water at 25 °C?



$$\Delta n_g = \text{_____ mol}$$

$$\Delta n_g RT = \text{_____ kJ}$$

$$\Delta E = \text{_____ kJ}$$

Note that the energy difference between a mole of liquid and a mole of gas is less than the amount of energy that must be supplied to vaporize a mole of liquid because some energy is used by the escaping gases to “push back the atmosphere.”

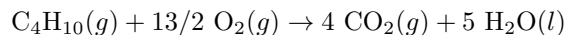
### 3.4-3. Enthalpy-Energy Exercise

#### **EXERCISE 3.10:**

Determine  $\Delta H_{\text{comb}}$  for butane given that  $\Delta E = -244.9$  kJ for the combustion of 5.000 g of butane at 25 °C.

Method:

1. Write the chemical equation for the combustion reaction.



2. Determine the number of moles of butane that react. ( $M_m = 58.12$  g/mol)

$$n = \text{_____ mol}$$

3. Use the given values to determine  $\Delta E$  for combustion of one mole of butane.

$$\Delta E_{\text{comb}} = \text{_____ kJ/mol}$$

4. Determine  $\Delta n_g$  for the combustion of one mole of butane.

$$\Delta n_g = \text{_____ mol}$$

5. Determine the amount of energy that is in the form of work.

$$\Delta n_g RT = \text{_____ kJ/mol}$$

6. Use Equation 3.11 to determine the heat of combustion.

$$\Delta H_{\text{comb}} = \text{_____ kJ/mol}$$

## 3.5 Standard States and Properties of Enthalpy Changes

### Introduction

The enthalpy of a reaction depends upon the states of the reactants (solid, liquid, gas, or solution) and upon the amounts of each of the substances. Thus, thermodynamic data are tabulated at reference states and apply to specific chemical equations. In this section, we discuss these reference states and how the enthalpy is dependent upon how the chemical equation is balanced.

### Objectives

- Identify the standard state of a substance.

#### 3.5-1. Standard States

The standard state is defined by a pressure (1 atm), but there is no standard temperature.

The enthalpy change of a reaction depends upon the concentrations and states of the substances. Consequently, most tabulated data refer to the situation in which all substances are in a specified state, called the **standard state**.

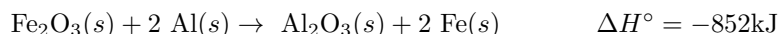
- The standard state of a pure substance is the most stable state at 1 atm pressure and the specified temperature. Solids and liquids are assumed to be pure unless specified otherwise.
- The standard state of a gas is a partial pressure of 1 atm.
- The standard state of a solute is a concentration of 1 *M*.

When considering standard states, 1 atm is the standard pressure, but there is no standard temperature. If no temperature is given, assume exactly 25 °C (298.15 K), which is the most common temperature used for tabulated data. The standard state of water is

- a solid at -10 °C
- a liquid at 25 °C

- a gas at 1 atm pressure at 110 °C

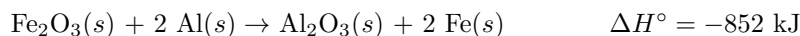
Most thermochemical data pertain to the reaction in which all of the products and reactants are in their standard states. These quantities are distinguished from their non-standard values with the use of a superscript. Thus,  $\Delta H^\circ$  is the standard enthalpy of reaction. Consider the following thermochemical equation:



No temperature is reported, so we assume a temperature of 298.15 K. The solid state is the standard state for each substance at 298.15 K, so the enthalpy change is the standard enthalpy of reaction as indicated by the superscript zero.

### 3.5-2. Properties of Enthalpy

The enthalpy change also depends upon the amount of reactant that reacts or product that is formed. For example, consider the following reaction:



$\Delta H^\circ = -852 \text{ kJ}$  in the above reaction as it is written. This means that 852 kJ are released for each mole of  $\text{Fe}_2\text{O}_3$  or every two moles of Al that react or every 2 mol Fe or 1 mole  $\text{Al}_2\text{O}_3$  that are produced. Thus, the following factors can be used to determine the amount of heat liberated from the amount of reactant consumed or product formed:

$$\frac{-852 \text{ kJ}}{1 \text{ mol Fe}_2\text{O}_3 \text{ reacting}}; \frac{-852 \text{ kJ}}{2 \text{ mol Al reacting}}; \frac{-852 \text{ kJ}}{1 \text{ mol Al}_2\text{O}_3 \text{ produced}}; \frac{-852 \text{ kJ}}{2 \text{ mol Fe produced}}$$

Enthalpy is a state function, so reversing the initial and final states simply changes the sign. Thus, 852 kJ would be *absorbed* when 1 mol of  $\text{Al}_2\text{O}_3$  reacts with 2 mol Fe to produce 1 mol  $\text{Fe}_2\text{O}_3$  and 2 mol Al.

The properties of the enthalpy change of a reaction can be summarized as the following:

- If a reaction is multiplied by some number, then the enthalpy change must be multiplied by the same number.
- If a reaction is reversed, the sign of its enthalpy change is reversed.

### 3.5-3. Balanced Chemical Equation and Enthalpy Change Exercise

#### **EXERCISE 3.11:**

The thermochemical equation for the thermite reaction is:



What is the standard enthalpy for the reaction of 1.00 mol of Al with an excess of  $\text{Fe}_2\text{O}_3$ ?

$$\Delta H^\circ = \text{_____ kJ}$$

What is the standard enthalpy for the reaction of 2.00 mol of Fe with an excess of  $\text{Al}_2\text{O}_3$ ?

$$\Delta H^\circ = \text{_____ kJ}$$

## 3.6 Hess's Law of Heat Summation

### Introduction

Enthalpy is a state function, so the enthalpy change of a process is independent of the path used to convert the initial state into the final state. This means that the enthalpy change of a process can be determined by breaking

the process into a series of smaller processes whose enthalpy changes are known. The steps we choose don't even have to be realistic; they only have to move the system from the initial to the final state.

## Objectives

- Apply Hess's Law of Heat Summation to determine the enthalpy of reaction.

### 3.6-1. Hess's Law

We will frequently use the fact that enthalpy is a state function to deduce its value from other known enthalpies with the use of Hess's Law of Heat Summation.

#### *Hess's Law of Heat Summation:*

- If a process can be expressed as the sum of several steps, then the enthalpy change of the process is the sum of the enthalpy changes of the steps.

### 3.6-2. A Heating Curve

Adding heat to a substance results in either a temperature change or a phase change. For example, consider the heating curve for heating water from 25 °C to 150 °C shown in Figure 3.3. Initially, the heat results only in a temperature change until the boiling point is reached. There is no temperature change as heat is added at the boiling point because all of the heat is used to vaporize the liquid. Once all of the liquid is vaporized, additional heat again causes the temperature to rise. The amount of heat required in each step is determined as follows:

- Temperature change: Combining Equation 3.2 and Equation 3.1, we see that the heat required to raise the temperature of  $m$  grams of a substance by  $\Delta T$  degrees is  $\Delta H = ms\Delta T$ .
- Phase change: Enthalpies of phase change are usually given in  $\text{kJ}\cdot\text{mol}^{-1}$ , so the enthalpy change required to change the phase of  $n$  moles is  $\Delta H = n\Delta H_{\text{phase change}}$ .

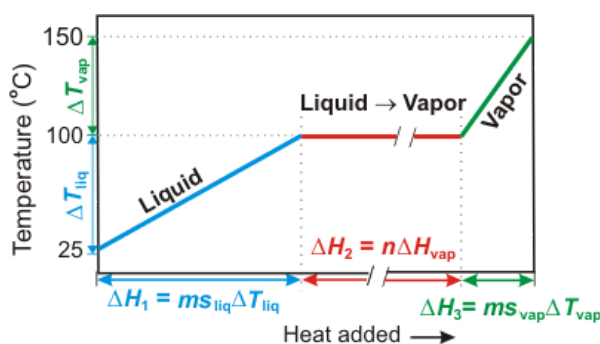


Figure 3.3: Heating Curve for Water from 25 °C to 150 °C

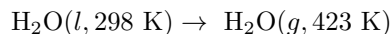
### 3.6-3. Hess's Law Example

Hess's Law, coupled with the fact that enthalpy change is path independent, allows us to determine enthalpy changes for complicated processes by considering simpler ones. Consider the process of heating water from 25 °C to 150 °C that was discussed above. To determine the heat required for the overall process, we would first break the process down into smaller processes (chemical equations) for which we can readily determine individual enthalpies. The processes are chosen so that they involve only one change, either temperature or phase, but not both.

Process	Chemical Equation
Heat the liquid from 25 °C to its boiling point.	$\text{H}_2\text{O}(l, 298 \text{ K}) \rightarrow \text{H}_2\text{O}(l, 373 \text{ K})$
Vaporize the liquid at its boiling point.	$\text{H}_2\text{O}(l, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(g, 373 \text{ K})$
Heat the steam to 150 °C.	$\text{H}_2\text{O}(g, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(g, 423 \text{ K})$

Table 3.2

Note that the final state of each process is the same as the initial state of the following process, so these two states cancel when the three processes are added to leave only the initial state of the first process and the final state of the last process (the two states in bold):



Since the process can be represented as the sum of three processes, the enthalpy change for the overall process is the sum of the three enthalpy changes. The enthalpy changes are determined for an expanded problem in the following section.

### 3.6-4. State Change Exercise

#### **EXERCISE 3.12:**

Use the following table for the thermal properties of water to determine how much heat is required to convert 1.00 mole of ice at  $-20.^\circ\text{C}$  to steam at  $120.^\circ\text{C}$ .

	<b>Specific Heats</b> <b><math>\text{J}\cdot\text{g}^{-1}\cdot^\circ\text{C}</math></b>
solid	2.0
liquid	4.18
gas	2.0
	<b>Enthalpies</b> <b><math>(\text{kJ}\cdot\text{mol}^{-1})</math></b>
fusion	6.01
vaporization	40.7

**Table 3.3: Some Thermal Properties of Water**

First, break the overall process down into a series of smaller processes and determine the value of  $\Delta H$  for each of the simple processes. Note: the enthalpy units must be the same for each process in order to add them. In this example, we determine the enthalpies in kJ.

<b>Process</b>	<b><math>\Delta H</math> (kJ/mol)</b>
$\text{H}_2\text{O}(s, 253\text{ K}) \rightarrow \text{H}_2\text{O}(s, 273\text{ K})$	
$\text{H}_2\text{O}(s, 273\text{ K}) \rightarrow \text{H}_2\text{O}(l, 273\text{ K})$	
$\text{H}_2\text{O}(l, 273\text{ K}) \rightarrow \text{H}_2\text{O}(l, 373\text{ K})$	
$\text{H}_2\text{O}(l, 373\text{ K}) \rightarrow \text{H}_2\text{O}(g, 373\text{ K})$	
$\text{H}_2\text{O}(g, 373\text{ K}) \rightarrow \text{H}_2\text{O}(g, 393\text{ K})$	

Use the above values and Hess's Law to determine  $\Delta H$  for the entire process.

<b>Process</b>	<b><math>\Delta H</math> (kJ/mol)</b>
$\text{H}_2\text{O}(s, 253\text{ K}) \rightarrow \text{H}_2\text{O}(g, 393\text{ K})$	

### 3.6-5. Any Path Will Do

Although some ice may sublime, and some of the water vaporizes prior to the boiling point, the processes used in the preceding example follow closely those that actually occur during the heating process. However, enthalpy is

a state function, so we are free to choose any path, even one that is totally unrelated to the overall process under consideration. As long as the sum of the processes in the path chosen sum to the overall process, we can use Hess's Law. One path that we can sometimes use is to combust all of the reactants and then let the products of the combustion recombine to produce the desired products. To do this, we use heats of combustion, which are defined as follows:

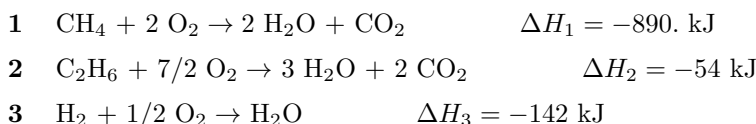
- **Enthalpy of combustion** is the heat absorbed when one mole of a substance reacts with oxygen.

Tables of heats (enthalpies) of combustion are common. In the following example, we determine the enthalpy of a reaction from the enthalpies of combustion of the reactants and products.

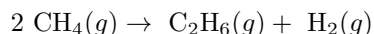
### 3.6-6. Using Heats of Combustion in the Path

#### **EXERCISE 3.13:**

Given the following combustion reactions:



Determine the enthalpy change for the following reaction:



We must rearrange the given chemical equations (multiply each by a number and/or reverse the reaction) so that the sum of the resulting equations produces the desired equation. Reversing the direction of a reaction changes its sign, so **use a minus sign with the multiplier to indicate that the reaction must be reversed**.

Each reactant and product appears in only one of the given reactions, so we can construct the desired reaction from the individual molecules.

Two molecules of CH<sub>4</sub> appear on the reactant side of the desired reaction, and one molecule appears on the reactant side of Equation 1.

The multiplier that should be applied to Equation 1 is \_\_\_\_\_

The resulting chemical equation is the following. (Denote any subscripts with an underscore. For example, NH\_3 for NH<sub>3</sub>. Place a single space between the coefficient and the compound. Omit any coefficients of 1.)



The enthalpy change is  $\Delta H_A =$  \_\_\_\_\_ kJ

One molecule of C<sub>2</sub>H<sub>6</sub> is required on the product side, and one molecule of C<sub>2</sub>H<sub>6</sub> appears on the reactant side of Equation 2.

The multiplier that should be applied to Equation 2 is \_\_\_\_\_

The resulting chemical equation is the following. (Denote any subscripts with an underscore. For example, NH\_3 for NH<sub>3</sub>. Place a single space between the coefficient and the compound. Omit any coefficients of 1.)



The enthalpy change is  $\Delta H_B =$  \_\_\_\_\_ kJ

One molecule of H<sub>2</sub> appears on the product side of the desired equation, and one molecule appears as a reactant in Equation 3.

The multiplier that should be applied to Equation 3 is \_\_\_\_\_

The resulting chemical equation is the following. (Denote any subscripts with an underscore. For example, NH\_3 for NH<sub>3</sub>. Place a single space between the coefficient and the compound. Omit any coefficients of 1.)



The enthalpy change is  $\Delta H_C =$  \_\_\_\_\_ kJ

The chemical equation produced by the sum of equations A, B, and C is the following. (Denote any subscripts with an underscore. For example, NH\_3 for NH<sub>3</sub>. Place a single space between the coefficient and the compound. Omit any coefficients of 1.)



The enthalpy change for the above reaction is  $\Delta H =$  \_\_\_\_\_ kJ

### 3.6-7. Heats of Combustion Summary

We saw in the preceding example that the enthalpy of the reaction



can be determined from the heats of combustion of the reactants and products as

$$\Delta H = 2\Delta H_{\text{comb}}(\text{CH}_4) - \Delta H_{\text{comb}}(\text{C}_2\text{H}_6) - \Delta H_{\text{comb}}(\text{H}_2)$$

In other words, the enthalpy of this reaction can be determined as the heats of combustion of the reactants minus the heats of combustion of the products, where each heat of combustion is multiplied by the coefficient in the balanced equation.

## 3.7 Enthalpies (or Heats) of Formation

### Introduction

In the previous section, we saw that the enthalpy of a reaction can be determined from the heats of combustion of the reactants and products. This would be an excellent method to use to determine enthalpies of reactions, but it is limited to reactions in which all reactants and products react with oxygen, and not all compounds do. Thus, another, more general, reaction needs to be used. The reaction that is used is the formation reaction; not all compounds combust, but they all form.

### Objectives

- Determine the enthalpy of reaction given the heats of formation of the reactants and products.
- Determine the enthalpy of formation of one of the reactants or products of a reaction given the  $\Delta H$  of the reaction and the heats of formation of all other participants in the reaction.

#### 3.7-1. Definition

The *standard heat of formation*,  $\Delta H_f^\circ$ , of a compound is the heat absorbed when one mole of the compound is formed from its elements in their standard states. For example, saying that “the heat of formation of hydrogen chloride is  $-92.3 \text{ kJ/mol}$ ” implies the following thermochemical equation.





The equation obtained by multiplying the above by 2 to eliminate the fractions corresponds to twice the heat of formation of HCl because it involves the production of 2 mol HCl.

The heat of formation of an element in its standard state is zero because there is no reaction required to produce an element from its elements. For example, consider the formation reaction for elemental oxygen:

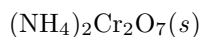
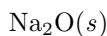
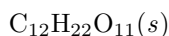


The enthalpy change for the above reaction is zero because the final and initial states are the same.

### 3.7-2. Writing Formation Reaction Exercise

#### EXERCISE 3.14:

Write the formation reaction for each of the following. Order the elements in the same order they appear in the given compound. Denote any subscripts with an underscore. For example, NH<sub>3</sub> for NH<sub>3</sub>. Place a single space between the coefficient and the compound. Omit any coefficients of 1. Be sure to indicate the state of each substance as (s), (l), or (g) and express non-integer coefficients as fractions.



### 3.7-3. Using Heats of Formation

The path that is assumed when heats of formation are used involves breaking up the reactant molecules into their elements, then combining the elements that were produced to form the products. The application of Hess's Law to the process can be summarized as follows:

- The enthalpy of any reaction can be determined as the sum of the enthalpies of formation of the products, each multiplied by its coefficient in the balanced equation, minus the sum of the enthalpies of formation of the reactants, each multiplied by its coefficient in the balanced equation.

$$\Delta H^\circ = \sum c_P(\Delta H_f^\circ)_P - \sum c_R(\Delta H_f^\circ)_R \quad (3.12)$$

- ( $\Delta H_f^\circ$ )<sub>P</sub> is the standard heat of formation of the product whose coefficient in the balanced equation is  $c_P$ .
- ( $\Delta H_f^\circ$ )<sub>R</sub> is the standard heat of formation of the reactant whose coefficient in the balanced equation is  $c_R$ .

For example, the enthalpy for the reaction  $\text{Al}_2\text{O}_3(s) + 3 \text{CO}(g) \rightarrow 2 \text{Al}(s) + 3 \text{CO}_2(g)$  could be determined as

$$\Delta H^\circ = 2\Delta H_f^\circ(\text{Al}) + 3\Delta H_f^\circ(\text{CO}_2) - \Delta H_f^\circ(\text{Al}_2\text{O}_3) - 3\Delta H_f^\circ(\text{CO})$$

Heats of formation are available in tables (See Thermodynamic Properties in the Resources). Substitution of the tabulated values yields

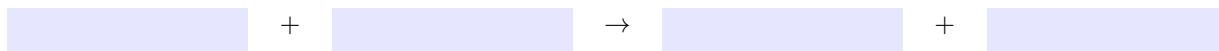
$$\Delta H^\circ = 2(0) + 3(-393.51) - (-1676) - 3(-110.52) = 827 \text{ kJ}$$

### 3.7-4. Heat of Combustion from Heats of Formation Exercise

#### **EXERCISE 3.15:**

Determine the standard heat of combustion of ethanol,  $\text{C}_2\text{H}_5\text{OH}(l)$ , at 298 K.

First, write the combustion reaction for  $\text{C}_2\text{H}_5\text{OH}(l)$ . The carbon and hydrogen atoms are oxidized to carbon dioxide and water, respectively. At 298 K, the water is a liquid. Denote any subscripts with an underscore. For example,  $\text{NH}_3$  for  $\text{NH}_3$ . Place a single space between the coefficient and the compound. Omit any coefficients of 1. When writing the reaction, be sure to include the states of matter and express noninteger coefficients as fractions.



Next, use the resource titled Thermodynamic Properties to determine the heat of formation of each product and reactant.

$\text{C}_2\text{H}_5\text{OH}(l)$  \_\_\_\_\_ kJ/mol

$\text{O}_2(g)$  \_\_\_\_\_ kJ/mol

$\text{CO}_2(g)$  \_\_\_\_\_ kJ/mol

$\text{H}_2\text{O}(l)$  \_\_\_\_\_ kJ/mol

Finally, use Equation 3.12 to determine the enthalpy of combustion of ethanol.

$$\Delta H_{\text{comb}} = \text{_____ kJ/mol}$$

### 3.7-5. Heats of Formation from Heat of Combustion Exercise

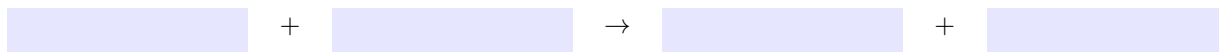
Heats of formation are not always determined from direct measurement. For example, when  $\text{C}(s)$  and  $\text{H}_2(g)$  react, a number of different compounds will be produced. Consequently, the heat of formation of something like  $\text{C}_6\text{H}_6$  cannot be determined directly. Instead, the heat of reaction for a different reaction is measured and used with known heats of formation to determine the unknown heat of formation. The heat of formation of octane is determined from its heat of combustion in the following example.

### 3.7-6. Exercise

#### **EXERCISE 3.16:**

The enthalpy of combustion of octane ( $\text{C}_8\text{H}_{18}$  is  $-5494 \text{ kJ/mol}$ ). What is the heat of formation of octane?

First, write the combustion reaction for  $\text{C}_8\text{H}_{18}(l)$ . The carbon and hydrogen atoms are all oxidized to carbon dioxide and water. At 298 K, the water is a liquid. Denote any subscripts with an underscore. For example,  $\text{NH}_3$  for  $\text{NH}_3$ . Place a single space between the coefficient and the compound. Omit any coefficients of 1. Express all noninteger coefficients as fractions and include the states of matter.



Next, use the resource titled Thermodynamic Properties to determine the heat of formation of each of the other compounds in the reaction.



Write the expression for the heat of combustion in terms of the heats of formation and solve it for the heat of formation of octane.

$$\Delta H_f = \text{_____} \quad \text{kJ/mol}$$

## 3.8 Bond Dissociation Energies

### Introduction

Although tables of heats of formation are extensive, there are still many compounds whose heats of formation are unknown. However, all chemical reactions involve breaking and forming bonds and the enthalpy of a reaction can be approximated from the energies of the broken and formed bonds. In this section, we define the bond or dissociation energy, show how bond energies can be determined from heats of formation, and finally show how bond energies can be used to approximate the enthalpy of any reaction.

### Prerequisites

- (CAMS) 9.4 Bond Energies

### Objectives

- Determine the enthalpy of atomization of a molecule and the average bond energy of its bonds when all of the bonds are between the same pair of atoms.
- Use bond energies to estimate enthalpies of gas-phase reactions.

### 3.8-1. Definition

The **bond energy** or **dissociation energy**,  $D$ , is the energy required to break a mole of bonds in the gas phase. When all of the bonds in a gas phase molecule are broken to produce the constituent atoms in the gas phase, the molecule is said to be atomized and the energy required to atomize a mole of molecules is called the **atomization energy**,  $\Delta H_{\text{atom}}$ . Note that *the atoms, not the elements in their standard states, are the products of atomization*. The chemical equation for the atomization of  $\text{CH}_4$  is



The atomization energy is the sum of the bond energies of all of the broken bonds, but it can also be determined from the heats of formation of the products and reactants. We next combine both methods for the above process.

$$\Delta H_{\text{atom}} = \Delta H_f(\text{C}) + 4\Delta H_f(\text{H}) - \Delta H_f(\text{CH}_4) = 4D_{\text{C-H}}$$

The atomization of  $\text{CH}_4$  requires breaking the four C–H bonds, so  $D_{\text{C-H}}$ , which is the average C–H bond energy in  $\text{CH}_4$ , can be determined as  $\Delta H_{\text{atom}}/4$ . Atomization energies are often used to estimate bond energies.

### 3.8-2. Determining a Bond Energy Exercise

#### EXERCISE 3.17:

What is the average N–O bond energy in NO<sub>2</sub>?

Our strategy is to determine the atomization energy from heats of formation and then relate that to the N–O bond energy.

Write the atomization reaction for NO<sub>2</sub>. (Denote any subscripts with an underscore. For example, NH\_3 for NH<sub>3</sub>. Place a single space between the coefficient and the compound. Omit any coefficients of 1. Include states of matter.)



Look up the required heats of formation (Thermodynamic Properties).

NO<sub>2</sub> \_\_\_\_\_ kJ/mol                      N \_\_\_\_\_ kJ/mol  
O \_\_\_\_\_ kJ/mol

Use the heats of formation to determine the atomization energy of NO<sub>2</sub>.

$$\Delta H_{\text{atom}} = \text{_____ kJ/mol}$$

Determine the average bond strength given that two N–O bonds must be broken to atomize the molecule.

$$D_{\text{N-O}} = \text{_____ kJ/mol}$$

### 3.8-3. Determining a Bond Energy Exercise

#### EXERCISE 3.18:

Determine the average C–F bond energy in CHF<sub>3</sub> from the following data.

- Enthalpies of formation: C = 717; F = 79; H = 218; CHF<sub>3</sub> = –695 kJ/mol
- C–H bond energy = 413 kJ/mol

Write the atomization reaction for CHF<sub>3</sub>. (Denote any subscripts with an underscore. For example, NH\_3 for NH<sub>3</sub>. Place a single space between the coefficient and the compound. Omit any coefficients of 1. Include states of matter.)



Determine the atomization energy of CHF<sub>3</sub>.

$$\Delta H_{\text{atom}} = \text{_____ kJ/mol}$$

Use the given bond energy to determine the energy of three C–F bonds.

$$3D_{\text{C-F}} = \text{_____}$$

Determine the average C–F bond energy in CHF<sub>3</sub>.

$$D_{\text{C-F}} = \text{_____ kJ/mol}$$

### 3.8-4. Enthalpies of Reaction from Bond Energies

Reactions involve breaking and forming bonds, so enthalpies of reaction can be estimated with bond energies. The path assumed for a reaction when bond energies are used involves breaking all of the relevant reactant bonds to produce fragments and then combining the fragments so as to produce the desired products. Application of Hess's Law to the process can again be summarized in a simple fashion.

- The enthalpy of a reaction can be *estimated* as the energy required to break the reactant bonds minus the energy released when the product bonds are formed.

$$\Delta H \approx \sum (D_{\text{broken bonds}}) - \sum (D_{\text{formed bonds}}) \quad (3.13)$$

The above is only an approximation because the energy of a bond depends on its environment (the other atoms attached to the bound atoms). In addition, bond energies are sometimes used to estimate enthalpies in solution, but the tabulated values are average values for gas phase bonds only, so such approximations should be treated with care.

### 3.8-5. Bond Energy Table

Bond energies are a convenient way to estimate reaction enthalpies, and a table of bond energies of common bonds can be found in the resource titled Bond Energies. For completeness, it is also given below.

C-H	413	N-H	391	O-H	463	H-H	436				
C-F	485	N-F	272	O-F	190	H-F	565	F-F	159		
C-Cl	328	N-Cl	200	O-Cl	203	H-Cl	431	Cl-Cl	243		
C-Br	276	N-Br	243	O-Br	235	H-Br	366	Br-Br	193		
C-I	234			O-I	234	H-I	299	I-I	151		
C-C	347	N-N	163	N-O	201	C-N	293	C-O	358	O-O	146
C=C	612	N=N	418	N=O	607	C=N	615	C=O	799	O=O	495
C≡C	820	N≡N	941			C≡N	891	C≡O	1072		

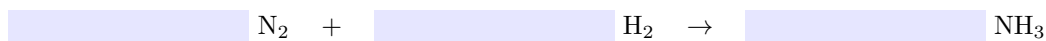
Table 3.4: Common Bond Energies (kJ·mol<sup>-1</sup>)

### 3.8-6. Using Bond Energies Exercise

#### **EXERCISE 3.19:**

Use bond energies to estimate the heat of formation of NH<sub>3</sub>.

- Write the chemical equation (no states needed) for the formation reaction. (Express all noninteger coefficients as fractions.)



- Draw Lewis structures for each compound to identify multiple bonds.
- Use a table of bond energies (Bond Energies) to determine the energy of the reactant bonds.

Energy Reactant Bonds \_\_\_\_\_ kJ/mol

- Use a table of bond energies (Bond Energies) to determine the energy of the produced bonds.

Energy Required to Break Reactant Bonds \_\_\_\_\_ kJ/mol

Use the results of 3 and 4 to determine the enthalpy of formation.

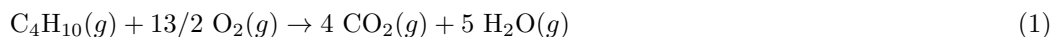
$$\Delta H_f = \text{_____ kJ/mol}$$

### 3.8-7. Using Bond Energies in Reactions that Involve a Simple Solid or Liquid

Bond energies should be applied directly only when all substances in a reaction are gases. However, they can be combined with other thermodynamic quantities to produce valid results for reactions that involve a simple solid or liquid. This is done by applying Hess's Law of Heat Summation to the enthalpy of reaction determined with bond energies and the energy required to convert the solid or liquid into a gas. Consider the example where the heat of combustion of butane at 298 K is determined from bond energies.

#### **EXAMPLE:**

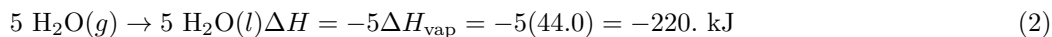
Bond energies apply only to molecules in the gas phase, so using bond energies alone we would obtain the enthalpy of the following reaction.



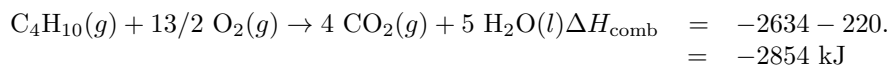
Using a table of bond energies (Bond Energies), we can determine the enthalpy of Reaction 1 as follows.

$$\begin{aligned} \Delta H &= 3D_{\text{C-C}} + 10D_{\text{C-H}} + 6.5D_{\text{O=O}} - 8D_{\text{C=O}} - 10D_{\text{O-H}} \\ &= 3(347) + 10(413) + 6.5(495) - 8(799) - 10(463) \\ &= -2634 \text{ kJ} \end{aligned}$$

However, water is a liquid at 298 K, not a gas, so the heat of vaporization of water must be combined with Reaction 1 to convert the gas to a liquid. Five moles of  $\text{H}_2\text{O}$  are produced, so we use the following:



Adding Reactions 1 and 2 provides the chemical equation for the combustion as the  $5 \text{H}_2\text{O}(g)$  cancels in the addition. Adding their enthalpy changes provides the heat of combustion.



### 3.8-8. Using Bond Energies for a Reaction with a Solid Exercise

#### **EXERCISE 3.20:**

Use bond energies to estimate the heat of formation of ethene ( $\text{C}_2\text{H}_4$ ).

Write the balanced chemical equation for the formation as determined solely from bond energies. (Denote any subscripts with an underscore. For example,  $\text{NH}_3$  for  $\text{NH}_3$ . Place a single space between the coefficient and the compound. Omit any coefficients of 1. Include states of matter.)



Draw Lewis structures and use bond energies to determine the enthalpy for Reaction 1:

$$\Delta H_1 = \text{_____ kJ}$$

The standard state of carbon is graphite. What equation must be added to the above to convert  $C(g)$  to  $C(s)$ ? (Denote any subscripts with an underscore. For example,  $NH_3$  for  $NH_3$ . Place a single space between the coefficient and the compound. Omit any coefficients of 1. Include states of matter.)

Reaction 2:  →

What is the enthalpy of Reaction 2?

$\Delta H_2 =$  \_\_\_\_\_ kJ

The enthalpy of formation of ethene is:

$\Delta H_f =$  \_\_\_\_\_ kJ

## 3.9 Calorimetry

### Introduction

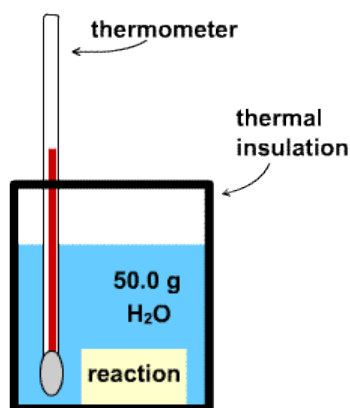
Heats of formation, heats of combustion, and bond energies are all available in tables and can be used to determine or approximate the enthalpy change of other reactions. However, these tabulated numbers are based on experimental values. In this section, we discuss how those values are obtained. Measuring the amount of heat absorbed or liberated in a process is called calorimetry.

### Objectives

- Calculate the heat of a reaction from the temperature change it causes in a calorimeter with known heat capacity, and decide whether the heat is an enthalpy change or a change in the energy of the system.

#### 3.9-1. A Calorimeter

Calorimetry is the measurement of the heat flow of a process, and a schematic of a simple calorimeter is shown in Figure 3.4. The calorimeter consists of a thermally insulated container, a thermometer, and a carefully measured amount of water. The thermal insulation can range from styrofoam as found in insulated cups to evacuated jackets as found in Thermos bottles. A heat source or sink, which is often a reaction, is then placed in the calorimeter, and the temperature change of the calorimeter is measured.



**Figure 3.4** The amount of heat that is released or absorbed in a reaction is determined experimentally in a *calorimeter*. The reaction is usually carried out in a container that is submerged in the water, so the heat flow is determined by measuring the temperature change in the water.

### 3.9-2. The Calorimetry Equations

Since the water and the reaction are in a thermally insulated container, no heat can enter or leave the system; i.e.,  $q_{\text{rxn}} + q_{\text{cal}} = 0$ , which can be rearranged to the following:

$$q_{\text{rxn}} = -q_{\text{cal}} \quad \text{Calorimetry Equation 1} \quad (3.14)$$

The heat of the reaction causes only a temperature change in the calorimeter, so we can express  $q_{\text{cal}}$  as

$$q_{\text{cal}} = C_{\text{cal}}\Delta T_{\text{cal}}$$

Substituting this expression into Calorimetry Equation 1, we obtain

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta T_{\text{cal}} \quad \text{Calorimetry Equation 2} \quad (3.15)$$

Almost all of the heat that is absorbed by the calorimeter is absorbed by the water, so we can make the following approximation:

$$C_{\text{cal}} \approx m_{\text{water}}s_{\text{water}}$$

Substitution of the above into Calorimetry Equation 2 yields a commonly used approximation that relates the heat of reaction to the mass and temperature change of the water in the calorimeter.

$$q_{\text{rxn}} = -m_{\text{water}}s_{\text{water}}\Delta T_{\text{water}} \quad \text{Calorimetry Equation 3} \quad (3.16)$$

### 3.9-3. Using a Calorimeter Exercise

#### **EXERCISE 3.21:**

When the reaction in the simulation online is the reaction of 0.0225 mol X, the temperature of the 50.0 g of water rises from 22.5 °C to 26.4 °C and there is no volume change.

A video or simulation is available online.

The reaction is \_\_\_\_\_.  
exothermic  
endothermic

$$\Delta T_{\text{water}} = \text{_____ } ^\circ\text{C}$$

$$s_{\text{water}} = 4.18 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$$

$$q_{\text{cal}} = \text{_____ } \text{J}$$

$$q_{\text{rxn}} = \text{_____ } \text{J}$$

$$\Delta H = \text{_____ } \text{kJ/mol}$$



### 3.9-4. Determining Specific Heat Exercise

#### **EXERCISE 3.22:**

9.0 g of Al at 100.0 °C are placed in 20.0 mL of water at 20.0 °C contained in a Styrofoam cup. At thermal equilibrium, the temperature of the water and aluminum is 27.1 °C. What is the specific heat of aluminum?

The heat absorbed by the water:

$$m_{\text{water}} = \text{_____ g}$$

$$s_{\text{water}} = 4.18 \text{ J}\cdot\text{g}^{-1}\cdot\text{°C}^{-1}$$

$$\Delta T_{\text{water}} = \text{_____ °C}$$

$$q_{\text{water}} = \text{_____ J}$$

The specific heat of Al:

$$q_{\text{Al}} = \text{_____ J}$$

$$m_{\text{Al}} = \text{_____ g}$$

$$\Delta T_{\text{Al}} = \text{_____ °C}$$

$$s_{\text{Al}} = \text{_____ J}\cdot\text{g}^{-1}\cdot\text{°C}^{-1}$$

### 3.9-5. Energy or Enthalpy

The heat of reaction determined in a bomb calorimeter is  $\Delta E$ , but the heat determined in an open calorimeter is  $\Delta H$ .

The state function assigned to  $q_{\text{rxn}}$  depends upon how the reaction is carried out.

- No gases are involved in the reaction or the number of moles of gas does not change. Under these conditions, no  $P\Delta V$  work can be done. This is the case in most reactions that occur in solution.
  - $q_{\text{rxn}} = \Delta E = \Delta H$
- The number of moles of gas does change. Under these conditions, some  $P\Delta V$  work can be done.
  - **at constant pressure:**  $q_{\text{rxn}} = \Delta H$  because  $P\Delta V$  work can be done. Any reaction open to the atmosphere or carried out in a piston/cylinder is carried out at constant pressure.
  - **at constant volume:**  $q_{\text{rxn}} = \Delta E$  because no  $P\Delta V$  work can be done. This is the case in a **bomb calorimeter**, where the reaction is carried out in a steel vessel with a cap that is screwed on so no volume change (no work) can take place.

### 3.9-6. Bomb Calorimeter Exercise

#### **EXERCISE 3.23:**

What temperature rise would occur in a bomb calorimeter with a heat capacity of 4.877 kJ/°C when 0.00750 mol C<sub>4</sub>H<sub>10</sub> is burned at 25 °C?

First, decide which thermodynamic property should be used to determine  $q_{\text{rxn}}$ .

$$\Delta H_{\text{comb}} = -2856 \text{ kJ/mol}$$

$$\Delta E_{\text{comb}} = -2847 \text{ kJ/mol}$$

Next, determine  $q_{\text{rxn}}$  for the combustion of 0.00750 mol C<sub>4</sub>H<sub>10</sub>.

$$q_{\text{rxn}} = \text{_____ kJ}$$

Finally, solve Equation 3.15 for  $\Delta T$ .

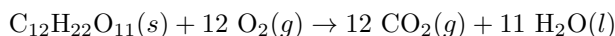
$$\Delta T = \text{_____ °C}$$

### 3.9-7. Heat of Formation from Calorimetry Exercise

#### **EXERCISE 3.24:**

Combustion of 1.00 g of sucrose ( $C_{12}H_{22}O_{11}$ ) causes the temperature in a bomb calorimeter with a heat capacity of  $4.90 \text{ kJ}/^\circ\text{C}$  to rise from  $24.92$  to  $28.33$   $^\circ\text{C}$ . What is the standard heat of formation of sucrose? The heats of formation of  $CO_2(g)$  and  $H_2O(l)$  are  $-393.5 \text{ kJ/mol}$  and  $-285.8 \text{ kJ/mol}$ , respectively.

The combustion reaction:



heat of reaction in calorimeter  $q_{\text{rxn}} = \text{_____ kJ}$

moles of sucrose reacting  $n = \text{_____ mol } C_{12}H_{22}O_{11}$

energy change for combustion (reaction is carried out in a bomb)  $\Delta E_{\text{comb}} = \text{_____ kJ/mol}$

change in number of moles of gas in balanced equation  $\Delta n_g = \text{_____ mol}$

heat of combustion of sucrose  $\Delta H_{\text{comb}} = \text{_____ kJ/mol}$

heat of formation of sucrose  $\Delta H_{\text{comb}} = \text{_____ kJ/mol}$

## 3.10 Combustion: Food as Fuel

### Introduction

The energy that is derived from the metabolism of carbohydrates and fats is essentially the same as is produced by their combustion in a calorimeter. Thus, the calorie content used in nutrition is the same as that derived from calorimetry.

#### 3.10-1. Nutrition Labels

In the last example of the previous section, we showed that the heat of combustion of 1 g of  $C_{12}H_{22}O_{11}$ , a carbohydrate, is 17 kJ. Indeed, the heat of combustion of most carbohydrates is 17 kJ/g. The heats of combustion of proteins are also 17 kJ/g, while those of fats are 38 kJ/g. These are approximately the same values derived from their metabolism in the body.

A dietary calorie (Cal, upper case "C") is actually a kcal of energy and  $1 \text{ kcal} = 4.18 \text{ kJ}$ . We can summarize the heats of combustion as follows:

Substance	$\Delta H_{\text{comb}}$ (kJ/g)	$\Delta H_{\text{comb}}$ (Cal/g)
carbohydrates	17	4
proteins	17	4
fats	38	9

Table 3.5

### 3.10-2. Nutrition Label Exercise

**EXERCISE 3.25:**

Use the heats of combustion given above to determine the number of calories derived from each substance and the total number of calories in one serving of a can of soup with the following nutrition information on one serving.

- Total Fat 1 g
- Total Carbohydrates 31 g
- Total Protein 7 g

Calories from Fat \_\_\_\_\_ Cal

Calories from Carbohydrates \_\_\_\_\_ Cal

Calories from Protein \_\_\_\_\_ Cal

Total Calories \_\_\_\_\_ Cal

### 3.11 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.