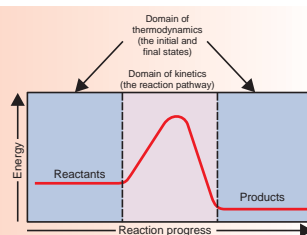


UNIT 3



Introduction to Chemical Thermodynamics

Unit Outcomes

After completing this unit, you will be able to:

- *understand the terms system, open system, closed system and isolated system, spontaneous process, state and path function, intensive and extensive property, internal energy, heat and work;*
- *understand the first and second laws of thermodynamics;*
- *compare the energy change observed when chemical bonds are formed and broken, and relate these changes to endothermic and exothermic reactions;*
- *identify ways in which the terms reactant, product, and heat are combined to form thermodynamic equations representing endothermic and exothermic chemical change;*
- *understand concepts such as enthalpy change, entropy change and free-energy changes;*
- *determine the spontaneity of a given reaction; and*
- *demonstrate scientific enquiry skills including: communicating, measuring, applying concepts and asking questions.*



MAIN CONTENTS

- 3.1 Common Thermodynamic Terms
- 3.2 The First Law of Thermodynamics and Some Thermodynamic Quantities
- 3.3 Thermochemistry
- 3.4 Entropy and the Second Law of Thermodynamics
 - Unit Summary
 - Review Exercises

Start-up Activity

Form a group and discuss the following issues:

How do you describe the following in relation to energy? How do they benefit the society? Which of them are widely used in Ethiopia?

1. Fuels such as oil, wood, coal and natural gas.
2. Fertilizers.
3. Plastics, fiber glass and ceramic materials.
4. Solar energy.
5. Hydroelectric power.

Write a short report and present it to the class.

In Grade 11 Chemistry, you learned about chemical kinetics. What are the main concerns of chemical kinetics? How do you relate it to thermodynamics?

Thermodynamics is the study of energy and its transformation. In a chemical reaction, thermodynamics determines whether a reaction is possible and how much product can be formed.

Thermodynamics deals with energy changes and applies to physical as well as chemical changes. However, it does not give any information about the duration of time required for the related processes. *Which area of chemistry is concerned with that topic?*

Figure 3.1 depicts the concern of chemical kinetics and chemical thermodynamics.

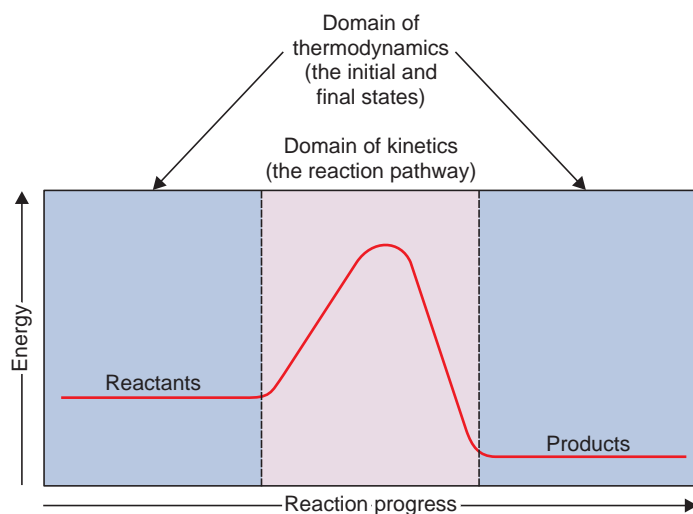


Figure 3.1 Concerns of kinetics and thermodynamics.

Activity 3.1



Read chemistry books and other resource materials, and define the following terms:

- | | |
|----------------------|---------------------|
| a thermodynamics | g equation of state |
| b system | h heat capacity |
| c surroundings | i specific heat |
| d isothermal process | j state function |
| e adiabatic process | k state variable |
| f state | |

Try to explain these terms verbally to your classmates.

3.1 COMMON THERMODYNAMIC TERMS

At the end of this topic, you will be able to:

- define chemical thermodynamics;
- define system;
- give examples of system;
- explain open, closed and isolated systems;
- classify system as open, closed and isolated;



- define state function and path function;
- distinguish between intensive and extensive properties; and
- define spontaneous and non-spontaneous process.

When we study a set of energy changes, we focus our attention on a limited and well-defined part of the universe. In your discussion of **Activity 3.1**, have you recognized that we are considering systems? A thermodynamic system may be a solution in a beaker, a gas in a cylinder, a reaction vessel, an engine, an electrochemical cell, a biological cell, etc.

What do you call the rest of the universe outside a system? Because energy is neither created nor destroyed, any gain or loss of energy by a system must be accompanied by an equivalent loss or gain of energy in the surroundings.

There are three types of thermodynamic systems based on the boundary between the system and its surroundings.

An open system – is a system that can exchange mass and energy, usually in the form of heat, with its surroundings.

For example, an open system may consist of a quantity of water in an open container, as shown in **Figure 3.2 a**.

A closed system – is a system which transfers energy, but not mass across its boundary with its surroundings. If you close the flask, as in **Figure 3.2 b**, so that no water vapor can escape from or condense into the container, you create a closed system.

An isolated system – is a system in which neither the transfer of mass nor that of energy takes place across its boundary with the surroundings. By placing the water in a totally insulated container, as shown in **Figure 3.2 c**, we construct an isolated system.

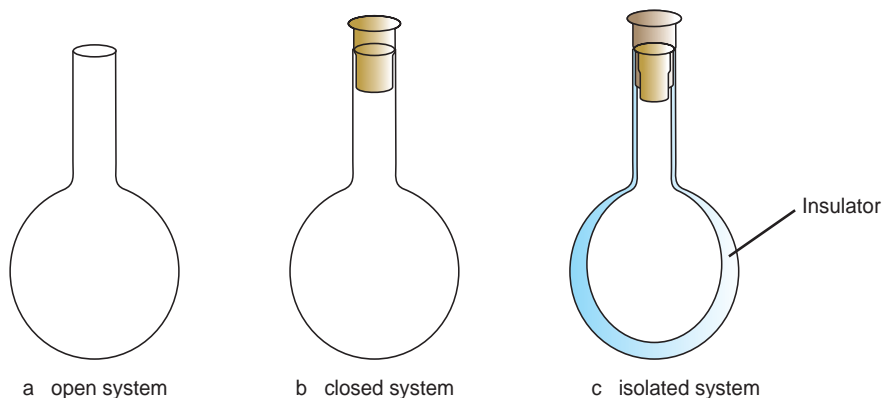


Figure 3.2 The three classes of system.

A system is said to be in a certain state if T, P, V, n (*observable variables*) do not change with time. An equation that relates these observable variables is called an equation of state. An ideal-gas equation is an example of equation of state. A thermodynamic function (*expressed in quantity*) that depends on the initial and final state of a system, regardless of how that condition was achieved, is called a *state function*. Examples are energy, volume, pressure, etc. Functions that depend on the path are *path functions*. Examples are heat, work, etc.

The properties of a system can be **intensive** or **extensive** based on its dependence on amount of a substance.

Intensive properties are those that do not depend on the amount of matter present. Some examples include colour, temperature and density.

Extensive properties are those properties, that depend on the amount of matter, for example, mass, internal energy, volume, and pressure.

Activity 3.2



In your group list properties of a system you know. Classify them as intensive or extensive. Record your conclusions by copying and filling out the following table. Follow the example that is given in the first line of the tabulation.

Properties	Intensive	Extensive
Colour	✓	

A **spontaneous process** is a process that occurs without external influence. Once started, requires no action from outside in order to continue. On the other hand, a **non-spontaneous** process will not occur unless some external action is continuously applied.

A rock that is rolling down from the top of a hill continues to roll down. Heat flows from an object of high temperature to an object of low temperature. Iron rusts in moist air. Each of these processes occurs spontaneously, without requiring an outside force or agency. If these processes were to go in the opposite direction, they would be non spontaneous.

Can you mention some other examples of spontaneous and nonspontaneous processes you encounter in your daily life?



An **isothermal process** is a process in which temperature remains constant, $\Delta T = 0$. This typically occurs when a system in contact with an outside thermal reservoir (*heat bath*), and the change occurs slowly enough to allow the system to continually adjust to the temperature of the reservoir through heat exchange.

An alternative special case in which a system exchanges no heat with the surroundings ($\Delta q = 0$) is called an **adiabatic process**. In an isothermal process, the value of $\Delta T = 0$ but $\Delta q \neq 0$, while in an adiabatic process, $\Delta T \neq 0$ but $\Delta q = 0$.

3.2 THE FIRST LAW OF THERMODYNAMICS AND SOME THERMODYNAMIC QUANTITIES

At the end of this topic, you will be able to:

- explain internal energy in relation to the concepts of thermodynamics;
- explain heat in relation to the concepts of thermodynamics;
- explain work in relation to the concepts of thermodynamics;
- state the first law of thermodynamics;
- explain the first law of thermodynamics; and
- calculate the change in the internal energy of a system based on a given information.

3.2.1 Internal Energy (E)

Activity 3.3



If you have pumped air into a bicycle tyre, you probably noticed a warming effect in the valve stem. Discuss in a group from where this heat is originated and write a short report and present to the class.

The internal energy (E) of a system is the total energy contained within a system, partly as kinetic energy and partly as potential energy. When a chemical system changes from reactants to products and the product return to the starting reactant, the internal energy has changed. To determine this change, ΔE , we measure the difference between the systems internal energy after the change (E_{final}) and before the change (E_{initial}).

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

The kinetic energy component of internal energy consists of various types of molecular motion and the movement of electrons within molecules.

Potential energy is a factor of:

- * attractive and repulsive interaction between molecules;
- * attractive interactions between electrons and nuclei within molecules;
- * repulsive interactions between electrons within molecules; and
- * repulsive interactions between nuclei within molecule.

Activity 3.4



Take ordinary electric bulbs of 100 W, and 150 W; put separate white papers (of equal size and weight) above the bulbs; after noting the initial temperature of the paper, switch the bulbs on. Note the temperature of the papers after 15 minutes and 30 minutes respectively. Do you observe any change in temperature of the papers? Discuss the results with your classmates.

3.2.2 Heat (Q)

Heat (*thermal energy*) is the energy transferred between a system and its surroundings as a result of a difference in their temperatures. Heat passes spontaneously from the region of higher temperature to the region of lower temperature. Heat transfer stops when the system and surroundings reach the same temperature and therefore the system and surroundings are at **thermal equilibrium**.

Heat and Calorimetry

A chemical reaction or a physical change that releases heat is said to be an **exothermic process**. The burning of charcoal, for example, is an exothermic process. A reaction or a physical change that absorbs heat is an **endothermic process**. The melting of ice is an endothermic process, because heat is absorbed when ice melts. The SI unit of heat is joule (J). Another unit of heat is calorie. A calorie (Cal) is the amount of heat, or other energy, necessary to raise the temperature of 1 g of water by 1 degree Celsius. A kilocalorie (kCal) is 1000 calories, and 4.184 Joules is equivalent to 1.0 calorie.

Experimentally, we can determine the heat flow associated with chemical reaction by measuring the temperature change it produces. The measurement of heat flow is called **calorimetry**. An apparatus that measures heat is called a **calorimeter**.



The temperature change experienced by an object when it absorbs a certain amount of energy is determined by its **heat capacity**. Heat capacity is defined as the amount of heat energy required to raise its temperature by 1° (or 1 K). For pure substances, heat capacity is usually given for a specified amount of the substance. The heat capacity of 1 mol of a substance is called its **molar heat capacity**. In all thermodynamic calculations temperature must be expressed in Kelvin (K).

The heat capacity of 1 g of a substance is called its **specific heat**. Specific heat of a substance can be determined experimentally by measuring the temperature change (ΔT) for a known mass (m) of a substance that gains or loses a specific quantity of heat, q .

$$\begin{aligned}\text{Specific heat} &= \frac{\text{quantity of heat transferred}}{(\text{grams of substance}) \times (\text{temperature change})} \\ &= \frac{q}{m \times \Delta T}\end{aligned}$$

Table 3.1 shows the specific heat of some common substances.

Table 3.1 The specific heat of some common substances.

Substance	Specific heat [$\text{Jg}^{-1}\text{K}^{-1}$]
Aluminum, Al (s)	0.90
Gold, Au (s)	0.13
Carbon (<i>graphite</i>)	0.72
Carbon (<i>diamond</i>)	0.50
Copper, Cu (s)	0.38
Iron, Fe (s)	0.45
Mercury, Hg (l)	0.14
Water, H_2O (l)	4.18
Ethanol, $\text{C}_2\text{H}_5\text{OH}$ (l)	2.46

Example 3.1

A 466 g sample of water is heated from 8.5°C to 74.6°C. Calculate the amount of heat absorbed by the water in kilojoules.

Solution:

We know the quantity of water and the specific heat of water (4.18 J/g.K). On applying the equation:

$$\text{Specific heat} = \frac{q}{m \times \Delta T}$$

$$4.18 \text{ J/g}\cdot\text{K} = \frac{q}{466 \text{ g} \times (347.60 \text{ K} - 281.5 \text{ K})}$$

$$q = 4.18 \text{ J/g}\cdot\text{K} \times 466 \text{ g} \times 66.1 \text{ K} = 129 \text{ kJ}$$

Exercise 3.1

1. How much heat is required to raise the temperature of 250 g of water from 22°C to near its boiling point, 98°C?
2. What is the molar heat capacity of water?

Activity 3.5



Take 50 mL water in two different beakers; heat one beaker to 10°C above room temperature and cool the other beaker 10°C below room temperature. Note the time taken by both the beakers to attain the room temperature. Discuss the results with your teacher.

3.2.3 Work (W)

How do you determine the pressure-volume work of a gas?

Work, like heat, is an energy transferred between a system and its surroundings. There are several types of work, but here we will consider only the pressure-volume work that is done when gases are compressed or expanded.

Suppose we have a gas confined to a cylindrical container that is fitted with a movable piston as shown in **Figure 3.3**, where F is the force acting on the piston of area A . Since

pressure is defined as force per unit area, the pressure of the gas is $P = \frac{F}{A}$.

Work is defined as a force applied over a given distance, so if the piston moves a distance Δh , as shown in **Figure 3.3**, then the magnitude of the work is

$$\text{Work} = \text{force} \times \text{distance} = F \times \Delta h$$

Since $P = \frac{F}{A}$, or $F = P \times A$, then

$$\text{Work} = F \times \Delta h = P \times A \times \Delta h$$

The product of the cross-sectional area of the cylinder, A , and the height, Δh , represents the change in volume of the gas, which is designated by the symbol ΔV . By replacing $A \times \Delta h$ with its equivalent, ΔV , we see that the work associated with a gas that expands at constant pressure is described by the following equation.

$$\text{Work} = P \times A \times \Delta h = P\Delta V$$

The product of pressure and a change in volume is usually called “pressure-volume” work. When a gas expands, ΔV is positive, and the work is negative.

$$\text{Work (} W \text{)} = - P\Delta V$$

A negative quantity of work signifies that the system loses energy, and that this, energy is transferred from the system to the surroundings.

When a gas is compressed by its surroundings, ΔV is negative, the quantity of work is positive and energy is gained by the system.

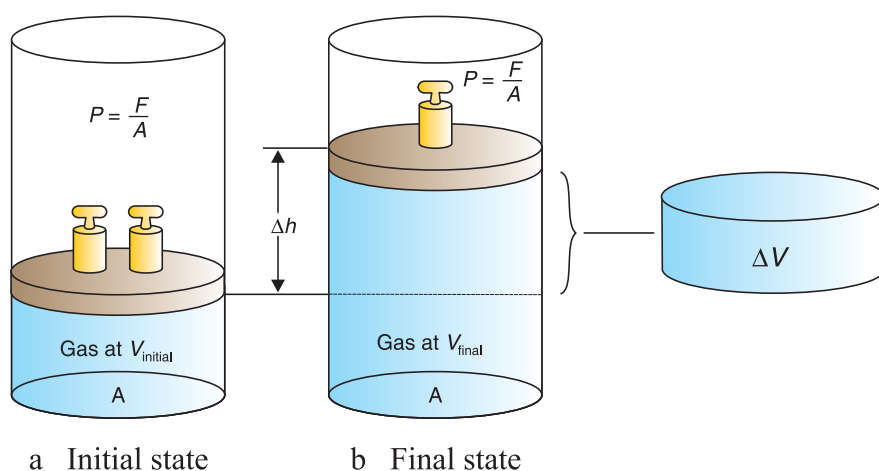


Figure 3.3 a The piston, moving a distance Δh against a pressure P , does work on the surroundings.

b Since the volume of a cylinder is the area of the base times its height, the change in volume of the gas (ΔV) is given by $A \times \Delta h$.

Activity 3.6



Observe different types of energy transformations occurring at home and around you, and make a list of these. Discuss the nature and type of transformations with your friends and present your findings in the class.

3.2.4 The First Law of Thermodynamics

What are the concepts studied in the first law of thermodynamics?

The first law of thermodynamics, which is a restatement of the law of conservation of energy, states that the total amount of energy in the universe is constant. When a system undergoes any chemical or physical change, the accompanying change in its internal energy, ΔE , is given by the heat added to the system, q , plus the work done by the system, W .

$$\Delta E = q + W$$

Thermodynamic quantities always consist of two parts:

- * a number plus units, which gives the magnitude of the change; and
- * a sign that indicates the direction of the flow.

The sign reflects the system's point of view. For example, if a quantity of energy flows into the system as heat, q is equal to $+q$, where the positive sign indicates that the system's energy is increasing. On the other hand, when energy flows out of the system as heat, q is equal to $-q$, where the negative sign indicates that the system's energy is decreasing.

This suggests that we need sign conventions to be used with the first law of thermodynamics. The conventions are as follows:

- * If heat is absorbed by the system, $q > 0$. If work is done on a system, $W > 0$.
- * If heat is given off by a system, $q < 0$. If work is done by a system, $W < 0$.

Example 3.2

A gas does 135 J of work while expanding and at the same time, it absorbs 156 J of heat. What is the change in internal energy?

Solution:

Note that heat is absorbed by the system (a positive quantity, $+156$ J) and work is done by the system (a negative quantity, -135 J). Because more heat is absorbed than work done, the internal energy increases:

$$\Delta E = q + W = (+156 \text{ J}) + (-135 \text{ J}) = +21 \text{ J}$$

Exercise 3.2

1. Calculate ΔE for a process in which the system absorbs 65 J of heat and 12 J of work is done on it by the surroundings.
2. A balloon is inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 4.00×10^6 L to 4.50×10^6 L by addition of 1.3×10^8 J of energy as heat. Assuming the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process.

3.3 THERMOCHEMISTRY

At the end of this topic, you will be able to:

- define enthalpy change, ΔH ;
- derive an expression for the enthalpy change of an ideal gas, based on the first law of thermodynamics;
- calculate enthalpy change for ideal gases, from a given information;
- define standard state;
- define standard molar enthalpy of combustion, ΔH_c° ;
- describe how heats of combustion can be used to estimate the energy available from foods;
- define standard molar enthalpy of formation, ΔH_f° ;
- define standard molar enthalpy of neutralization, $\Delta H_{\text{neut}}^\circ$;
- carry out an activity to measure standard molar enthalpy of neutralization;
- state Hess's law;
- apply Hess's law to solve problems on enthalpy changes of chemical reactions;
- explain bond energy;
- calculate the bond energies of substances in a given chemical reaction; and
- calculate the standard enthalpy changes of reaction from given enthalpy changes of reactants and products.

Activity 3.7



Form a group and discuss the following questions:

Can water freeze at room temperature; why?

When ice melts at room temperature, the enthalpy decreases or increases? Explain.

Write a short report and present it to the class.

Thermochemistry is the study of energy changes that occur during chemical reactions. Usually we assess these energy changes in terms of losing and gaining energy in a system.

When we warm our cold hands over a campfire, the burning wood gives off energy *as heat* and our hands gain energy, raising their temperature.

3.3.1 Heats of Reactions

In the first law of thermodynamics, you have learned that,

$$\Delta E = q + p\Delta V$$

If a reaction occurs at constant volume, then $\Delta V = 0$ and no pressure-volume work is done. Thus, $\Delta E = (q)_V$. Where the subscript V indicates a constant-volume process.

Constant volume conditions are often inconvenient, and sometimes impossible, to measure.

What is enthalpy?

Most physical and chemical changes, including those in living systems, take place under the constant pressure of the earth's atmosphere. In the laboratory, for example, reactions are generally carried out in containers that are open to the atmosphere, such as beakers and test tubes. For most processes, especially those that do not involve gases, only small amount of work is performed as the system expands or contracts slightly against the pressure of the atmosphere. Thus, most of the energy gained or lost by the system during these processes is in the form of heat. The heat absorbed or released by a system at constant pressure is called enthalpy (H).

Enthalpy is defined as the sum of the internal energy and the pressure-volume product of a system.

$$H = E + PV$$

or $\Delta H = \Delta E + P\Delta V$ (at constant pressure)

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

then $\Delta H = q - P\Delta V + P\Delta V$

$$\Delta H = (q)_p$$

Thus, the change in enthalpy equals the heat gained or lost at constant pressure.

What is the relationship between ΔH and ΔE ?

In case of an ideal gas, we can express change in enthalpy, using the ideal-gas law:

$$PV = nRT$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + \Delta(nRT)$$

If the temperature is constant

$$\Delta H = \Delta E + \Delta nRT$$

or
$$\Delta E = \Delta H - \Delta nRT$$

where $\Delta n = \sum n_p - \sum n_r$ of the gaseous substances.

Example 3.3

Calculate the change in enthalpy when 2 moles of CO is converted to 2 moles of CO₂ at 1 atm and 25°C.



Solution:

Given T = 25°C = 298 K

$$\Delta E = -563.5 \text{ kJ}$$

$$\begin{aligned} \Delta n &= \text{number of moles of gaseous products} - \text{number of moles of gaseous reactants} \\ &= 2 - 3 = -1 \end{aligned}$$

$$R = 0.082 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = 8.314 \text{ J/mol} \cdot \text{K}$$

$$\begin{aligned} \Delta H &= \Delta E + \Delta nRT \\ &= -563.5 \text{ kJ} + (8.314 \text{ J/mol} \cdot \text{K} \times 298 \text{ K} \times -1 \text{ mol}) \\ &= -563.5 \text{ kJ} - (8.314 \times 298) \text{ J} \\ &= -563.5 \text{ kJ} - 2477.6 \text{ J} \\ &= -563.5 \text{ kJ} - 2.5 \text{ kJ} \\ &= -566.0 \text{ kJ} \end{aligned}$$

Is there a significant difference between the values of ΔH and ΔE ?

Note that if a physical process or reaction occurs under constant-volume conditions, then the heat change, $(q)_v$, is equal to ΔE . On the other hand, when a physical process or reaction is carried out at constant pressure, the heat change, $(q)_p$, is equal to ΔH .

Consider the combustion of methane:



We say that the enthalpy change in the combustion of 1 mol CH₄(g) at 25°C is 890.3 kJ. The negative value of ΔH shows that the combustion of methane at constant pressure is an exothermic reaction.

Some Properties of Enthalpy

1. Enthalpy is an extensive property. The enthalpy of a system depends on the quantities of substances present. Consider the formation of ammonia from nitrogen and hydrogen;



It is found experimentally that -45.9 kJ of heat is produced when $\frac{1}{2}$ mole of nitrogen reacts with $\frac{3}{2}$ moles of hydrogen to produce 1 mole of ammonia at constant pressure system.

1 mole of nitrogen reacts with 3 moles of hydrogen to form 2 moles of NH_3 and -91.8 kJ of heat is produced.

2. The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction. For example, if we assume for the reverse reaction of the formation of ammonia (forward reaction for decomposition of ammonia):

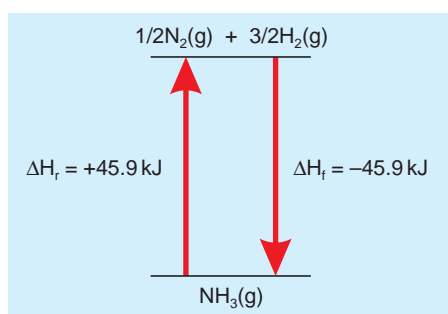


Figure 3.4 Reversing a reaction changes the sign but not the magnitude of the enthalpy change: $\Delta H_r = -\Delta H_f$.

3. The enthalpy change for a reaction depends on the state of the reactants and the products. If the product in the combustion of methane were gaseous H_2O instead of liquid H_2O , ΔH would be -802 kJ instead of -890.3 kJ . This is due to the absorption of 88 kJ of heat when 2 mol of liquid water is changed to gaseous water.



Therefore, the states of the reactants and products must be specified.

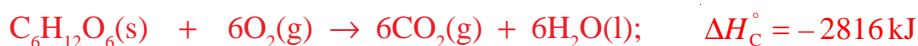


3.3.2 Standard States

Is there any difference between standard states of ideal gases and standard states of thermodynamic properties?

The **standard state** for a substance is the most stable form at temperature of 25°C and at atmospheric pressure of 1 atm. We can define the standard enthalpy of combustion, ΔH_c° , as the change in enthalpy that accompanies the combustion of 1 mole of a substance in oxygen at standard conditions. Most chemical reactions that produce heat are combustion reactions. The food we eat is combusted in our bodies in order to give us energy. Most of the energy our bodies need comes from carbohydrates and fats. Carbohydrates are decomposed in the intestines into glucose, $C_6H_{12}O_6$.

Glucose is soluble in blood and is known as blood sugar. It is transported by the blood to cells, where it reacts with O_2 in a series of steps, eventually producing $CO_2(g)$, $H_2O(l)$, and energy.



The breakdown of carbohydrates is rapid, so their energy is quickly supplied to the body.

Standard Enthalpies of Formation

The standard enthalpy of formation, ΔH_f° , is the change in enthalpy in the reaction when one mole of a substance is formed from the elements in their standard states. By definition, the standard enthalpy of formation of the most stable form of any element is zero.

Table 3.2 Standard enthalpies of formation, ΔH_f° , of some substances at 25°C.

Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7
Ammonia	$NH_3(g)$	- 46.11
Benzene	$C_6H_6(l)$	48.99
Calcium carbonate	$CaCO_3(s)$	- 1207.1
Calcium oxide	$CaO(s)$	- 635.5
Carbon dioxide	$CO_2(g)$	- 393.5
Diamond	$C(s)$	1.88
Ethane	$C_2H_6(g)$	- 84.68
Ethanol	$C_2H_5OH(l)$	- 277.7
Ethylene	$C_2H_4(g)$	52.26
Glucose	$C_6H_{12}O_6(s)$	- 1260

Substance	Formula	ΔH_f° (kJ/mol)
Hydrogen bromide	HBr(g)	- 36.23
Hydrogen chloride	HCl(g)	- 92.30
Hydrogen fluoride	HF(g)	- 271.1
Hydrogen iodide	HI(g)	26.48
Methane	CH ₄ (g)	- 74.85
Methanol	CH ₃ OH(l)	- 238.6
Nitric oxide	NO(g)	90.25
Nitrous oxide	N ₂ O(g)	82.05
Nitrogen dioxide	NO ₂ (g)	33.18
Propane	C ₃ H ₈ (g)	- 103.85
Silver chloride	AgCl(s)	- 127.0
Sodium bicarbonate	NaHCO ₃ (s)	- 947.7
Sodium carbonate	Na ₂ CO ₃ (s)	- 1130.9
Sodium chloride	NaCl(s)	- 441.0
Sulfur dioxide	SO ₂ (g)	- 296.8
Sulfur trioxide	SO ₃ (g)	- 395.7
Water	H ₂ O(l)	- 285.8
Water vapor	H ₂ O(g)	- 241.8

Now let us explore how we can use standard enthalpies of formation to determine standard enthalpy changes of chemical reactions.

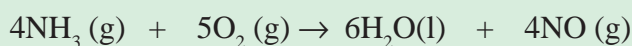
We sum the enthalpies of formation of all reaction products, taking care to multiply each molar enthalpy of formation by the coefficient of that substance in a balanced equation. From this, we subtract a similar sum of the enthalpies of formation for the reactants:

$$\Delta H_{\text{rxn}}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

where, n and m are the stoichiometric coefficients of the chemical reaction.

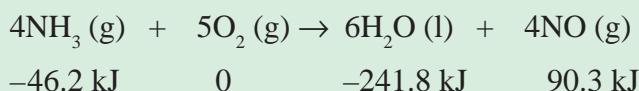
Example 3.4

The standard enthalpies of formation of NH₃, H₂O and NO are -46.2, -241.8 and 90.3 kJ/mol, respectively. Calculate the enthalpy of the reaction:



**Solution:**

The convenient way to begin this kind of calculation is to list ΔH_f° under the formula of each substance in the equation.

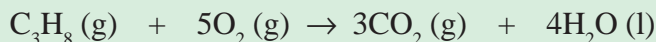


Now we can multiply these ΔH_f° values by the numbers of moles given by the coefficients in the equation. In substituting these values into the general equation for $\Delta H_{\text{rxn}}^\circ$, remember that we must subtract the sum of the terms for the reactants from the sum of the terms for products.

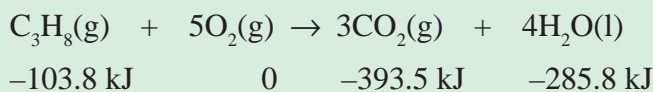
$$\begin{aligned}
 \Delta H_{\text{rxn}}^\circ &= 6[\Delta H_f^\circ(\text{H}_2\text{O})] + 4[\Delta H_f^\circ(\text{NO})] - 4[\Delta H_f^\circ(\text{NH}_3)] - 5[\Delta H_f^\circ(\text{O}_2)] \\
 &= 6(-241.8 \text{ kJ/mol}) + 4(90.3 \text{ kJ/mol}) - 4(-46.2 \text{ kJ/mol}) - 5(0 \text{ kJ/mol}) \\
 &= -1450.8 \text{ kJ} + 361.2 \text{ kJ} + 184.8 \text{ kJ} - 0 \\
 &= -904.8 \text{ kJ}
 \end{aligned}$$

Example 3.5

Calculate ΔH° for combustion of propane, C_3H_8 , from the ΔH_f° values of the products and reactants.

**Solution:**

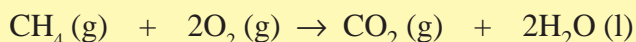
As usual, first we list ΔH_f° under the formula of each substance in the equation:



$$\begin{aligned}
 \Delta H_{\text{rxn}}^\circ &= 3(-393.5 \text{ kJ/mol}) + 4(-285.8 \text{ kJ/mol}) - (-103.8 \text{ kJ/mol}) - 5(0) \\
 &= (-2324) - (-103.8) \\
 &= -2220 \text{ kJ}
 \end{aligned}$$

Exercise 3.3

- Using the standard enthalpies of formations given in [Table 3.2](#), calculate the ΔH° for the reaction:



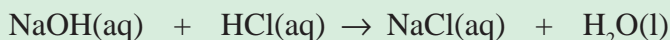
2. Compare the quantity of heat produced by combustion of 1.00 g of propane, C_3H_8 , with that produced by 1.00 g of benzene, C_6H_6 . (Hint: refer to Example 3.5, above).

The standard molar enthalpy of neutralization is the change in enthalpy, ΔH_{neut} , when one mole of an acid or a base is completely neutralized. For example, the heat of neutralization for



Example 3.6

1.00×10^2 mL of 0.5 M HCl was mixed with 1.00×10^2 mL of 0.5 M NaOH. The initial temperature of the HCl and NaOH solution was the same, i.e., 22.5°C , and the final temperature of the mixed solution was 25.86°C . Calculate the heat change for the neutralization reaction on a molar basis.



Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL, and 4.184 J/g $^\circ\text{C}$, respectively)

Solution:

Assuming no heat lost to the surroundings, $q_{\text{sys}} = q_{\text{soln}} + q_{\text{rxn}} = 0$, so $q_{\text{rxn}} = -q_{\text{soln}}$, where q_{soln} is the heat absorbed by the combined solution. Because the density of the solution is 1.00 g/mL, the mass of a 100 mL solution is 100 g. Thus

$$\text{Specific heat} = \frac{q}{m \times \Delta T}$$

$$\begin{aligned} q_{\text{soln}} &= m \times C \Delta T \\ &= (1.00 \times 10^2 \text{ g} + 1.00 \times 10^2 \text{ g}) (4.184 \text{ J/g}^\circ\text{C}) (25.86^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 2.81 \times 10^3 \text{ J} = 2.81 \text{ kJ} \end{aligned}$$

Because $q_{\text{rxn}} = -q_{\text{soln}}$, $q_{\text{rxn}} = -2.81 \text{ kJ}$

The number of moles of both HCl and NaOH in 1.00×10^2 mL solution is:

$$\frac{0.5 \text{ mol}}{1 \text{ L}} \times 0.1 \text{ L} = 0.05 \text{ mol}$$

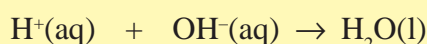
Therefore, the heat of neutralization when 1.00 moles of HCl react with 1.00

$$\text{moles of NaOH is } -\frac{2.81 \text{ kJ}}{0.05 \text{ mol}} = -56.2 \text{ kJ/mol}$$

Exercise 3.4

2.00×10^2 mL of 0.862 M HCl is mixed with 2.00×10^2 mL of 0.431 M Ba(OH)₂ in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and Ba(OH)₂ solution is the same, at 20.48°C.

For the process

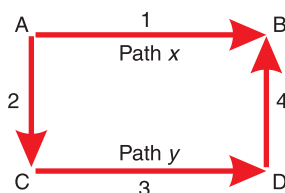


the heat of neutralization is -56.2 kJ/mol. What is the final temperature of the mixed solution?

3.3.3 Hess's Law

Hess's law states that if different processes are used to bring about the same change the enthalpy changes during these processes are the same.

Consider the following cycle, in which Path x from step A \rightarrow B, represents one process, and path y represents second process through three steps: A \rightarrow C, C \rightarrow D, and D \rightarrow B. Both paths result in the same change.



$$\Delta H_1 = H_B - H_A$$

If we know how to calculate the enthalpy from A to C, from C to D, and from D to B, then we can calculate the enthalpy from A to B for path x. This is possible because enthalpy is a state function. By definition,

$$\Delta H_2 = H_C - H_A$$

$$\Delta H_3 = H_D - H_C$$

$$\Delta H_4 = H_B - H_D$$

According to **Hess's Law**, if we add up ΔH_2 , ΔH_3 and ΔH_4 , we get:

$$\Delta H_2 + \Delta H_3 + \Delta H_4 = (H_C - H_A) + (H_D - H_C) + (H_B - H_D) = H_B - H_A = \Delta H_1$$

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

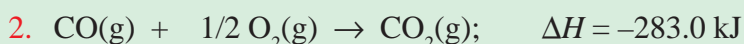
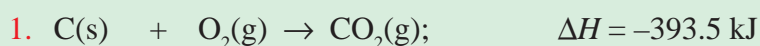
This shows that the change in the heat of a reaction is constant, whether the reaction is carried out directly in one step or through a number of steps.

To apply Hess's law, you can generally expect to do the following.

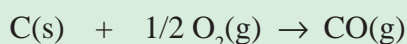
Reverse certain equations and change the signs of their ΔH values. Multiply certain quantities and their ΔH values by appropriate factors. The factors may be whole numbers or fractions.

Example 3.7

The enthalpies of combustions, of C to CO_2 and CO to CO_2 are -393.5 kJ/mol and -283.0 kJ/mol , respectively.



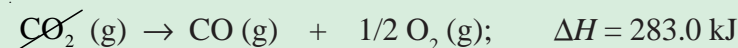
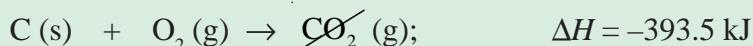
Using these data, calculate the enthalpy of combustion of C to CO.



Solution:

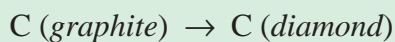
To apply **Hess's Law**, we need to arrange the above equations, (Equation (1) and equation (2)) so that C(s) on the reactant side and CO(g) on the product side of the arrow are the same, as we can see in the target equation.

To do this, we need to reverse *equation (2)* so that CO(g) is a product. Remember that when reactions are reversed, the sign of ΔH is also reversed. We arrange the two equations so that they can be added to give the target equation:

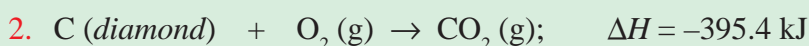
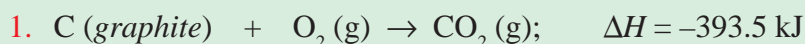


Example 3.8

Calculate the enthalpy for the following reaction:

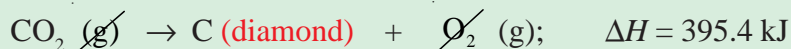
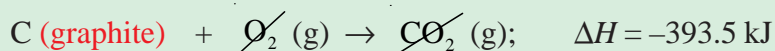


Given the data:

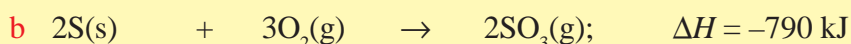
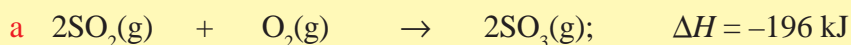


Solution:

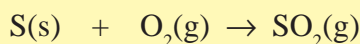
To get the target equation C (graphite) \rightarrow C (diamond) from equation (1) and (2), we reverse equation (2) and add to equation (1).

**Exercise 3.5**

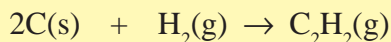
1. From the following enthalpies of reaction:



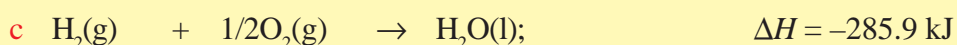
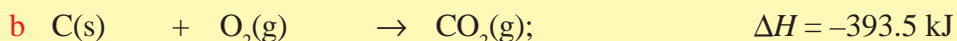
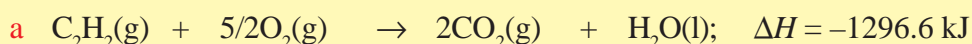
Calculate the enthalpy change for the reaction:



2. Calculate ΔH for the reaction:



Given the following reactions and their respective enthalpy changes:

**3.3.4 Bond Energies**

Why is bond energy defined only for gases?

Bond energy is the enthalpy required to break a particular bond in 1 mole of gaseous molecules. This energy is generally expressed in kilojoules per mole of bonds (kJ/mol).

It is easy to understand bond-dissociation energy (D) for diatomic molecules because there is only one bond (single, double or triple) per molecule. We can represent bond-dissociation energy as an enthalpy change or a heat of reaction. The enthalpy change for the reverse reaction, which is bond formation, is the negative of the bond-dissociation energy. For example





Notice that the bond energy is always a positive quantity; energy is always required to break chemical bonds. Conversely, energy is released when a bond forms between two gaseous atoms or molecular fragments. Of course, the greater the bond energy, the stronger the bond.

Calculations Involving Bond Energies

How do we apply bond energies to calculate ΔH ?

For chemists, reactions involve the breaking and remaking of bonds. So, we can imagine a process in which we break all the reactant molecules into their respective atoms, and then recombine the atoms in the way we want. In other words the process we follow is:



The enthalpy of the reaction is estimated as the total energy required to break the bonds minus the total bond energies of the new bonds formed.

$$\Delta H = \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed})$$

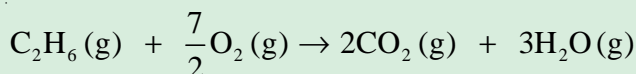
Table 3.3 Average bond energies of some substances (kJ/mol).

Bond	Bond Energy	Bond	Bond Energy
H—H	436	N—H	389
H—F	565	N—N	163
H—Cl	427	N—O	201
H—Br	366	N—F	272
H—I	295	N—Br	243
C—H	413	N—I	159
C—C	348	O—H	463
C—N	305	O—F	190
C—O	358	O—Cl	203
C—F	485	O—I	234
C—Cl	328	F—F	155
C—Br	276	Cl—F	253
C—I	240	Br—Br	193
Multiple bonds			
C=C	614	N=N	418
C≡C	839	N=O	607
C≡N	615	O=O	498
C=O	799	N≡N	945
C≡O	1072		



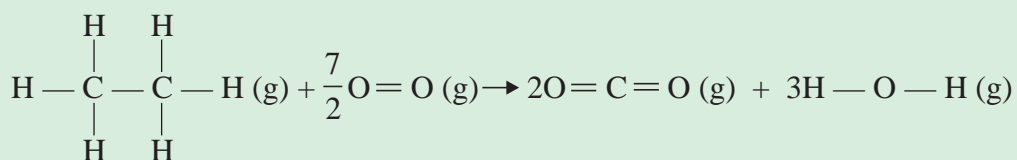
Example 3.9

Estimate ΔH for the following reaction:



Solution:

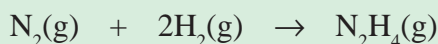
Among the reactants, we must break six C – H bonds and one C – C bond in C_2H_6 . We also break $\frac{7}{2}\text{O} = \text{O}$ bonds. Among the products, we form four C = O bonds (two in each CO_2) and six O – H bonds (two in each H_2O). We may rewrite the equation, using Lewis structures of each substance involved in the reaction.



$$\begin{aligned} \Delta H &= \left(6(\text{C} - \text{H}) + (\text{C} - \text{C}) + \frac{7}{2}(\text{O} = \text{O}) \right) - \left(4(\text{C} = \text{O}) + 6(\text{H} - \text{O}) \right) \\ &= 6(413 \text{ kJ}) + 348 \text{ kJ/mol} + \frac{7}{2}(498 \text{ kJ/mol}) - 4(799 \text{ kJ/mol}) - 6(463 \text{ kJ/mol}) \\ &= 4558 \text{ kJ/mol} - 5974 \text{ kJ/mol} = -1416 \text{ kJ/mol} \end{aligned}$$

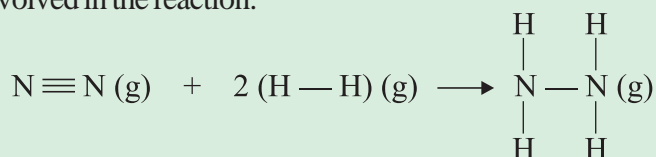
Example 3.10

Estimate the enthalpy of the formation of gaseous hydrazine, $\text{N}_2\text{H}_4(\text{g})$



Solution:

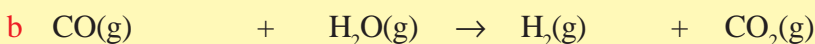
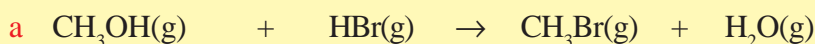
To know the bond energies, we need to write a Lewis structure for each substance involved in the reaction.



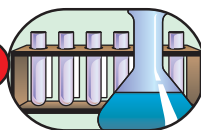
$$\begin{aligned} \Delta H &= 945 \text{ kJ} + 2(436 \text{ kJ}) - 4(389 \text{ kJ}) - 163 \text{ kJ} \\ &= 1818 \text{ kJ} - 1719 \text{ kJ} \\ &= 99 \text{ kJ} \end{aligned}$$

Exercise 3.6

Using bond energies given in Table 3.3, estimate ΔH for each of the following gas-phase reactions.



Experiment 3.1



Measuring the standard molar enthalpy of neutralization

Objective: To measure the standard molar enthalpy of the neutralization of sodium hydroxide and hydrochloric acid.

Apparatus: Plastic cup, beaker, thermometer, measuring cylinder, cotton wool.

Chemicals: Sodium hydroxide, hydrochloric acid.

Procedure:

1. Measure 50 mL of 1M NaOH solution and put it in the plastic cup. Measure its initial temperature and record it.
2. Add 50 mL of 1 M HCl to the beaker containing 50 mL of 1 M NaOH and stir the solution with the thermometer. Record the maximum temperature of the mixture.

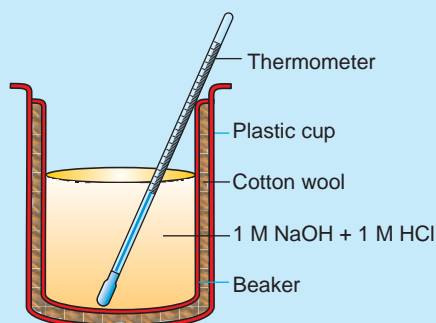


Figure 3.5 Apparatus to measure standard molar enthalpy of neutralization.

3. Record the temperature as follows:

Initial temperature of NaOH

Temperature of the mixture of NaOH and HCl

Change in temperature, $\Delta T =$



4. The total mass of the solution is 100 g (100 mL), and the specific heat of the solution is

[Given: Specific heat of water = 4.18 J/g.°C]

Observations and analysis:

1. Calculate the heat of neutralization.
2. Is the value obtained for the heat of neutralization larger or smaller than 57.3 kJ? Why?
3. If more acid is added after neutralization, no more rise in temperature will take place. What is the reason?

3.4 ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

At the end of this topic, you will be able to:

- explain entropy and entropy change;
- calculate entropy change, from the given standard entropies of substances;
- state the second law of thermodynamics;
- explain the second law of thermodynamics;
- calculate the entropy changes from the given enthalpy changes of the system and absolute temperature;
- explain free energy and free-energy change;
- calculate the standard free-energy change, ΔG° , from given standard free energies of reactants and products;
- describe the relationship between ΔG° , ΔH° and S° of a reaction; and
- determine the spontaneity of a given reaction.

3.4.1 Entropy and Spontaneous Process

Activity 3.8



Discuss the following issues in group and present your ideas to the class.

1. Why a ball rolls down a hill but not up?

2. Does this rolling of ball down a hill need any action from outside to occur?
3. List any process that can occur in a system by itself.
4. Decide whether the following become ordered or disordered.
 - a Solids melt to liquids.
 - b Solids or liquids vaporize to form gases.
 - c Solids or liquids dissolve in a solvent to form solutions.
 - d A chemical reaction produces more number of molecules of gases.

A **spontaneous process** (change) is a change in a system that proceeds without any outside influence on the system. For example, when we add solid salt to water, the solid dissolves without any outside influence. The dissolution is spontaneous. Liquid water freezes to ice spontaneously below 0°C ; ice melts spontaneously at 25°C . When a solution of an acid is added to a solution of a base, the hydronium ions and hydroxide ions combine spontaneously.

We know well that certain other processes don't occur by themselves. They are said to be **non-spontaneous**. For example, water does not freeze to form ice at room temperature. The iron oxide of a rusty nail does not revert to iron metal and oxygen gas, solid sodium chloride does not decompose into sodium metal and chloride gas.

A non-spontaneous process is one that cannot take place without outside influence on the system.

The fact that a process is spontaneous does not mean that it will occur at an observable rate. A spontaneous reaction may be very fast, as in the case of acid-base neutralization, or very slow, as in the case of the rusting of iron. Thermodynamics can tell us the direction and extent of a reaction, but it can say nothing about its speed. Which field of chemistry studies the rates of reactions?

What factors make a process spontaneous?

In the previous section, we have seen that the enthalpy change, ΔH , for a process is an important factor in determining whether the process is favorable. Those exothermic processes for which ΔH is very negative are frequently spontaneous. For example, enough heat to melt and ignite the metal may be produced by the spontaneous reaction of sodium with water, and the reaction is exothermic.



However, we shall see that considering only the enthalpy change of a process is not enough. The spontaneity of a process also depends on how the disorder of the system changes during the process.



Entropy and Entropy Change

Entropy (S) is the thermodynamic property of a system that is related to its degree of randomness, or disorder. The greater the randomness, or disorder, in a system, the higher is its **entropy**. Entropy is one of the most important scientific concepts.

The SI unit of entropy is JK^{-1} (Joule per Kelvin), which is the same unit as that of heat capacity. Every substance has entropy as one of its characteristic properties, just as it has colour, hardness, volume, melting point, density and enthalpy. Is entropy an intensive or extensive property?

The entropy change, ΔS , for a chemical change is equal to the sum of the entropies of the products minus the sum of the entropies of the reactants.

$$\Delta S_{\text{rxn}} = \sum mS_{(\text{product})} - \sum nS_{(\text{reactant})}$$

where m and n are the amounts of the individual species represented by their coefficients in the balanced equation. For a reaction,

$aA + bB \rightarrow cC + dD$, the entropy change is

$$\Delta S = [(c \times S_C) + (d \times S_D)] - [(a \times S_A) + (b \times S_B)]$$

where S_A is the entropy of A, S_B is the entropy of B, and so on.

- * $\Delta S > 0$ indicates an increase in randomness, or disorder, during the change.
- * $\Delta S < 0$ indicates a decrease in randomness, or an increase in order.

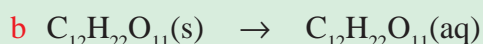
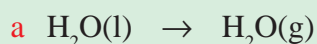
In **Activity 3.8**, in which case does the entropy increase? In which case does the entropy have a negative sign?

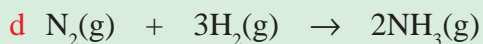
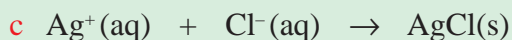
The difference between the entropy change for a process at 298 K and that same process at some other temperature is generally small and is often ignored. It is common practice to make the approximation that ΔS_{298}° equals ΔS° for the same process.

$$\Delta S_{\text{rxn}}^\circ = \sum mS_{(\text{product})}^\circ - \sum nS_{(\text{reactant})}^\circ$$

Example 3.11

Predict whether each of the following leads to an increase or decrease in the entropy.





Solution:

a The vaporization of a liquid is accompanied by an increase in volume, because the molecules are distributed throughout a much larger volume in the gaseous state than in the liquid state, an increase in disorder accompanies vaporization, thus producing an increase in entropy.

b Sucrose molecules are highly ordered in the solid state, however they are randomly distributed in aqueous solution. We predict an increase in entropy.

c In this process, the ions that are free to move about the larger volume of the solution form a solid in which the ions are confined to highly ordered positions. Thus there is a decrease in entropy.

d Four moles of gaseous reactants produce two moles of gaseous products. Because two moles of gas in a highly disorganized state of matter are lost, we predict a decrease in entropy.

Exercise 3.7

- Indicate whether each of the following reactions produces an increase or decrease in the entropy of the system, and predict whether ΔS is positive or negative in each case.
 - $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$
 - $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s})$
 - $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
 - $2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$
- Predict the sign of entropy change for each of the following processes:
 - cooling nitrogen gas from 80°C to 20°C
 - freezing liquid bromine below its melting point
 - evaporating ethanol

3.4.2 The Second Law of Thermodynamics

Activity 3.9



Write a brief paragraph on the following topic and present it to the class.

If the processes of the universe are not at equilibrium, what would be the effect of the solar energy on living things?

The connection between entropy and the spontaneity of a reaction is expressed by the **second law of thermodynamics**, which states that “*The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.*” Because the universe is made up of the system and its surroundings, the entropy change in the universe (ΔS_{univ}) for any process is the sum of the entropy changes in the system (ΔS_{sys}) and the surroundings (ΔS_{sur}).

Mathematically, we can express the second law of thermodynamics as follows:

$$\text{For a spontaneous process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$$

$$\text{For an equilibrium process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$$

For a spontaneous process, the second law says that ΔS_{univ} must be greater than zero, but it does not place a restriction on either ΔS_{sys} or ΔS_{sur} . Thus it is possible for either ΔS_{sys} or ΔS_{sur} to be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process, ΔS_{univ} is zero. In this case ΔS_{sys} and ΔS_{sur} must be equal in magnitude but opposite in sign.

Free Energy and Free Energy Change

We have seen that the spontaneity of a reaction involves two thermodynamic concepts, enthalpy and entropy. A new quantity that tells us whether a reaction will be spontaneous was first developed by the American mathematician **J. Willard Gibbs**. He proposed a new state function, now called the **Gibbs free energy**, or just free energy, designated by G .

The **Gibbs** free energy, G , is defined as

$$G = H - TS$$

where T is the absolute temperature, S is an entropy and H is an enthalpy.

For a process occurring at constant temperature, the change in free energy is given by the expression

$$\Delta G = \Delta H - T\Delta S$$

The **Gibbs** free energy change gives an unambiguous prediction of the spontaneity of a chemical reaction run at constant temperature and pressure, because it combines the effect of both ΔH and ΔS . Since temperature, T , has positive value, ΔS determines the sign of $T\Delta S$ terms, and the following can be summarized for $\Delta G = \Delta H - T\Delta S$:

- * For a change in which $\Delta H < 0$ and $\Delta S > 0$, the change in Gibbs free energy becomes less than zero ($\Delta G < 0$), and the process is spontaneous.
- * If $\Delta H > 0$ and $\Delta S < 0$, the change in Gibbs free energy becomes positive ($\Delta G > 0$), and the process is non-spontaneous.
- * If $\Delta H > 0$ and $\Delta S > 0$, ΔG may or may not be negative, but only if $\Delta H < T\Delta S$, $\Delta G < 0$.
- * If $\Delta H < 0$ and $\Delta S < 0$, $\Delta G < 0$ if $T\Delta S$ is small. This occurs at small value of temperature.
- * If ΔG is zero, the process is at equilibrium and there is no driving force tending to make the reaction go in either direction.

Table 3.4 Criterion for spontaneous change: $\Delta G = \Delta H - T\Delta S$.

Case	ΔH	ΔS	ΔG	Result	Example
1.	-	+	-	Spontaneous at all T	$2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$
2.	-	-	-	Spontaneous toward low T	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
	-	-	+	Non-spontaneous toward high T	
3.	+	+	+	Non-spontaneous toward low T	$2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
	+	+	-	Spontaneous toward high T	
4.	+	-	+	Non-spontaneous at all T	$2\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g})$

Activity 3.10



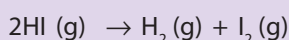
Do the following as a group assignment:

1. Given the following ΔH and ΔS values, determine the temperatures at which these reactions would be spontaneous:
 - a $\Delta H = 10.5 \text{ kJ}$; $\Delta S = 30 \text{ J/K}$



- b $\Delta H = 1.8 \text{ kJ}$; $\Delta S = 113 \text{ J/K}$
 c $\Delta H = -11.7 \text{ kJ}$; $\Delta S = -105 \text{ J/K}$

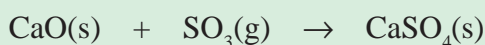
2. Consider the reaction:



- a Is $\Delta S^\circ > 0$, $\Delta S^\circ = 0$ or $\Delta S^\circ < 0$?
 b Indicate the sign of ΔG° at high and low temperature, and predict whether the reaction is spontaneous or non-spontaneous
 c What is the answer for the questions a and b if the reaction is reversed?

Example 3.12

The reaction of calcium oxide with the pollutant sulfur trioxide has been proposed as one way of removing SO_3 from burning high sulfur coal.



Using the following ΔH_f° and S_{298}° values, calculate the standard free-energy change for the reaction under standard state conditions and predict whether the reaction is spontaneous or non-spontaneous.

$$\text{CaO}(\text{s}): \quad \Delta H_f^\circ = -635.5 \text{ kJ/mol}; \quad S_{298}^\circ = 40 \text{ J/mol K}$$

$$\text{SO}_3(\text{g}): \quad \Delta H_f^\circ = -395.7 \text{ kJ/mol}; \quad S_{298}^\circ = 256.6 \text{ J/mol K}$$

$$\text{CaSO}_4(\text{s}); \quad \Delta H_f^\circ = -1432.7 \text{ kJ/mol}; \quad S_{298}^\circ = 107 \text{ J/mol K}$$

Solution:

We calculate ΔH_{298}° and S_{298}° for the reaction from the data and then calculate ΔG_{298}° from the free energy equation.

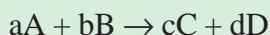
$$\begin{aligned} \Delta H_{298}^\circ &= \sum \Delta H_f^\circ(\text{product}) - \sum \Delta H_f^\circ(\text{reactant}) \\ &= \Delta H_f^\circ \text{CaSO}_4(\text{s}) - \Delta H_f^\circ \text{CaO}(\text{s}) - \Delta H_f^\circ \text{SO}_3(\text{g}) \\ &= 1 \text{ mol} (-1432.7 \text{ kJ/mol}) - 1 \text{ mol} (-635.5 \text{ kJ/mol}) - 1 \text{ mol} (395.7 \text{ kJ/mol}) \\ &= -401.5 \text{ kJ} = -401,500 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta S_{298}^\circ &= \sum S_{298}^\circ(\text{products}) - \sum S_{298}^\circ(\text{reactants}) \\ &= S_{298}^\circ \text{CaSO}_4(\text{s}) - S_{298}^\circ \text{CaO}(\text{s}) - S_{298}^\circ \text{SO}_3(\text{g}) \end{aligned}$$

$$\begin{aligned} \Delta S_{298}^\circ &= 1 \text{ mol} (107 \text{ J/mol K}) - 1 \text{ mol} (40 \text{ J/mol K}) - 1 \text{ mol} (256.6 \text{ J/mol K}) \\ &= -189.6 \text{ J/K} \end{aligned}$$

The free-energy change of a chemical process equals the sum of the free energies of formation of the products minus the sum of the free energies of formation of the reactants.

For the reaction



the free energy change is

$$\begin{aligned}\Delta G_{298}^{\circ} &= \sum \Delta G_{(\text{products})}^{\circ} - \sum \Delta G_{(\text{reactants})}^{\circ} \\ &= \left[(c \times \Delta G_{\text{fC}}^{\circ}) + (d \times \Delta G_{\text{fD}}^{\circ}) - (a \times \Delta G_{\text{fA}}^{\circ}) - (b \times \Delta G_{\text{fB}}^{\circ}) \right]\end{aligned}$$

The standard molar free energy of formation of any free element in its most stable state is zero. So, for the above example,

$$\begin{aligned}\Delta G_{298}^{\circ} &= \Delta H_{298}^{\circ} - T\Delta S_{298}^{\circ} \\ &= -401,500 \text{ J} - (298.15 \text{ K}) \times (-189.6 \text{ J/K}) \\ &= -344,971 \text{ J} \approx -345.0 \text{ kJ}\end{aligned}$$

Since, ΔG_{298}° is negative, therefore, the reaction will be spontaneous.

Exercise 3.8

Classify each of the following reactions as belonging to the four possible cases summarized in **Table 3.4**.

- $$\text{N}_2(\text{g}) + 3\text{F}_2(\text{g}) \rightarrow 2\text{NF}_3(\text{g})$$

$$\Delta H^{\circ} = -249 \text{ kJ}; \Delta S^{\circ} = -278 \text{ J/K}$$
- $$\text{N}_2(\text{g}) + 3\text{Cl}_2(\text{g}) \rightarrow 2\text{NCl}_3(\text{g})$$

$$\Delta H^{\circ} = 460 \text{ kJ}; \Delta S^{\circ} = -275 \text{ J/K}$$
- $$\text{N}_2\text{F}_4(\text{g}) \rightarrow 2\text{NF}_2(\text{g})$$

$$\Delta H^{\circ} = 85 \text{ kJ}; \Delta S^{\circ} = 198 \text{ J/K}$$
- Calculate the standard free energy change, for the reaction

$$2\text{Ag}_2\text{S}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{Ag}(\text{s}) + 2\text{H}_2\text{S}(\text{g}) + \text{O}_2(\text{g})$$

Standard molar free energies of formation of Ag_2S , H_2O and H_2S are -40.7 , -237.2 and -33.6 kJ/mol , respectively.

Unit Summary

- *Thermodynamics is the study of heat, work, and energy and the rules that govern their inter-conversion. Among its basic ideas are the notion of a system and its surroundings, the concepts of kinetic energy, potential energy, and the internal energy and the distinction between two types of energy exchanges, heat (q) and work (W).*
- *The first law of thermodynamics (the law of conservation of energy) tells us that the energy is conserved. That is the energy lost by a system equals that gained by its surroundings and vice versa.*
- *Enthalpy change (ΔH) can be written into chemical equations and incorporated into **conservation factors** that relate amounts of substances with quantities of heat released or absorbed in chemical reactions. In an exothermic reaction, enthalpy of the system decreases and heat is given off to the surroundings. In an endothermic reaction, enthalpy increases and heat is absorbed from the surroundings.*
- *The standard enthalpy change, ΔH° , and the standard enthalpy of formation (heat of formation), ΔH_f° , are important thermodynamic quantities. The standard enthalpy of formation of a substance is defined as the enthalpy change for the formation of 1 mole of that substance from the elements, with all reactants and products in their standard states.*

$$\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ (\text{products}) - \sum m \Delta H_f^\circ (\text{reactants})$$

- *A spontaneous change in a system occurs by itself without outside intervention. The enthalpy change of a system, ΔH , is a measure of the heat change in a process. Exothermic processes ($\Delta H < 0$) tend to occur spontaneously. The spontaneous character of a reaction is also determined by the change in randomness or disorder of the system, measured by the entropy, S . Processes that produce an increase in randomness or disorder of the system ($\Delta S > 0$) tend to occur spontaneously.*
- *The second law of thermodynamics tells us that in any spontaneous process the entropy of the universe increases. That is*

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

- *The standard entropy change in a system, ΔS° , can be calculated from tabulated standard entropy values, S° , as follows:*

$$\Delta S^\circ = \sum n S^\circ (\text{products}) - \sum m S^\circ (\text{reactants})$$

- The Gibbs free energy, G , is a thermodynamic state function that combines the two state functions enthalpy and entropy:
- $G = H - TS$. For processes that occur at constant temperature,
 $\Delta G = \Delta H - T\Delta S$
- For a spontaneous process at constant temperature and pressure, ΔG must be negative, that is $\Delta G < 0$. In many cases, the sign of ΔG can be predicted just by knowing the signs of ΔH and ΔS .
- The standard free energy change, ΔG° , for any process can be calculated from tabulated standard free energies of formation, ΔG_f° .

$$\Delta G^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants})$$

Check List

Key terms of the unit

- | | |
|-------------------------------|--------------------|
| • Calorie | • Heat of reaction |
| • Calorimeter | • Internal Energy |
| • Closed system | • Open system |
| • Endothermic process | • Specific heat |
| • Enthalpy | • Standard state |
| • Entropy | • State function |
| • Exothermic process | • Surroundings |
| • First law of thermodynamics | • System |
| • Free energy change | • Thermochemistry |
| • Gibbs free energy | • Work |

REVIEW EXERCISE ON UNIT 3

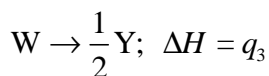
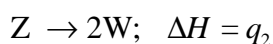
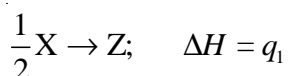
Part I: Multiple Choice Questions

1. In thermodynamics, a quantity whose value simply depends upon the initial and final state of the system is called:

a thermodynamic quantity	c adiabatic quantity
b state function	d path function



2. All naturally-occurring processes proceed spontaneously in a direction which leads to:
- increase in enthalpy of a system
 - decrease in entropy of a system
 - decrease in free energy of a system
 - increase in free energy of a system
3. A system absorbs 20 kJ of heat and also does 10 kJ of work. The net internal energy of the system:
- increases by 10 kJ
 - increases by 30 kJ
 - decreases by 10 kJ
 - decreases by 30 kJ
4. A hypothetical reaction $X \rightarrow 2Y$ proceeds by the following sequence of steps:



after applying Hess' law, the value of ΔH for the hypothetical reaction above is:

- $q_1 + q_2 + q_3$
 - $2(q_1 + 2q_2 + 2q_3)$
 - $2q_1 + 2q_2 + 2q_3$
 - $2(q_1 + q_2 + 2q_3)$
5. A certain system which can exchange energy but not matter with the surroundings is classified as:
- open system
 - closed system
 - isolated system
 - heterogeneous system
6. A human being requires 2700 kcal of energy per day. If ΔH_c of glucose is -1350 kcal/mol, how many grams of glucose a person has to consume every day:
- 360 g
 - 36.0 g
 - 3.6 kg
 - 360 mg
7. In a certain chemical process both ΔH and ΔS have values greater than zero. Under what conditions, the reaction would not be spontaneous?
- $\Delta H > T\Delta S$
 - $\Delta H = T\Delta S$
 - $T\Delta S - \Delta H > 0$
 - None

8. A mode of transference of energy involved when petrol undergoes combustion in an internal combustion engine is:
- heat as well as light
 - heat
 - work as well as heat
 - heat as well as electricity
9. If $\Delta H_{\text{CO}}^{\circ}$ and $\Delta H_{\text{CO}_2}^{\circ}$ are -111.3 kJ/mol and -393.5 kJ/mol respectively, the $\Delta H_{\text{C}}^{\circ}$ of CO (g) will be
- -282.2 kJ
 - $+282.2 \text{ kJ}$
 - 28.2 kJ
 - unpredictable because $\Delta H_{\text{O}_2}^{\circ}$ is not given
10. Which of the following processes involve decrease in the entropy of system?
- $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$
 - diamond to graphite
 - $\text{N}_2(\text{g}) (1\text{atm}) \rightarrow \text{N}_2(\text{g}) (10 \text{ atm})$
 - none

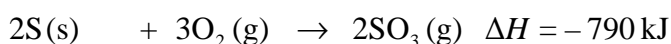
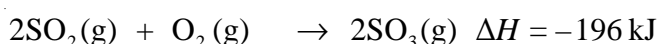
Part II: Short Answer Questions

11. Define the following terms:
- system
 - surroundings
 - open system
 - closed system
 - isolated system
 - thermochemistry
 - enthalpy
 - entropy
 - thermodynamics
 - adiabatic process
12. a What is work?
b How do we determine the amount of work done given the magnitude of the associated force?
13. What is the change in internal energy of a system that absorbs 455 J of heat and does 325 J of work?
14. How much heat, in J, is needed to raise the temperature of 324 g of H_2O from 15.3°C to 67.1°C .
15. a What is meant by the term state function?
b Give an example of a quantity that is a state function and one that is not?
c Is temperature a state function? Why?
16. State Hess's law. Explain with one example the usefulness of Hess's law in thermochemistry.

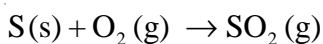


17. A large bed of rocks are used in some solar heated homes to store heat. Calculate the quantity of heat absorbed by 50.0 kg of rocks if their temperature increases by 12.0°C (Assume that the specific heat of the rock is 0.82 J/g.K).
18. a What is the specific heat of water?
b How many kilojoules of heat are needed to raise the temperature of 2.06 kg of water from 35.14°C to 76.37°C?

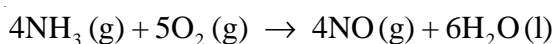
19. From the following enthalpies of reaction:



Calculate the enthalpy change for the reaction



20. Determine the enthalpy change for the oxidation of ammonia



From the following data



21. If a reaction is spontaneous, does this imply that it occurs rapidly? Explain.
22. Rank the three physical states in order of increasing entropies.
23. How does the entropy of the system change when the following processes occur?
- a A solid is melted.
b A liquid is vaporized.
c A solid is dissolved in water.
d A gas is liquidified.
24. Given the following bond energy data:
- | | |
|--------------|---------------------------------|
| N – N | $\Delta H = 160 \text{ kJ/mol}$ |
| N = N | $\Delta H = 481 \text{ kJ/mol}$ |
| N \equiv N | $\Delta H = 941 \text{ kJ/mol}$ |
| F – F | $\Delta H = 154 \text{ kJ/mol}$ |

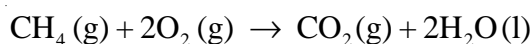
and the enthalpy change for the reaction $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{F}_2(\text{g}) \rightarrow \text{NF}_3(\text{g})$; $\Delta H = -103 \text{ kJ/mol}$; what is the bond energy for NF_3 ?

25. Find the temperature at which reactions with the following ΔH and ΔS values would become spontaneous.

a $\Delta H = -126 \text{ kJ/mol}$, $\Delta S = 84 \text{ J/K}\cdot\text{mol}$

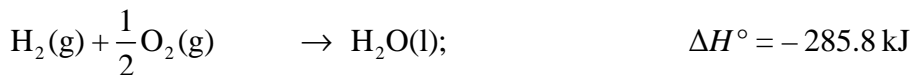
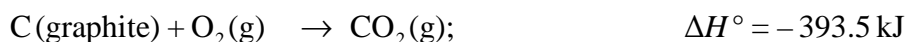
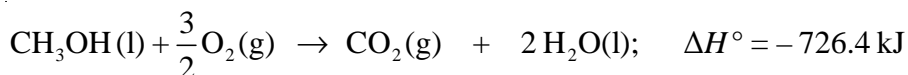
b $\Delta H = -117 \text{ kJ/mol}$, $\Delta S = -105 \text{ J/K}\cdot\text{mol}$

26. Calculate the standard free energy change, ΔG° , for the complete combustion of methane.

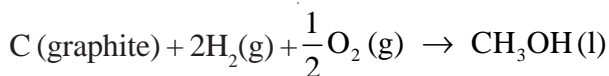


The standard free energies of formation for $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -51 kJ/mol , -394 kJ/mol and -237 kJ/mol , respectively.

27. From the following heats of combustion,



calculate the enthalpy of formation of methanol (CH_3OH) from its elements.



28. From the data given below:



Calculate the enthalpy change for the transformation

