



Richard Grifith/Shutterstock.com

Chapter 2

Thermodynamics and Thermochemistry

2.1 Heat, Work, and Energy

OBJECTIVES

After studying this topic, you should be able to:

- Explain, identify, or provide examples of the different types of systems, heat capacity, the meaning of the sign of q , intrinsic and extrinsic properties, state functions, pressure–volume work, the first law of thermodynamics, and internal energy.
- Determine the temperature change, the energy change, or any other variables for a particular process or reaction, when given the appropriate information.

WHAT IS THERMODYNAMICS?

Thermodynamics is the study of the energy changes involved in physical and chemical processes. Physical processes include the heating and cooling of substances, phase changes, and changes in physical parameters such as the volume and pressure of a gas. Chemical processes often involve chemical reactions. *Thermochemistry* is the branch of thermodynamics that investigates the heat flow that occurs during these reactions.

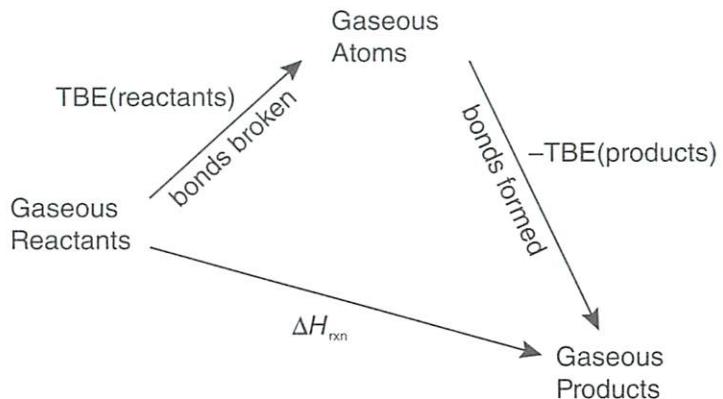
One of the many important applications of thermodynamics is the determination of the energy content of various foods. As you probably know, the nutritional value of a food item is usually stated in terms of energy units called calories. The “food calorie” or “large calorie” (abbreviated Cal), which you typically see on food packages, is actually equal to 1,000 “small calories” (cal) used in thermodynamics. 1 cal = 4.184 J, so 1 Cal is equivalent to 4.184 kJ, which is the amount of energy needed to raise the temperature of 1 kg of water by 1 degree Celsius.

Scientific discovery and scientific knowledge have been achieved only by those who have gone in pursuit of it without any practical purpose whatsoever in view.

Max Planck (1858–1947)

Topics Covered:

- 2.1 Heat, Work, and Energy
- 2.2 Enthalpy
- 2.3 Entropy and Spontaneous Change
- 2.4 Free Energy



Previously, the energy content of foods was measured directly. A food sample was placed in a calorimeter (see Section 2.2 below) and completely burned. The resulting rise in temperature was recorded and the calorie count of the sample was calculated from it. Nowadays, an indirect method is used, in which one first determines the amounts of three basic nutrient types (proteins, carbohydrates, and fats) present in a food sample and then uses tabulated standard calorie counts per 1 g of each type of nutrient to calculate the total nutritional value of the sample. The standard energy values of proteins, carbohydrates, and fats are still determined by burning. As part of this topic and among many other things, you will learn all the concepts and techniques necessary to perform such calculations and experiments.

SYSTEMS AND SURROUNDINGS

Many of the energy changes studied in this course take the form of heat flow, which is the transfer of thermal energy in the process being studied. *Heat always flows from the warmer object to the cooler object.*

In any study of heat flow, it is important to distinguish between a system and its surroundings. A system is that part of the universe that one wants to study. For example, when a chemical reaction takes place, chemists consider the reactants and products (or the entire reaction mixture) to be the system. The surroundings are the remaining parts of the universe that can interact (e.g., exchange energy) with a system under study. During a reaction, the surroundings would be the vessel (flask, test tube, etc.) in which the reaction takes place, including the air and any other material making thermal contact with the vessel, such as the solution in which the reaction occurs. The system and its surroundings thus constitute the universe.

Types of Systems

Depending on the interactions between a system and its surroundings, there are three common system types defined in chemistry:

1. An **open system**, which can exchange both matter and energy with its surroundings.
2. A **closed system**, which can exchange energy but not matter with its surroundings.
3. An **isolated system**, which exchanges neither matter nor energy with its surroundings.



For example, the unsealed flask in Figure 2.1.1 is partially filled with water and is an open system because gaseous water molecules can escape into the surroundings. The same flask with a stopper is a closed system because the water (matter) cannot escape, although thermal energy can be exchanged between the flask and the surroundings through the glass walls of the flask. If the stoppered flask is placed in an insulated chamber so that there is no heat exchange with the surroundings, it becomes an isolated system.

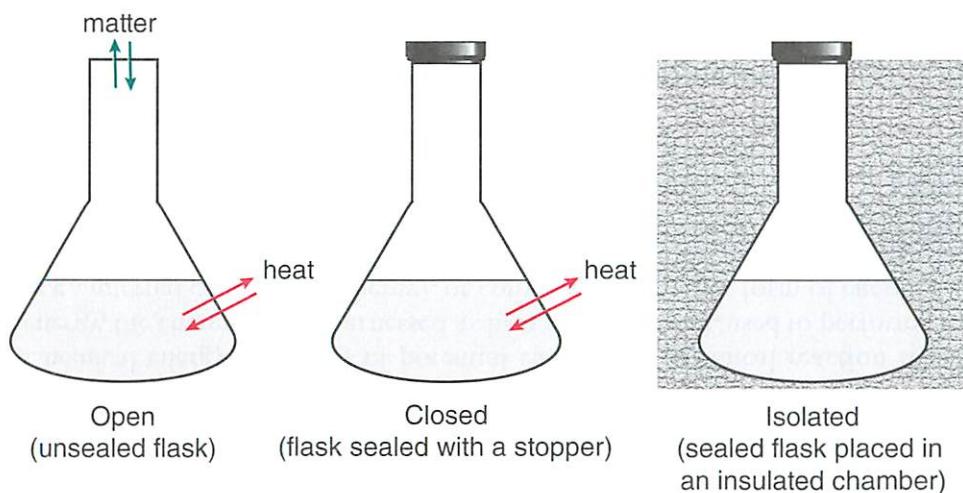


Figure 2.1.1 An open, closed, and isolated system.

WHAT IS ENERGY?

Energy can take many different forms, and because of this, an all-encompassing definition of energy is not possible. That being said, the most common definition of energy is “the capacity to do work.”

In turn, work, w , is defined as the product of a force, F , acting on an object, and the distance, d , that the object moves in response to the force. That is, $w = F \times d$. (The SI units for work are the joule (J) or newton-metre (Nm), where $1\text{ J} = 1\text{ Nm}$.)

Chemists are usually interested in a type of work called *pressure-volume (PV)* work, which is the work involved in the expansion or compression of gases.

Many chemical reactions produce or consume gases, and when gases expand or are compressed, work is involved. Pressure can be measured in kPa, and volume in L, giving rise to the units for PV work:

$$w = -P \times \Delta V \quad \text{with units of kPa L (where } 1 \text{ kPa L} = 1 \text{ J)}$$

Some types of energy are:

- Heat energy (thermal energy), which is the energy transferred due to a temperature difference between the system and the surroundings.
- Kinetic energy, which is the energy associated with motion.
- Potential energy, which is stored energy or the energy a body possesses due to its position. For instance, a rock on a hill has potential energy and, if it rolls down the hill, the potential energy is converted to kinetic energy.

Chemical energy is a form of potential energy. If a chemical reaction releases energy, the energy can be harnessed as heat (e.g., furnace), used to perform work (e.g., internal combustion energy), or converted to another form of energy.

It is important to realize that while energy cannot be created or destroyed, it can be converted from one form to another.

Units of Energy

The joule (J) has already been mentioned as being the SI unit for any form of energy, including heat. What can one do with one joule of energy? Not much at all! In fact, it would take about 4.2 joules of energy to heat up one gram of water by one degree Celsius. A microwave oven must provide about 52,250 J to heat up 250 mL of water from 25 °C to 75 °C. How was this number of joules determined? The heat energy associated with temperature changes can be estimated using a parameter called *heat capacity*, or a related quantity known as *specific heat capacity*.

HEAT CAPACITY AND ITS USES

As previously mentioned, heat is the energy transferred between the system and the surroundings, or from one object to another, as a result of a temperature difference. When two objects of different temperature contact each other, heat always flows from the warmer object to the cooler object and stops flowing when



thermal equilibrium is reached (i.e., both objects have the same temperature). The amount of heat transferred, q , is related to the temperature difference, ΔT , and another physical parameter called *heat capacity* or *specific heat capacity*.

Both of these terms are a measure of how many joules are required to change the temperature of a substance or object by one degree ($^{\circ}\text{C}^{-1}$ or K^{-1}). So why do we need two terms? Heat capacity is usually *used for objects*, like a piece of apparatus used in an experiment. The heat capacity, represented by the symbol C , is unique to each piece of apparatus and has units of $\text{J } ^{\circ}\text{C}^{-1}$. The relationship between the amount of heat energy (q), an object's heat capacity (C), and the temperature change (ΔT) is:

$$q = C \times \Delta T$$

Specific heat capacity (lowercase c) is similar to heat capacity, but *considers the mass of the substance*. It is the heat needed to warm one *mass unit* (g or kg) of a substance by one degree. The SI units for specific heat capacity are $\text{J kg}^{-1} \, ^{\circ}\text{C}^{-1}$, but the most commonly used are $\text{J g}^{-1} \, ^{\circ}\text{C}^{-1}$. It can be used to calculate q :

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

An alternative way to express the specific heat capacity is to indicate the energy required to warm 1 mole of substance by one degree. For instance, specific heat capacity expressed in units of $\text{J mol}^{-1} \, ^{\circ}\text{C}^{-1}$ describes the heat needed to increase the temperature of one mole of a substance by one degree, and is known as *molar heat capacity*. Another example would be $\text{J cm}^{-3} \, ^{\circ}\text{C}^{-1}$, a quantity known as *volumetric heat capacity*.

Table 2.1.1 lists selected specific and molar heat capacities. Note that $^{\circ}\text{C}^{-1}$ can be interchanged with K^{-1} only because temperature *differences* are used.

TABLE 2.1.1 HEAT CAPACITIES OF SELECTED SUBSTANCES AND MATERIALS

SUBSTANCE	SPECIFIC HEAT CAPACITY <i>c</i> (J g ⁻¹ K ⁻¹)	MOLAR HEAT CAPACITY <i>c</i> (J mol ⁻¹ K ⁻¹)
Brick	0.840	—
Copper, Cu(s)	0.386	24.47
Ethanol, CH ₃ CH ₂ OH(l)	2.44	112.0
Graphite, C(s)	0.710	8.53
Oxygen, O ₂ (g)	0.918	29.38
Glass (Pyrex)	0.753	—
Human tissue	3.5	—
Water, H ₂ O(s) (at -10 °C)	2.114	38.09
H ₂ O(l) (at 25 °C)	4.184	75.40
H ₂ O(g) (at 100 °C)	2.080	37.47
Wood	1.3 to 2.3	—

Temperature Change

Temperature change (ΔT) is the difference between final and initial temperatures:

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

The value of ΔT is the same whether in °C or K. For example, if the initial temperature is 25.0 °C and the final temperature is 14.7 °C, then ΔT is -10.3 °C. Using the same example, the initial temperature is 298.2 K, the final temperature is 287.9 K, and ΔT is -10.3 K. Make sure that both T_{final} and T_{initial} are using the same scale before taking the difference. It would be incorrect to determine the difference in Celsius and then add 273.15 to “convert” to Kelvin!

Example 2.1.1. Energy Required to Warm a Sample of Silver

Silver has a specific heat capacity of $0.237 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$. How many kJ of energy are needed to warm 100 g of silver from $25.0 \text{ }^{\circ}\text{C}$ to $90.0 \text{ }^{\circ}\text{C}$?

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

$$= 100 \text{ g} \times 0.237 \text{ J }^{\circ}\text{C}^{-1} \times (90 - 25) \text{ }^{\circ}\text{C}$$

$$= 1.54 \text{ kJ}$$

Example 2.1.2. Energy Required to Warm Flask and Water (In-Class Exercise)

An Erlenmeyer flask has a heat capacity of $175 \text{ J }^{\circ}\text{C}^{-1}$. 52.0 g of water are added. Assuming there are no heat losses, determine the energy required to raise the temperature of the assembly from $25.0 \text{ }^{\circ}\text{C}$ to $40.0 \text{ }^{\circ}\text{C}$. (Hint: Determine the energy required for the flask and water separately ($q_{\text{sys}} = q_{\text{flask}} + q_{\text{water}}$) and then add the results.)

Data: $c \text{ H}_2\text{O(l)} = 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$

Now suppose the flask and contents in the above “Flask and Water” In-Class Exercise example are allowed to cool from $40.0 \text{ }^{\circ}\text{C}$ to $25.0 \text{ }^{\circ}\text{C}$. How much heat energy is lost by the flask and the water as they cool down? Logic dictates that it must also be 5.89 kJ. How does one differentiate between energy lost and energy gained? The convention used is that when a system *absorbs* energy from the surroundings, the process is said to be *endothermic* and the change in energy is positive. Conversely, when the system *releases* energy to the surroundings, the process is said to be *exothermic* and the change in energy is negative. In the above “Flask and Water” In-Class Exercise example, the energy change (q) for the system (flask plus water), is +5.89 kJ as it heats up, and -5.89 kJ as it cools down.

When a system cools, ΔT will be negative. As a result, q will also be a negative number. Likewise, when a system is warmed, ΔT and q will be positive. In essence, the sign of q is determined by the sign of ΔT .

Thermal Equilibrium

When heat is transferred between objects, it can be more difficult to distinguish between the system and the surroundings. The warmer object loses heat and cools down, so its $\Delta T < 0$ and q_{lost} are negative. The cooler object gains heat and warms up, so its $\Delta T > 0$ and q_{gained} are positive.

The number of joules lost by the warmer object must equal the number of joules gained by the cooler object. However, this leads to a sign discrepancy between q_{lost} and q_{gained} . A negative number is obviously not equal to a positive number (e.g., $-300 \neq +300$). To correct this discrepancy, a negative sign is placed in front of q_{lost} in order to make $-q_{\text{lost}} = q_{\text{gained}}$.

Once the warmer object has transferred sufficient heat to the cooler object, and both objects reach the same final temperature (T_f), the heat flow stops and the objects are said to be in *thermal equilibrium*.

Example 2.1.3. Temperature at Thermal Equilibrium (In-Class Exercise)

A piece of aluminum weighing 40.0 g is heated to 80.0 °C and dropped into 100.0 g of water at 25.0 °C. What is the temperature once thermal equilibrium is attained?

All of the heat energy lost by the aluminum is gained by the water.

Data: $c_{\text{H}_2\text{O(l)}} = 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$; $c_{\text{Al(s)}} = 0.902 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$

INTENSIVE AND EXTENSIVE PROPERTIES

Suppose you take two samples of the same uniform system, one small and one large, and measure their properties. An *intensive (intrinsic) property* is a property that has the same value regardless of the sample size. Temperature (including melting and boiling points) and density are examples of intensive properties. An *extensive (extrinsic) property* is a physical property whose value increases with the sample size. Mass, volume, energy, enthalpy, and entropy are all examples of extensive properties.



STATE FUNCTIONS

A *state function* is a property whose value depends only on the current state of the system but not on how that state was reached. Examples of state functions are volume, pressure, and enthalpy. Heat and work are *not* state functions. One can “pump” different amounts of heat into the system, make the system use those different amounts of heat to perform different amounts of work (the more heat, the more work), and still end up in exactly the same final state every time.

To understand this, consider two states of n moles of an ideal gas: State 1, specified by P_1 and V_1 , and State 2, specified by P_2 and V_2 . There is no need to specify T_1 and T_2 because the temperature of the system is determined by P and V through the ideal gas law. Suppose that $V_2 > V_1$, that is, that the gas expands.

There are many different ways to change the system from State 1 to State 2. For instance: (a) by letting the gas expand while holding the pressure at $P_1 = \text{const}$ until the very end and then changing the pressure to P_2 ; (b) by changing the pressure to P_2 right away and holding it constant until the end of expansion (note that the second process would require more heat but would also enable the gas to do more work than in the first process); and (c) by changing the pressure gradually from P_1 to P_2 as the volume increases (see Figure 2.1.2).

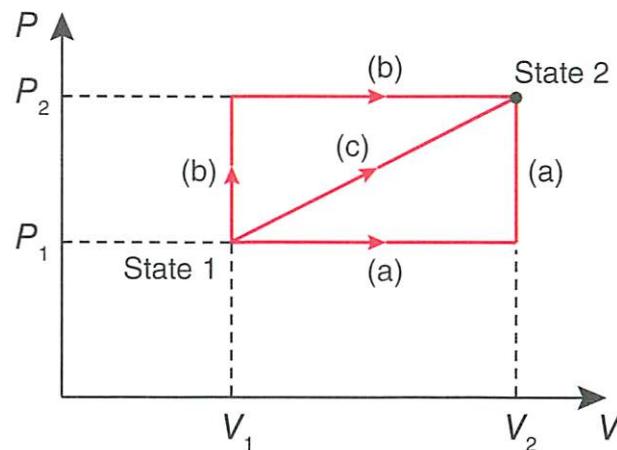


Figure 2.1.2 Different ways of changing the state of an ideal gas. The work done on the system in each case is equal to the area between V_1 and V_2 and under the arrows representing the corresponding path.

Now because it takes different amounts of heat to create different gas pressures for a given V and because the value of $P\Delta V$ depends on what $P = \text{const}$ is, the values of q and w will also depend on how the system gets from State 1 to State 2. However, the sum $\Delta E = q + w$ will be independent of those details. This is the meaning of the statement that q and w are not state functions, whereas internal energy is a state function.

The following mechanical analogy may also be useful. Imagine a person flying a small plane from Vancouver to St. John's. The person's initial position in Vancouver is a state function, because how he or she got there is irrelevant. The final position in St. John's is also a state function, because it doesn't matter if the person travelled there via the shortest route or decided to visit northern Canadian cities and towns along the way (Figure 2.1.3). However, the distance traveled from Vancouver and St. John's and the amount of fuel consumed during the trip are not state functions. Heat and work roughly correspond to the amount of fuel consumed and the distance traveled, respectively.

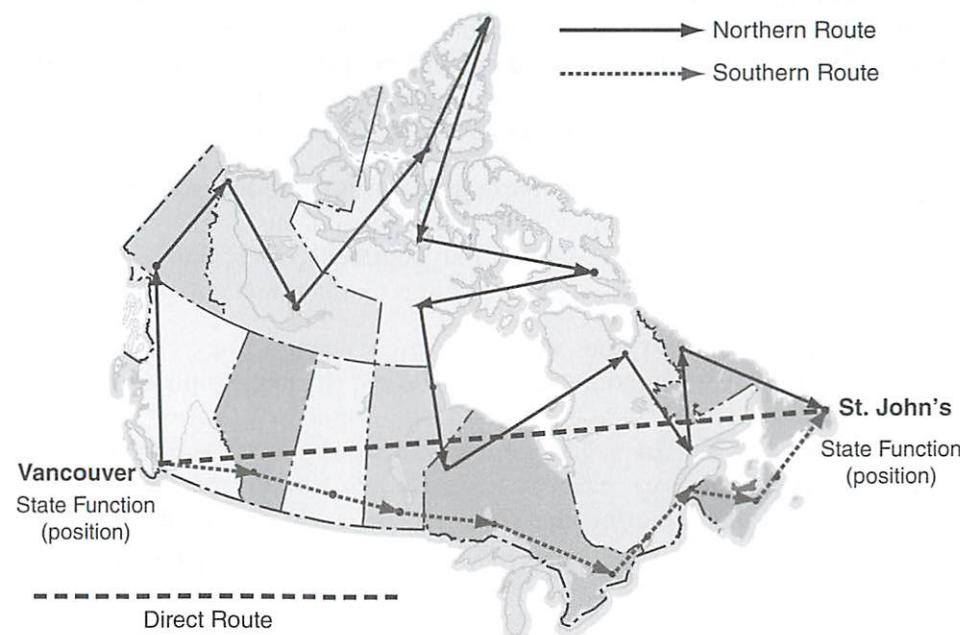


Figure 2.1.3 Position is an example of a state function.

FIRST LAW OF THERMODYNAMICS

Example 2.1.3 follows the first law of thermodynamics, which states that:

The total energy of an isolated system is conserved.

This means that energy can be transferred from one part of the system to another, or converted from one form to another, but it cannot be created or destroyed.

To keep track of the energy of a system, a thermodynamic function called *internal energy*, E , is used. E is the sum of all the kinetic and potential energies of all the atoms, ions, and molecules in the system. Internal energy is an extensive property and a state function.

For example, the internal energy of a monoatomic ideal gas is the total kinetic energy of all the atoms. For a gas consisting of molecules, E would be the total kinetic energy of all the molecules plus their total rotational and vibrational energies. If the gas is not ideal, then the internal energy would also include the potential energy of intermolecular interactions.

We have discussed two methods by which energy may be transferred: heat and work.

Heat is symbolized by q . If heat is added to a system, the sign of q is positive, and this signifies an endothermic process. If heat is released by a system, the sign of q is negative, and this signifies an exothermic process.

Work is symbolized by w . For a system at constant pressure, work may be calculated using: $w = -P \times \Delta V$. The sign of w tells us whether work is being done on the system, or whether it is the system that does the work. In an expansion, the gas (the system) is said to be doing work on the surroundings, and the value of w is negative (work energy has been used, so it has been removed from the system). In a compression, the surroundings are said to be doing work on the system, and the value of w is positive (the system has gained work energy). *However, if a process does not involve a compression or expansion, there is no volume change ($\Delta V = 0$) and the value of w is zero.*

In 1845, English physicist James Joule showed that heat and work are equivalent ways of transferring energy in or out of a system. Joule conducted an experiment in which the same rise in temperature of a sample of water was brought about by transferring a given quantity of energy *either* by electrically heating or by doing mechanical work on the water. His results are consistent with the first law of thermodynamics, which can be expressed mathematically as:

$$\Delta E = q + w$$

If the surroundings do work on, or supply heat to the system, the internal energy of the system increases ($\Delta E > 0$). If the system does work on, or supplies heat to the surroundings, the internal energy of the system decreases ($\Delta E < 0$).

If the system is kept at a constant volume, there is no expansion or compression work performed. That is, $w = 0$, assuming there are no other kinds of work done. The relationship then becomes $\Delta E = q$ and is commonly written as:

$$\Delta E = q_v$$

where the subscript V signifies that the volume of the system remains constant.

Therefore, the internal energy change of a system is equal to the heat transferred when the volume does not change.



Section 2.1 Practice Problems

1. The specific heat capacity of Al is $0.902 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$. What is its *molar* heat capacity? Use the molar heat capacity to find the amount of heat needed to warm 3.25 moles of Al from $24.5 \text{ }^{\circ}\text{C}$ to $46.5 \text{ }^{\circ}\text{C}$.
2. 250.0 J of heat is supplied to 20.00 g of $\text{O}_2(\text{g})$, and the resulting final temperature of the gas is $36.1 \text{ }^{\circ}\text{C}$. What was the initial temperature? The specific heat capacity of $\text{O}_2(\text{g})$ is $0.918 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$.
3. A 355 mL bottle of warm beer at $25.0 \text{ }^{\circ}\text{C}$ is placed into a fridge. How much energy must the fridge remove from the beer ($c = 4.06 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$) and the glass bottle ($c = 250 \text{ J }^{\circ}\text{C}^{-1}$) to cool the bottle of beer to a refreshing $4.0 \text{ }^{\circ}\text{C}$?
4. An unknown volume of water ($c = 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$) at $20.0 \text{ }^{\circ}\text{C}$ is added to 50 mL of water at $40.0 \text{ }^{\circ}\text{C}$. If the final temperature of the combined volumes is $24.5 \text{ }^{\circ}\text{C}$, what was the unknown volume of water at $20.0 \text{ }^{\circ}\text{C}$?
5. A 35 g sample of a metal alloy at $95 \text{ }^{\circ}\text{C}$ is placed in 50 g of water ($c = 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$) at $20 \text{ }^{\circ}\text{C}$. At thermal equilibrium, the temperature is $32 \text{ }^{\circ}\text{C}$. Find the specific heat capacity of the alloy.
6. A piece of copper at $120 \text{ }^{\circ}\text{C}$ has exactly twice the mass of another piece of copper at $40 \text{ }^{\circ}\text{C}$. The two pieces are brought into contact and allowed to reach thermal equilibrium. What is the final temperature?
7. A glass with a specific heat capacity of $0.84 \text{ J g}^{-1} \text{ K}^{-1}$ has a temperature of $20.0 \text{ }^{\circ}\text{C}$. It is then filled with 0.300 L of water ($c = 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$, $d = 1.00 \text{ g mL}^{-1}$) at $95.0 \text{ }^{\circ}\text{C}$. The resulting combined weight of the cup and water is 450 g. What is the temperature of the water at thermal equilibrium?
8. When 30.0 g of water at an unknown temperature were mixed with 27.0 g of water at $15.8 \text{ }^{\circ}\text{C}$, the final temperature of the mixture was $29.1 \text{ }^{\circ}\text{C}$. Heat exchange with the container walls was negligible. What was the initial temperature of the added water ($^{\circ}\text{C}$)?
9. Explain the difference between intensive and extensive properties. Provide examples of intensive and extensive properties.

10. Are the following quantities state functions? Explain.

- a. q
- b. w
- c. ΔE
- d. speed

11. When two objects of the same mass reach thermal equilibrium, their final temperatures are the same. However, their ΔT values may not be of the same magnitude. Explain. Under what circumstances, if any, would their ΔT values be of the same magnitude?



2.2 Enthalpy

OBJECTIVES

After studying this topic, you should be able to:

- Explain the difference between internal energy and enthalpy.
- Describe the possible phase transitions and use latent heats, in various units, to determine the amount of energy required for phase changes.
- Use data from a calorimetry experiment to calibrate a calorimeter, determine the heat of a reaction, or to find other variables.
- Define standard state, identify the standard state of common elements, and write formation reactions.
- Use Hess's law to determine enthalpy change or other variables.
- Write the appropriate reaction to determine the total bond energy (TBE) of a gaseous species, use average bond enthalpies to estimate the enthalpy change of a reaction, and explain why using heats of formation in thermodynamic calculations is more accurate than using average bond enthalpies.

ENTHALPY

As discussed in the previous topic, the change in internal energy (ΔE) of a system is equal to the heat flow (q) if the volume of the system remains constant ($w = 0$). However, many physical processes and chemical reactions of interest often take place at constant (atmospheric) pressure instead of constant volume.

Enthalpy (H) is a thermodynamic state function defined by

$$H = E + PV$$

where E is the internal energy, P is the pressure, and V is the volume of the system. Like internal energy, the absolute enthalpy of a system cannot be measured, but changes in enthalpy (ΔH) can be. At constant pressure:

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

Recall that $\Delta E = q + w$ and that $w = -P\Delta V$:

$$\Delta H = (q + w) + P\Delta V$$

$$\Delta H = (q - P\Delta V) + P\Delta V$$

$$\Delta H = q_p$$

This shows that, at constant pressure, the ΔH of a system is equal to the heat (q_p) flowing into or out of a system. Because many processes and reactions take place at constant pressure instead of constant volume, it is much more practical to measure heat flow in terms of ΔH instead of ΔE . In other words, provided the pressure of the system is kept constant, heat may be treated as if it were a state function, and that state function is known as enthalpy.

PHYSICAL PROCESSES AND LATENT HEAT

Latent heat is the energy change associated with physical processes that involve a change of state (phase). Melting (fusion), boiling (vapourization), and sublimation are endothermic processes (consume energy), while condensation, freezing, and deposition are exothermic (release energy). During any one of these processes, the temperature of the substance remains constant.

For example, when a mole of ice at 0 °C melts into a mole of water at 0 °C, the latent heat of fusion (q_{fusion}) is +6.01 kJ mol⁻¹. The positive sign of q indicates that the process is endothermic. The energy absorbed from the surroundings is used only to change the phase of the substance, not its temperature. Note that chemists often omit the adjective “latent” from the “latent heat of” expression, but it is understood to be there during state changes.



TABLE 2.2.1 MOLAR LATENT HEATS FOR H₂O STATE CHANGES

PROCESS	TERM	VALUE OF <i>q</i>
H ₂ O(s) → H ₂ O(l)	melting (fusion)	+6.01 kJ mol ⁻¹ at 0 °C
H ₂ O(l) → H ₂ O(s)	freezing	-6.01 kJ mol ⁻¹ at 0 °C
H ₂ O(l) → H ₂ O(g)	boiling (vapourization)	+40.66 kJ mol ⁻¹ at 100 °C
H ₂ O(g) → H ₂ O(l)	condensation	-40.66 kJ mol ⁻¹ at 100 °C
H ₂ O(s) → H ₂ O(g)	sublimation	+51.06 kJ mol ⁻¹ at 0 °C
H ₂ O(g) → H ₂ O(s)	deposition	-51.06 kJ mol ⁻¹ at 0 °C

If the phase changes are carried out at constant pressure, the latent heat values are also ΔH values. For example, at constant pressure, the ΔH of fusion (ΔH_{fus}) of ice is +6.01 kJ mol⁻¹. This is the difference in enthalpy between the product (liquid water) and the reactant (ice).

Observe that the values listed in Table 2.2.1 are not for standard conditions. If the processes are occurring under standard conditions, the corresponding latent heats (enthalpy changes) would be different. For example, the ΔH_{vap} of water would be +44 kJ mol⁻¹.

It is also important to note that the forward and reverse processes have *q* values of the same magnitude but of opposite sign. At 0 °C, 6.01 kJ mol⁻¹ of energy must be added to melt ice, but 6.01 kJ mol⁻¹ must be removed to freeze water.

Example 2.2.1. Energy Needed for Phase Change (In-Class Exercise)

How much energy is required to convert 22.0 g of ice at -15.0 °C to water vapour at 120.0 °C? Use the data provided below.

Data: $c(\text{H}_2\text{O}(s)) = 2.06 \text{ J g}^{-1} \text{ K}^{-1}$; $c(\text{H}_2\text{O}(l)) = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$;

$c(\text{H}_2\text{O}(g)) = 1.87 \text{ J g}^{-1} \text{ K}^{-1}$; $\Delta H_{\text{fus}}(\text{H}_2\text{O} \text{ at } 0 \text{ }^\circ\text{C}) = 6.01 \text{ kJ mol}^{-1}$;

$\Delta H_{\text{vap}}(\text{H}_2\text{O} \text{ at } 100 \text{ }^\circ\text{C}) = 40.66 \text{ kJ mol}^{-1}$

Enthalpy Change Under Standard Conditions (ΔH°)

Changes in enthalpy (ΔH) can be measured or determined, but the value of ΔH for a given process varies with temperature and pressure. It is therefore important to define a set of *standard conditions*. In the study of thermodynamics, the standard conditions used are 1 atm (101.33 kPa) and 25 °C (298.15 K), unless otherwise stated. Enthalpy changes under standard conditions are reported as ΔH° , where the superscript “o” denotes *under standard conditions*.

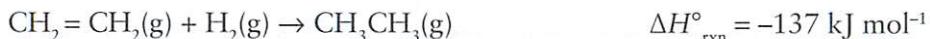
ΔH FOR CHEMICAL REACTIONS

For any reaction occurring under standard conditions, the enthalpy change for that reaction, ΔH_{rxn} , is the difference between the sum of the absolute molar enthalpies of the products and those of the reactants:

$$\Delta H_{\text{rxn}} = \sum H(\text{products}) - \sum H(\text{reactants}) \quad (2.2.1)$$

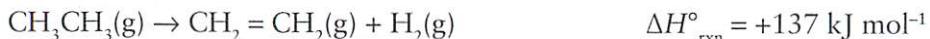
If a reaction releases heat into the surroundings, it is exothermic. That is, the system has lost energy, and the enthalpy has decreased ($\Delta H < 0$).

For example, if one mole of ethylene, $\text{CH}_2 = \text{CH}_2(\text{g})$, reacts with $\text{H}_2(\text{g})$ under standard conditions to form ethane, $\text{CH}_3\text{CH}_3(\text{g})$, the system releases 137 kJ mol⁻¹ of heat to the surroundings. The reaction is exothermic and the ΔH° is negative:



Conversely, if a reaction absorbs heat from the surroundings, it is endothermic. In endothermic reactions, the enthalpy of the system increases and the enthalpy change has a positive value ($\Delta H > 0$).

If the reaction above was reversed to give:



the process would be endothermic. The absolute value of ΔH is the same for both reactions but the sign is different.

ΔH for a reaction may be found experimentally by measuring the heat lost or gained when a process is carried out at constant pressure.

UNITS OF REACTION ENTHALPIES

From now on we will use the following two ways of reporting enthalpy changes for chemical reactions.

When $\Delta H^\circ_{\text{rxn}}$ is shown in units of kJ (not kJ mol^{-1}) next to a reaction, it means the enthalpy change for the reaction involving the numbers of moles equal to the stoichiometric coefficients of the balanced equation *as written*. A kJ value of $\Delta H^\circ_{\text{rxn}}$ is therefore proportional to the stoichiometric coefficients. For instance,



The first of these equations says that, when 1 mol of $\text{H}_2(\text{g})$ is reacted with 0.5 mol of $\text{O}_2(\text{g})$, 242 kJ of heat is produced. The second equation says that, when 2 mol of $\text{H}_2(\text{g})$ is reacted with 1 mol of $\text{O}_2(\text{g})$, 484 kJ of heat is produced.

When $\Delta H^\circ_{\text{rxn}}$ is shown in kJ mol^{-1} , it means the enthalpy change for the reaction per 1 mole of a particular substance that is either stated or implied by the context. $\Delta H^\circ_{\text{rxn}}$ values expressed in kJ mol^{-1} in reference to a particular substance do not change when stoichiometric coefficients are scaled. To avoid confusion with units of kJ mol^{-1} , we will always write the reaction in such a way that the substance in question has a stoichiometric coefficient of 1. For instance, if we write



it would mean that the enthalpy change is -242 kJ per 1 mole of H_2O (and, incidentally, of H_2). Note that the enthalpy change for this reaction per 1 mole of O_2 would be -484 kJ mol^{-1} .

The above two ways of reporting $\Delta H^\circ_{\text{rxn}}$ values are equivalent and may be used interchangeably.

MEASUREMENT OF ΔH

An experimental technique called *calorimetry* is used to study the heat flow of physical and chemical processes. In this technique, the processes are allowed to occur in a piece of apparatus known as a *calorimeter*.

Simple Calorimeter

A simple, low-tech calorimeter can be constructed using a low-cost insulated vessel (such as two styrofoam cups, one inside the other, with a lid), thermometer, and stirrer (magnetic stir bar or stirring rod), as shown in Figure 2.2.1. Such calorimeters can be used to study both exothermic and endothermic reactions in solution.

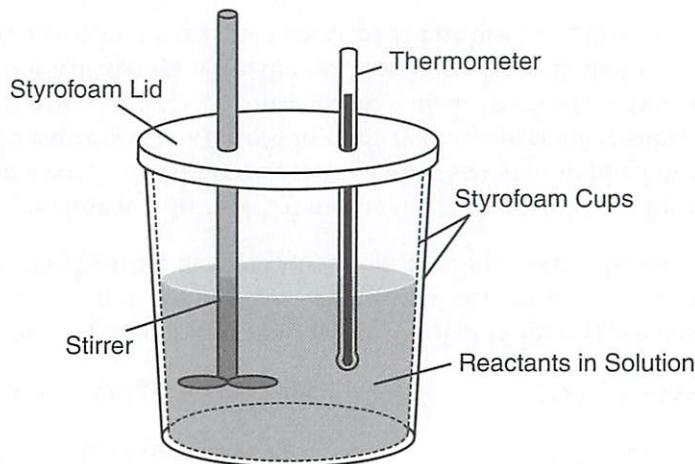


Figure 2.2.1 A simple calorimeter.

In the context of calorimetry, we will define the “system” as the calorimeter assembly (the styrofoam cups, the lid, the stirrer, and the thermometer) and all of its contents. The “surroundings” are the rest of the universe. The styrofoam cups of the simple calorimeter prevent the exchange of heat between the system and the surroundings, so the system can be treated as isolated. The thermometer is used to measure the temperature change of the system that is caused by the chemical reaction (or some other process).

For example, if HCl(aq) and NaOH(aq) are reacted in a calorimeter to produce NaCl(aq), the temperature of the system increases. Knowing the heat capacity of the solution and the heat capacity of the calorimeter assembly, one can use the observed temperature change to calculate the amount of heat produced by the reaction.

The “system” as defined on the previous page consists of three parts: the chemical reactants (the “reaction”), the solvent, and the dry calorimeter assembly. Within the system, heat flows from the reactants to the solvent and to the calorimeter (or in the opposite direction). We will denote the amounts of heat *gained* by these three parts as q_{rxn} , q_{sol} , and q_{cal} , respectively.

For an isolated system, there is no heat exchange between the system and the surroundings, so we can write

$$q_{\text{surr}} = -q_{\text{sys}} = -(q_{\text{rxn}} + q_{\text{sol}} + q_{\text{cal}}) = 0$$

Therefore,

$$q_{\text{rxn}} = -(q_{\text{sol}} + q_{\text{cal}})$$

If we also assume that the calorimeter assembly has a zero heat capacity, then $q_{\text{cal}} = 0$ and the above equation reduces to

$$q_{\text{rxn}} = -q_{\text{sol}}$$

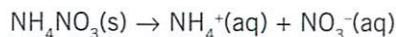
The heat absorbed or released by the solvent can be related to its heat capacity:

$$q_{\text{sol}} = m_{\text{sol}} c_{\text{sol}} \Delta T_{\text{sol}}$$

If the calorimetry experiment is performed at constant pressure, the value of q_{rxn} is also the ΔH for the reaction being studied. Furthermore, if the experiment is performed under standard conditions (1 atm and 298.15 K), the value of q_{rxn} is the standard enthalpy change (ΔH°) for the associated reaction.

Example 2.2.2. ΔH of Reaction from a Simple Calorimeter (In-Class Exercise)

Ammonium nitrate (NH_4NO_3) is the compound present in many “instant” cold packs found in first aid kits. The process of dissolving $\text{NH}_4\text{NO}_3(s)$ in water is endothermic, which causes the cold pack to become cold. The ΔH associated with the dissolution of a substance in water is called the *enthalpy of (dis)solution*.



When 1.00 g of NH_4NO_3 is dissolved in 50.00 g water in a simple calorimeter, the water cools from 25.00 to 23.32 °C. Assuming that the heat capacity of the solvent is $4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$, and that the heat released by the calorimeter assembly is negligible, find the enthalpy change for this process.

Molar Enthalpy of Reaction

It is often useful to express ΔH as an amount of energy per 1 mole of a particular reactant or product. The resultant value for ΔH is termed the molar enthalpy of reaction. Note that this value always refers to a specific species participating in that reaction.

Example 2.2.3. Molar Enthalpy of Dissolution (In-Class Exercise)

Using the ΔH determined in Example 2.2.2, find the molar enthalpy of dissolution of ammonium nitrate, in units of kJ mol^{-1} .

Calorimeter Calibration

So far, we have assumed that the calorimeter assembly itself does not absorb or release heat. To obtain more accurate experimental data, the heat absorbed or released by the calorimeter (q_{cal}) needs to be taken into account. Therefore:

$$q_{\text{rxn}} = -q_{\text{sol}} \text{ becomes } q_{\text{rxn}} = -(q_{\text{cal}} + q_{\text{sol}})$$

The q_{cal} term can be calculated from $q_{\text{cal}} = C_{\text{cal}} \times \Delta T$, but we first require the heat capacity of the calorimeter, C_{cal} . The process of determining C_{cal} (also called the *calorimeter constant*) is called *calorimeter calibration*.



Two common methods used for calorimeter calibration are:

1. Adding a known amount of hot water, with a known initial temperature, to the calorimeter and then measuring the temperature when the water and calorimeter are at thermal equilibrium. The heat lost by the water is absorbed by the calorimeter. There is no chemical reaction taking place. The calorimeter constant can be found from:

$$q_{\text{water}} = -q_{\text{cal}}$$

$$m_{\text{water}} \times c_{\text{water}} \times \Delta T_{\text{water}} = -(C_{\text{cal}} \times \Delta T_{\text{cal}})$$

$$C_{\text{cal}} = -\frac{m_{\text{water}} c_{\text{water}} \Delta T_{\text{water}}}{\Delta T_{\text{cal}}}$$

2. Carrying out a chemical reaction, with a known heat of reaction, inside the calorimeter. The heat released by the reaction is absorbed by the calorimeter. If there is no solution or water in the calorimeter, the calorimeter constant can be determined from:

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

$$C_{\text{cal}} = -\frac{q_{\text{rxn}}}{\Delta T_{\text{cal}}}$$

Example 2.2.4. ΔH of Reaction from a Calibrated Calorimeter (In-Class Exercise)

Calibration (Method 1). A calorimeter consists of a glass beaker surrounded by a styrofoam insulating jacket. When 25.0 mL of hot water is added to the calorimeter, the temperature of the hot water decreases by 4.5 °C and that of the calorimeter increases by 10.0 °C.

Actual experiment. 15.0 mL of 3.00 M HCl and 15.0 mL of 3.00 M NaOH, both initially at 22.6 °C, are mixed inside the calorimeter. After the reaction, the temperature of the solution is 38.2 °C. The mass of the final solution is 31.5 g, and it has a specific heat capacity of 3.79 J g⁻¹ K⁻¹.

Determine the ΔH of neutralization per mole of HCl reacted.

Bomb Calorimeter

While simple calorimeters are suitable for reactions occurring in liquids, they are not very useful for reactions involving gases or combustion. A *bomb calorimeter* (Figure 2.2.2) is typically used to measure the heat liberated from gaseous or combustion reactions. The reaction takes place in a heavy-duty vessel (the “bomb”) that is immersed in water. The entire bomb calorimeter assembly is therefore comprised of the vessel, the water surrounding it, and any other accessories (stirrer, thermometer, sample tray, etc.).

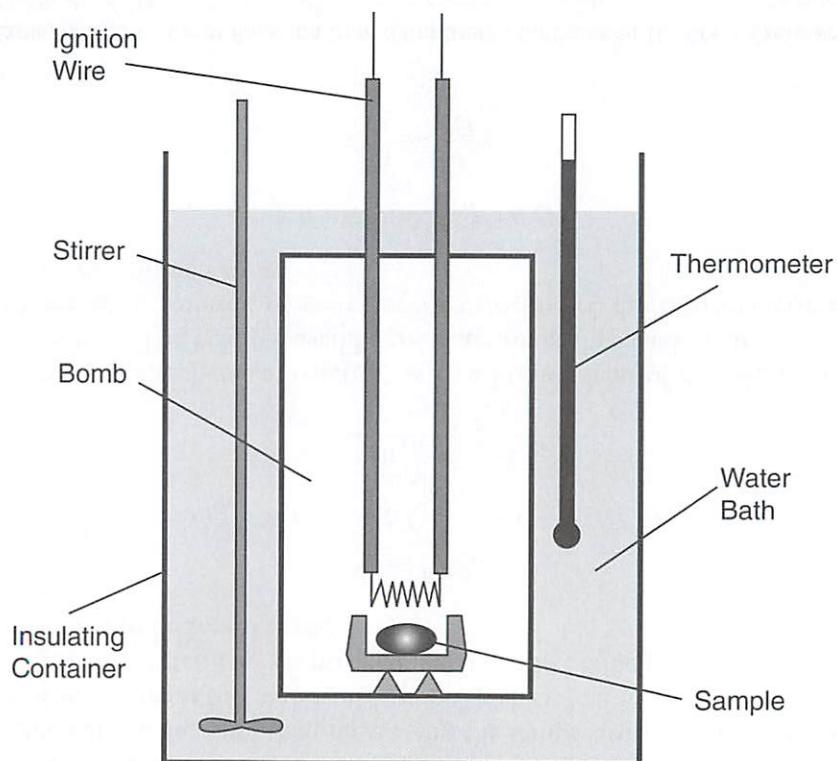


Figure 2.2.2 Bomb calorimeter.

Because of the complexity of the bomb calorimeter, it is necessary to calibrate the bomb calorimeter (determine its C_{cal}) prior to use. Note, however, that the value of C_{cal} typically does not include the water around the vessel.

In contrast to the simple calorimeter in the previous section, reactions in a bomb calorimeter take place under constant volume, and thus the measured heat transfer corresponds to ΔE . In practice, a bomb calorimeter is filled with a large excess of oxygen, so that the total pressure change due to the combustion is negligible. Since the pressure remains approximately constant, the heat transfer recorded is equal to ΔH .

The amount of heat produced by the chemical reaction in a bomb calorimeter can be calculated as follows

$$q_{\text{rxn}} = -(q_{\text{cal}} + q_{\text{water}}) = -(C_{\text{cal}} + c_{\text{water}} m_{\text{water}}) \Delta T$$

where ΔT is the change in the temperature of the calorimeter and the water bath.

Example 2.2.5. Determination of the Calorimeter Constant (In-Class Exercise)

1.22 grams of benzoic acid (C_6H_5COOH , 122 g mol⁻¹) are placed in a bomb calorimeter along with excess oxygen and burned completely. The heat of combustion of benzoic acid is known to be -3230 kJ mol⁻¹. The initial temperature of the water (1500 g) and the bomb calorimeter is 25.0 °C. After combustion, the temperature of the water bath and the bomb calorimeter is 28.2 °C. What is the calorimeter constant, C_{cal} ?

Example 2.2.6. Calorimeter Temperature Change after Reaction (In-Class Exercise)

Ethanol, CH_3CH_2OH , is a renewable biofuel and a component of certain beverages. 11.5 g of ethanol are placed into a bomb calorimeter with a heat capacity of 650 J K⁻¹ and surrounded by 10.0 kg of water. By how many degrees does the water temperature rise when the ethanol is completely burned to produce $CO_2(g)$ and $H_2O(l)$? The heat of combustion of ethanol is -1366.7 kJ mol⁻¹.

STANDARD ENTHALPY OF FORMATION

Standard enthalpy of formation, ΔH_f° , also known as the *standard heat of formation*, is the enthalpy change for the reaction in which 1 mole of a substance under standard conditions (1 atm and 298.15 K) is formed from the constituent elements in their reference states under standard conditions. This reaction is called a *formation reaction*:

elements (reference state, standard conditions) \rightarrow 1 mole of a substance (standard conditions)

The state of a substance under standard conditions is often called a *standard state*. The *reference state* of an element is that form of the element which is the most stable under standard conditions. The reference states of selected elements are given in Table 2.2.2. Realize that the elemental form need not be an atom; elements can also be molecules.

TABLE 2.2.2 REFERENCE STATES OF SELECTED ELEMENTS

ELEMENT	REFERENCE STATE	ELEMENT	REFERENCE STATE
Hydrogen	$H_2(g)$	Sulfur	S(rhombic, s)
Carbon	C(graphite, s)	Bromine	$Br_2(l)$
Nitrogen	$N_2(g)$	Iodine	$I_2(s)$
Oxygen	$O_2(g)$	Mercury	$Hg(l)$

Some chemical elements can exist in two or more different forms called *allotropes*. For instance, the allotropes of carbon include graphite, graphene, diamond, and fullerene (buckyball). Graphite is the most stable allotrope and so it is chosen as the reference state of carbon.



Examples of formation reactions include:



Example 2.2.7. Writing ΔH_f° for Reactions (In-Class Exercise)

Write formation reactions for $\text{C}_2\text{H}_5\text{OH}(\text{l})$, $\text{Mg}(\text{NO}_3)_2(\text{s})$, and $\text{NH}_4\text{Br}(\text{s})$.

The standard enthalpy of formation of an element in its reference state under standard conditions is arbitrarily defined as zero, i.e.,

$$\Delta H_f^\circ (\text{element in the reference state under standard conditions}) = 0$$

This sets a “reference point” of enthalpies for each chemical element. Note that the standard enthalpy of formation of an element under standard conditions is *not* zero if the element is not in its reference state. For example,

$$\Delta H_f^\circ [\text{Br}_2(\text{g})] = +30.9 \text{ kJ mol}^{-1}$$

Standard enthalpies of formation of substances that are not in their reference states have to be determined empirically. The experimental values of ΔH_f° for common substances are listed in Table 2.2.3.

TABLE 2.2.3 STANDARD ENTHALPIES OF FORMATION (kJ mol⁻¹)

AgBr(s)	-100.4
AgCl(s)	-127.1
AgI(s)	-61.8
AgNO ₃ (s)	-124.4
Ag ₂ O(s)	-31.0
Al ₂ O ₃ (s)	-1675.7
B(g)	+590
B ₂ Cl ₄ (g)	-490
BaCl ₂ (s)	-858.6
BaCO ₃ (s)	-1216.3
BaO(s)	-553.5
BaSO ₄ (s)	-1473.2
Br(atomic, g)	+111.9
Br ₂ (g)	+30.9
C(atomic, g)	+715.0
CCl ₄ (l)	-135.4
CHCl ₃ (l)	-134.5
CH ₄ (g)	-74.8
CHCH(g)	+226.7
CH ₂ CH ₂ (g)	+52.3
CH ₃ CH ₃ (g)	-84.7
C ₃ H ₈ (g)	-103.8
CH ₃ OH(l)	-238.7
C ₂ H ₅ OH(l)	-277.7
Cl(atomic, g)	+122.0
CO ₂ (g)	-393.5
CaCl ₂ (s)	-798.5
CaCO ₃ (s)	-1206.9
CaO(s)	-635.1
Ca(OH) ₂ (s)	-986.1
CaSO ₄ (s)	-1434.1
CdCl ₂ (s)	-391.5
CdO(s)	-258.2
Cr ₂ O ₃ (s)	-1139.7
CuO(s)	-157.3
CuS(s)	-53.1
Cu ₂ S(s)	-79.5
CuSO ₄ (s)	-771.4
F(atomic, g)	+76.5
Fe(OH) ₃ (s)	-823.0
Fe ₂ O ₃ (s)	-824.2
Fe ₃ O ₄ (s)	-1118.4
H(atomic, g)	+218.0
HBr(g)	-36.4
HCl(g)	-92.3
HF(g)	-271.1
HI(g)	+26.5
HNO ₃ (l)	-174.1
H ₂ O(g)	-241.8
H ₂ O(l)	-285.8
H ₂ O ₂ (l)	-187.8
H ₂ S(g)	-20.6
H ₂ SO ₄ (l)	-814.0
HgO(s)	-90.8
I ₂ (g)	+62.4
KBr(s)	-393.8
KCl(s)	-436.7
KClO ₃ (s)	-397.7
KClO ₄ (s)	-432.8
KNO ₃ (s)	-494.6
MgCl ₂ (s)	-641.3
MgCO ₃ (s)	-1095.8
MgO(s)	-601.7
Mg(OH) ₂ (s)	-924.5
MgSO ₄ (s)	-1284.9
MnO(s)	-385.2
MnO ₂ (s)	-520.0
N(atomic, g)	+470.5
NH ₃ (g)	-46.1
N ₂ H ₄ (l)	+50.6
NH ₄ Cl(s)	-314.4
NH ₄ NO ₃ (s)	-365.6
NO(g)	+90.2
NO ₂ (g)	+33.2
N ₂ O ₄ (g)	+9.2
NaCl(s)	-411.2
NaF(s)	-573.6
NaOH(s)	-425.6
O(atomic, g)	+249.0
PbBr ₂ (s)	-278.7
PbCl ₂ (s)	-359.4
PbO(s)	-219.0
PbO ₂ (s)	-277.4
PCl ₃ (g)	-287.0
PCl ₅ (g)	-347.9
SiCl ₄ (l)	-687.0
SiO ₂ (s)	-910.9
SnO ₂ (s)	-580.7
SO ₂ (g)	-296.8
SO ₃ (g)	-395.7
ZnI ₂ (s)	-208.0
ZnO(s)	-348.3
ZnS(s)	-206.0



HESS'S LAW OF THERMOCHEMISTRY

Standard enthalpies of formation ΔH_f° (or any other ΔH° , for that matter) may be used to predict the ΔH° of a reaction, using Hess's law, which states:

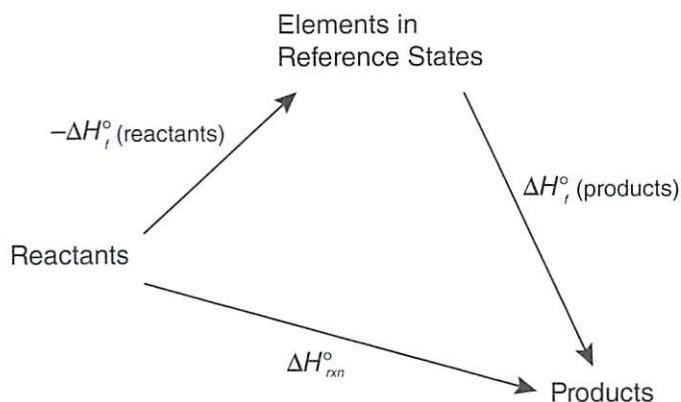
The enthalpy change for a reaction is the sum of the enthalpy changes for the individual steps of the reaction.

Consequently, an unknown ΔH° can be found for any reaction that is a combination of other reactions for which ΔH° is known. For example, if the reaction enthalpies for two reactions are known, the reaction enthalpy for a third related reaction can be derived. This is possible because enthalpy is a state function.

In general, standard enthalpies of formation (ΔH_f°) can be used as shown on the next page to predict the enthalpy change for a reaction. The reactants are hypothetically “unformed” in a reaction that is the reverse of formation, after which the resulting elements combine to form the products.



$$\text{Therefore: } \Delta H_{rxn}^\circ = \Delta H_f^\circ \text{ (products)} - \Delta H_f^\circ \text{ (reactants)}$$



If there is more than one product or reactant, the enthalpy change for a reaction must be summed over all the products and reactants:

$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

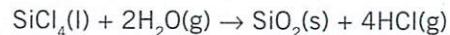
For a generic reaction: $aA + bB \rightarrow cC + dD$

$$\Delta H^\circ_{\text{rxn}} = [c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D)] - [a\Delta H_f^\circ(A) + b\Delta H_f^\circ(B)]$$

Note that the stoichiometric coefficients are essential in this equation because ΔH is an extensive property. Also, remember that elements in their standard state have an enthalpy of formation of zero.

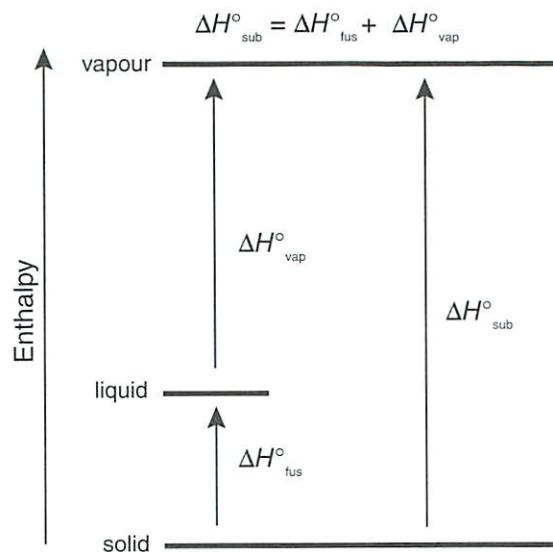
Example 2.2.8. Calculation of $\Delta H^\circ_{\text{rxn}}$ from ΔH_f° Values (In-Class Exercise)

Use the standard enthalpy of formation data from Table 2.2.3 to determine $\Delta H^\circ_{\text{rxn}}$ for the following reaction:



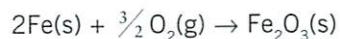
Hess's law is versatile in that it can be used to combine any set of ΔH° values, not just ΔH_f° values, to determine the ΔH° of another reaction or process. For instance, it can be used to predict enthalpy of sublimation, which is often difficult to measure. Again, the combination of ΔH° values is possible because enthalpy is a state function. The same change in enthalpy must be obtained both in the direct conversion of solid to vapour, and in the indirect conversion of solid to liquid and then to vapour (see the following diagram).



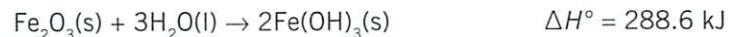
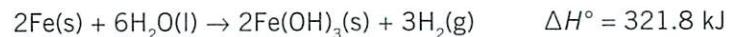


Example 2.2.9. Calculation of $\Delta H^\circ_{\text{rxn}}$ from ΔH° Values for Other Reactions (In-Class Exercise)

The oxidation (rusting) of iron occurs according to the reaction:



Given the following data, what is the heat of reaction for this process? Also note that the ΔH° for this process is the ΔH°_f of Fe_2O_3 .

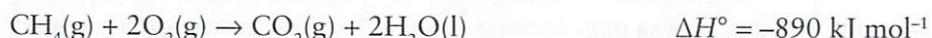


Combustion

Hess's law can be used to predict the ΔH° of combustion, a very important class of reactions in everyday life. The ΔH° for a given combustion reaction is termed the *standard enthalpy of combustion* or more commonly the *heat of combustion*, and it is a useful measure of the energy available from a particular fuel.

The heat of combustion is the energy released when one mole of a fuel in its standard state undergoes *complete* combustion with oxygen to form products in their standard state. Typically, the products formed from the complete combustion of an organic fuel are $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$; incomplete combustion results in undesirable compounds such as carbon monoxide, $\text{CO}(\text{g})$.

Heats of combustion can be expressed as heat per mole of fuel (e.g., kJ mol^{-1}). For example, the heat of combustion for methane, CH_4 , is 890 kJ mol^{-1} .



Note that the product side of the reaction includes *liquid* water. Although the water will initially be in the vapour form after the reaction, the measurements are taken after the products have cooled to 25°C .

Table 2.2.4 lists the standard enthalpies of combustion for some compounds.

TABLE 2.2.4 STANDARD ENTHALPIES OF COMBUSTION (kJ mol^{-1})

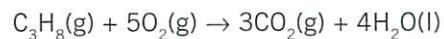
Benzene, $\text{C}_6\text{H}_6(\text{l})$	-3268	Hydrogen, $\text{H}_2(\text{g})$	-286
Carbon, C(graphite,s)	-394	Methane, $\text{CH}_4(\text{g})$	-890
Carbon monoxide, $\text{CO}(\text{g})$	-283	Ethane, $\text{CH}_3\text{CH}_3(\text{g})$	-1560
Ethanol, $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$	-1368	Ethyne, $\text{HCCH}(\text{g})$	-1300
Glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-2808*	Butane, $\text{CH}_3(\text{CH}_2)_2\text{CH}_3(\text{g})$	-2874

*When the human body metabolizes glucose, the same amount of energy is released!

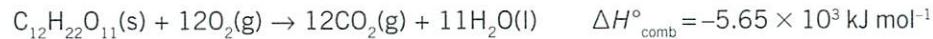


Example 2.2.10. Calculation of $\Delta H^\circ_{\text{combustion}}$ from ΔH_f° Values (In-Class Exercise)

Propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, is the fuel used in most home barbecues. Use the standard enthalpy of formation data from Table 2.2.3 to determine the ΔH° for the combustion of propane.

**Example 2.2.11. Calculation of ΔH° from $\Delta H^\circ_{\text{combustion}}$ (In-Class Exercise)**

The heat of combustion of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$, is given by:



Determine the standard enthalpy of formation, ΔH_f° , for sucrose.

Bond Enthalpy

Bond enthalpy (BE) is the energy required to break one mole of a specific type of bond (single, double, or triple) between two atoms, provided the reactants and products are both gases. When bonds are formed between atoms in the gas phase, energy is always released (exothermic). Breaking bonds to form atoms, therefore, requires an input of energy (endothermic), so bond enthalpies are always positive: for example, 431 kJ is required to break one mole of the single bond in $\text{HCl}(\text{g})$.

**Total Bond Enthalpy**

Total bond enthalpy (TBE), also known as the *enthalpy of atomization*, is the energy required to break all of the bonds in one mole of a gaseous compound:

one mole of gaseous compound \rightarrow gaseous atoms

There are no bonds between any of the gaseous atoms on the product side. For example, the TBE required to break up methane (CH_4) is:



Average Bond Enthalpy

The average bond enthalpy can be determined by dividing the TBE of a molecule which contains only one type of bonds by the total number of those bonds. For example, given that the TBE of $\text{CH}_4(\text{g})$ is $1661.8 \text{ kJ mol}^{-1}$, the average bond enthalpy of the C–H bond is $(1661.8 \text{ kJ mol}^{-1})/4 = 415.5 \text{ kJ mol}^{-1}$.

The following example illustrates how structural differences affect the numerical value for the enthalpy of a particular type of bond:



Both of these reactions involve breaking one mole of O–H bond, but the bond enthalpies, measured experimentally, are obviously different. Therefore, an average bond enthalpy of 464 kJ mol^{-1} is listed in Table 2.2.5 for the O–H bond.

TABLE 2.2.5 SELECTED AVERAGE BOND ENTHALPIES (kJ mol^{-1})

SINGLE BONDS									
	H	C	N	O	S	F	Cl	Br	I
H	436	414	389	464	339	565	431	366	298
C		347	293	351	259	485	331	288	216
N			159	222		272	201		
O				138			205		
S					226	285	255		
F						153	255		
Cl							244		
Br								193	
I									151

MULTIPLE BONDS

C=C	820	S=O	498	N=N	418	C=N	615
C=C	612	C=N	890	N=O	604	O=O	498
C=S	477	C=O	799	N=N	941		

Bond strength increases with bond order. For example, the CC triple bond (820 kJ mol^{-1}) is stronger than the CC double bond (612 kJ mol^{-1}), which is stronger than the CC single bond (347 kJ mol^{-1}). Note the double- and triple-bond values are not double or triple that of a single bond, respectively.



Example 2.2.12. Writing Total Bond Enthalpy Reactions (In-Class Exercise)

For each of the following compounds, write the reaction whose ΔH° is equal to the TBE: NH_3 , CH_3COOH , CH_2CH_2 .

Determination of Total Bond Enthalpies

There are two methods that can be used to determine the total bond enthalpy of a molecule, and both are shown below for methane.

Method 1: The TBE reaction can be treated like any reaction. Determine the ΔH° using the standard enthalpy of formation (ΔH_f°) data from Table 2.2.3:

$$\text{TBE}_{\text{CH}_4} = \Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

$$\begin{aligned}\text{TBE}_{\text{CH}_4} &= [(1 \times 715.0 \text{ kJ mol}^{-1}) + (4 \times 218.0 \text{ kJ mol}^{-1})] \\ &\quad - [(1 \times -74.8 \text{ kJ mol}^{-1})] \\ &= 1661.8 \text{ kJ mol}^{-1}\end{aligned}$$

Method 2: Determine the TBE by summing up the enthalpies of all the bonds in the molecule, using the *average bond enthalpies* from Table 2.2.5:

$$\begin{aligned}\text{TBE}_{\text{CH}_4} &= 4 \times \text{BE}(\text{C-H}) \\ &= 4 \times 414 \text{ kJ mol}^{-1} \\ &= 1656 \text{ kJ mol}^{-1}\end{aligned}$$

Obviously, the first method can only be used if the ΔH_f° values for all of the species in the reaction are known. A similar condition applies to the second method, which is suitable only if the average bond enthalpies, as well as the number and types of bonds in the molecule, are known.

Note that the two methods gave slightly different values for the TBE of CH₄. This is because molecular structure has an impact on bond enthalpy; that is, the enthalpy of the C–H bond in CH₄ is expected to be slightly different than the one in, for instance, ethane, CH₃CH₃. The bond enthalpies listed in Table 2.2.5 are *average values* only. Therefore, it is normally more accurate to determine TBE using ΔH°_f

Yet, the differences in TBE obtained using the two methods are usually small enough to allow the following approximation to be made:

$$\text{TBE} \text{ (using } \Delta H^\circ_f \text{)} \approx \text{TBE} \text{ (using bond enthalpies)}$$

ΔH of Gas-Phase Reactions

As previously discussed, the ΔH° of reactions can be determined using standard enthalpies of formation (ΔH°_f):

$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_f \text{ (products)} - \sum \Delta H^\circ_f \text{ (reactants)}$$

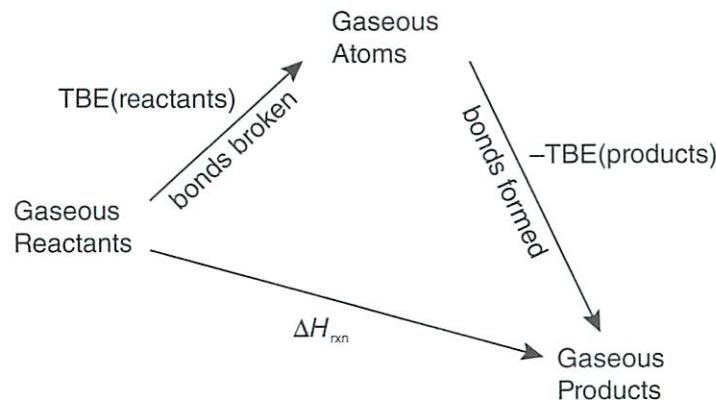
If a reaction is one where all of the reactants and products are in the gas phase, it is possible to estimate the enthalpy change of the gas-phase reaction using average bond enthalpies. The gaseous reactants are hypothetically broken up into gaseous atoms, after which the gaseous atoms combine to form new bonds in different arrangements, resulting in products in the gas phase.

reactants(g) → atoms(g)	TBE(reactants)
atoms(g) → products(g)	-TBE(products)
Overall: reactants(g) → products(g)	ΔH _{rxn}

$$\text{Therefore: } \Delta H_{\text{rxn}} = \text{TBE}_{\text{reactants}} - \text{TBE}_{\text{products}}$$

The equation above can be rewritten as:

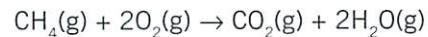
$$\Delta H_{rxn} = \sum \text{enthalpies of bonds broken} - \sum \text{enthalpies of bonds formed}$$



Remember, this equation works only if all of the reactants and products are in the gas phase!

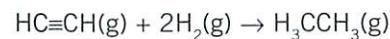
Example 2.2.13. Calculation ΔH°_{rxn} from Average Bond Enthalpies

Using the average bond enthalpies provided in Table 2.2.5, find ΔH° for the reaction below.



Example 2.2.14. Calculation of Bond Enthalpy from ΔH°_{rxn} and Other Bond Enthalpies

The hydrogenation reaction of acetylene, C_2H_2 , has $\Delta H^\circ = -311 \text{ kJ mol}^{-1}$. Use this value and the H–H, C–C, and C–H bond enthalpies from Table 2.2.5 to find the average bond enthalpy of the $\text{C}\equiv\text{C}$ bond. Compare it to the value given in Table 2.2.5.



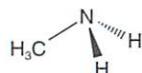
Using Gas-Phase Reactions

As seen previously, both enthalpies of formation and bond enthalpies can be used to determine ΔH for gaseous reactions. As the ΔH values obtained using these two methods are usually very similar, the ΔH value may be used interchangeably in the two relationships.

We can make use of this concept to determine enthalpies of formation or bond enthalpies of participant species in gaseous reactions.

Example 2.2.15. Calculation of ΔH°_f from Average Bond Enthalpies and Other ΔH° Values (In-Class Exercise)

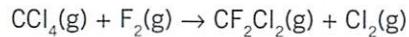
Determine the enthalpy of formation of gaseous methylamine, CH_3NH_2 , which has the structure:



Use Enthalpy of Formation values found on Table 2.2.3 and Bond Enthalpies found in Table 2.2.5.

Example 2.2.16. Calculation of ΔH°_f from a Combination of Thermochemical Data (In-Class Exercise)

Using only the data below, determine the ΔH°_f of CF_2Cl_2 using the reaction:

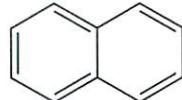


Data: ΔH°_f (kJ mol⁻¹): $\text{CCl}_4(\text{g}) = -96$; F(atomic, g) = 76.5

Avg. bond enthalpies (kJ mol⁻¹): (C–Cl) = 331; (C–F) = 485; (Cl–Cl) = 244

Section 2.2 Practice Problems

1. A student writes in an essay, “During melting of a pure substance, no heat is absorbed because the temperature does not change.” Is this true? Explain.
2. How many kJ of energy are required to convert 1.00 mol of Hg(l) at 20 °C to Hg(g) at its boiling point of 357 °C? Applicable data are 0.138 J g⁻¹ K⁻¹ and 59,400 J mol⁻¹. Again, examine the units to determine the relevance of the data.
3. Hg, the only metal that is a liquid under standard conditions, freezes at –39 °C. What is the ΔH° when 1.00 mL of Hg at 23 °C is cooled to –39 °C and frozen? Applicable data are 13.6 g mL⁻¹, 0.138 J g⁻¹ K⁻¹, and 11 J g⁻¹. Hint: Examine the units to determine what the data are.
4. What is the maximum mass of ice at –15.0 °C that can be converted to water vapour at 100.0 °C using 8.00×10^3 kJ of energy? Use other necessary data.
5. 505 mg of naphthalene ($C_{10}H_8$) reacts with excess oxygen in a bomb calorimeter. The heat released causes temperature to increase from 25.62 °C to 29.06 °C. The calorimeter constant, which includes the water bath, has been determined to be 5.90 kJ K⁻¹. Find the total heat released from the combustion and the molar heat of combustion of naphthalene.



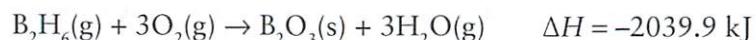
Did you know that naphthalene was once used as an ingredient in mothballs?

6. When 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) was combusted in a calorimeter to give $CO_2(g)$ and $H_2O(l)$, the temperature rose from 25.00 to 27.32 °C. The calorimeter itself had a heat capacity of 837 J °C⁻¹ and was submersed in 1500.0 g of water. Find the heat of combustion for sucrose.
7. A sample of sulfur, mass 2.56 g, is burned in excess oxygen inside a calorimeter of heat capacity 923 J K⁻¹ and insulated by 815 g of water. If the sole product of combustion is $SO_2(g)$, what is the expected increase in temperature?

8. Which of these reactions, when performed under standard conditions with the number moles as written, has a ΔH of reaction equal to the ΔH_f° of the product? Hint: Before punching numbers into the calculator, think about what the question is asking.

- a. $C(\text{diamond, s}) + O_2(\text{g}) \rightarrow CO_2(\text{g})$
- b. $H_2O(\text{l}) + \frac{1}{2}O_2(\text{g}) \rightarrow H_2O_2(\text{l})$
- c. $Fe(\text{s}) + 3Cl(\text{g}) \rightarrow FeCl_3(\text{s})$
- d. $C_2H_4(\text{g}) + H_2(\text{g}) \rightarrow C_2H_6(\text{g})$
- e. $CH_4(\text{g}) + CO(\text{g}) + H_2(\text{g}) \rightarrow C_2H_5OH(\text{l})$
- f. $H_2(\text{g}) + \frac{1}{2}O_2(\text{g}) \rightarrow H_2O(\text{l})$
- g. $C_2H_6(\text{g}) + \frac{1}{2}O_2(\text{g}) \rightarrow C_2H_5OH(\text{l})$
- h. $4C(\text{graphite, s}) + 6H_2(\text{g}) + O_2(\text{g}) \rightarrow 2C_2H_5OH(\text{l})$
- i. $2C(\text{g}) + 6H(\text{g}) + O(\text{g}) \rightarrow C_2H_5OH(\text{l})$
- j. $Hg(\text{s}) + Cl_2(\text{g}) \rightarrow HgCl_2(\text{g})$
- k. $H_2(\text{g}) + \frac{1}{8}S_8(\text{g}) \rightarrow H_2S(\text{g})$

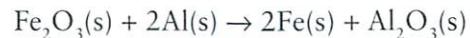
9. Use the data below to find the standard heat of formation for $B_2H_6(\text{g})$.



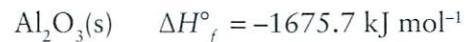
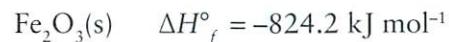
10. What is the ΔH when $PCl_3(\text{l})$ reacts with $Cl_2(\text{g})$ to give $PCl_5(\text{s})$? Use data below.



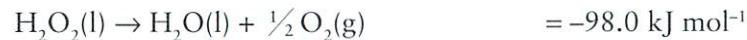
11. The thermite reaction is highly exothermic and is used to weld large pieces of metal, such as railroad rails, together:



Given the following data, how many kJ of heat are released when 5.00 g $\text{Fe}_2\text{O}_3(\text{s})$ reacts with excess $\text{Al}(\text{s})$?

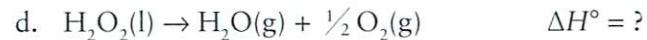
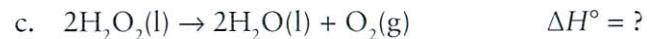
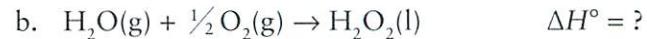


12. The enthalpies of the following two processes are known:

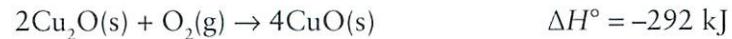


Find the following:

- a. The heat is released when 100 g $\text{H}_2\text{O}_2(\text{l})$ reacts via the first reaction.

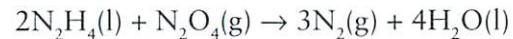


13. Consider the reaction below. What is the ΔH_f° of $\text{Cu}_2\text{O}(\text{s})$, in kJ mol^{-1} ?



14. How much heat energy is involved when 5.58 g of Fe metal reacts with excess oxygen to produce Fe_2O_3 ? Use the ΔH_f° of Fe_2O_3 .

15. Consider the following reaction of hydrazine, a rocket fuel:



Determine how much heat will be released if 32 kg hydrazine is used under standard conditions. Use the necessary ΔH_f° values from Table 2.2.3.

16. The standard heat of combustion for gaseous cyclopropane (C_3H_6) is $-2091 \text{ kJ mol}^{-1}$. What is its standard enthalpy of formation? Use data from Table 2.2.3 and Table 2.2.4.
17. The standard heat of combustion of gaseous ethylene oxide (C_2H_4O) is $-1264 \text{ kJ mol}^{-1}$. What is the ΔH_f° of gaseous ethylene oxide? Use data from Table 2.2.3 and Table 2.2.4.
18. The complete combustion of a certain quantity of acetylene (C_2H_2) at 25°C releases 650 kJ of energy. What was the quantity (in g) of acetylene combusted? Use data from Table 2.2.3.
19. A fuel mixture contains 90.0% octane, $C_8H_{18}(l)$, and 10.0% ethanol, $CH_3CH_2OH(l)$, by weight. How many kJ of energy are produced when 100.0 g of this mixture burns completely to $CO_2(g)$ and $H_2O(l)$? The ΔH_f° of octane is -250 kJ mol^{-1} . Use other necessary ΔH_f° values from Table 2.2.3.
20. The TBE of benzene (C_6H_6) is equal to the ΔH of which reaction?
- $C_6H_6(l) \rightarrow 6C(\text{s, graphite}) + 3H_2(g)$
 - $C_6H_6(l) \rightarrow 6C(\text{g}) + 6H(\text{g})$
 - $C_6H_6(g) \rightarrow 6C(\text{s, diamond}) + 3H_2(g)$
 - $C_6H_6(g) \rightarrow 6C(\text{s, graphite}) + 3H_2(g)$
 - $C_6H_6(g) \rightarrow 6C(\text{g}) + 6H(\text{g})$
21. Consider the statement, “The ΔH_f° of atomic oxygen, $O(\text{g})$ is exactly twice the bond energy of $O_2(\text{g})$.” Explain whether the statement is true or false.
22. Bond enthalpies reported in the literature are *average* values. Why *average*?
23. If the ΔH_f° for ethene gas (C_2H_4) is $+52 \text{ kJ mol}^{-1}$, what is the TBE (in kJ mol^{-1}) of ethene? Use data from Tables 2.2.3 and 2.2.5.
24. Using the ΔH_f° for atomic oxygen, $O(\text{g})$, find the bond enthalpy of the oxygen–oxygen bond in $O_2(\text{g})$.

25. Ozone gas (O_3) has a bent structure with two oxygen–oxygen linkages. If ozone has a ΔH_f° of +143 kJ mol⁻¹, what is the average oxygen–oxygen bond enthalpy in O_3 ? Does this suggest a reason why ozone is much more reactive than molecular oxygen, O_2 ? Use other necessary data.

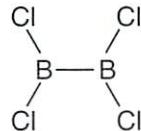
26. Consider the reaction below. If the I–I bond enthalpy is 152 kJ mol⁻¹, find the I–F bond enthalpy.



27. The ΔH_f° values in kJ mol⁻¹ for the carbon tetrahalides are respectively: $\text{CF}_4(\text{g}), -933$; $\text{CCl}_4(\text{g}), -96$; $\text{CBr}_4(\text{g}), +79$. Use this and data on Table 2.2.3 to find the C–F, C–Cl, and C–Br bond enthalpies.

28. Hexafluoroethane, $\text{F}_3\text{C}-\text{CF}_3(\text{g})$, has $\Delta H_f^\circ = -1343$ kJ mol⁻¹. Find the TBE of this compound and use this in conjunction with the C–F bond energy from the previous problem, plus data on Table 2.2.3, to find the energy of the C–C bond in hexafluoroethane.

29. Given the structure shown below, what is the average bond enthalpy (kJ mol⁻¹) of a boron–chlorine bond in B_2Cl_4 ? (Data: Bond enthalpy of B–B = 309 kJ mol⁻¹)



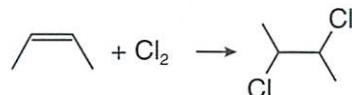
30. Estimate the standard enthalpy of formation (ΔH_f°) of acetaldehyde(g) from the structure and data below.



Bond energies (kJ mol⁻¹): C–H 414; C–C 347; C=O 715

ΔH_f° (kJ mol⁻¹): C(g,at) 715; H(g,at) 218; O(g,at) 249

31. The ΔH for the reaction below, where all molecules are gases, is -152 kJ mol^{-1} .
Using bond energies, calculate the average bond energy for the C–Cl bond.



Bond energies (kJ mol^{-1}): C–H 414; C–C 347; C=C 612

ΔH_f° (kJ mol^{-1}): Cl(g,at) 122

■ 2.3 Entropy and Spontaneous Change

OBJECTIVES

After studying this topic, you should be able to:

- Determine the standard molar entropy change of chemical reactions given tabulated values of standard molar entropies for elements and compounds.
- Predict the sign (+ or –) of an entropy change for phase transitions.
- Predict the sign (+ or –) of an entropy change based on the change in the total number of molecules during a chemical reaction.
- Explain and apply the first and second laws of thermodynamics.

SPONTANEITY

In addition to the determination of enthalpy changes in chemical reactions, thermodynamics allows us to determine whether a process will proceed spontaneously. In the case of a process at equilibrium (rate forward = rate reverse), we can determine whether the equilibrium will favour the reactants or the products.

SPONTANEOUS PROCESSES

A spontaneous process is one that occurs in the absence of any ongoing outside intervention. The transfer of heat from a hot object to a cold object is spontaneous. Sugar will spontaneously dissolve in hot coffee. Wet laundry will spontaneously dry and a piece of iron will spontaneously rust. The combustion of propane, once ignited, is spontaneous.

Processes that are spontaneous in one direction are nonspontaneous in the reverse direction. A car that is rolling backward does not spontaneously produce gasoline from CO_2 and H_2O .

How can we determine if a process will occur spontaneously? Enthalpy, which is related to internal energy and the first law of thermodynamics, is not sufficient on its own for predicting spontaneity. Rather, we must examine *free energy*, a thermodynamic quantity that encompasses both enthalpy and *entropy*.

WHY IS THE FIRST LAW OF THERMODYNAMICS INSUFFICIENT?

For a process where no work has been done ($w = 0$), $\Delta E = \Delta H$. In our study of thermodynamics, we saw that if ΔE_{sys} or ΔH_{sys} were negative quantities, then energy was released into the surroundings, and the products were at a lower energy than the reactants.

While one might think that a negative ΔE_{sys} or ΔH_{sys} is the only criterion needed for a reaction to occur spontaneously, it is not necessarily so. Sometimes, an exothermic reaction will not occur spontaneously, and sometimes, an endothermic reaction will occur spontaneously.

Clearly, the first law of thermodynamics alone is not enough to predict whether a process will occur spontaneously or not. This is illustrated by the two processes shown in Figure 2.3.1.

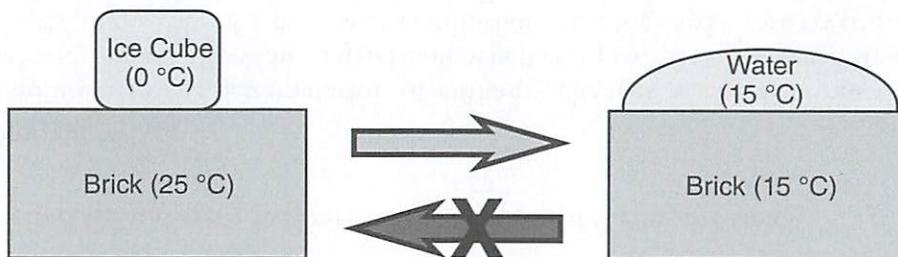


Figure 2.3.1 The melting of ice is a spontaneous process.

1. The forward process. An ice cube (system) placed on a warm brick will melt. The thermal energy provided by the brick disrupts the intermolecular forces that hold the H_2O molecules in the ice together, thereby turning the solid into a liquid. This lowers the temperature of the brick (say, from 25 °C to 15 °C) such that the overall energy of the two bodies is conserved. The process does not violate the first law, and one knows from experience that it will occur spontaneously.
2. The reverse process. A sample of liquid water is placed on the same brick. Both the water and brick are at an initial temperature of 15 °C. Is it possible for the brick to absorb heat from the water, thereby cooling the water so it turns to ice? This process would not violate the first law, but it will not happen spontaneously.

The previous examples demonstrate that energetic considerations alone are insufficient for predicting the direction of spontaneous change. In order to determine whether a process will occur spontaneously, it is necessary to consider another quantity known as *entropy*.

ENTROPY

A simple definition of entropy is that it is a measure of the randomness, or the disorder, of a system. The higher the number of possible arrangements of a system, the greater the entropy. For example, Figure 2.3.2 shows a container divided into two equal volumes. The left half of the container is filled with 1 mole of nitrogen, while the right half is filled with 1 mole of oxygen. The gases are at the same temperature and the two halves are initially separated by a barrier. Once the barrier is removed, mixing takes place. After some time, both sides of the container will be filled with a random mixture of the two gases. The final (mixed) state is more disordered than the initial state. Mixing is a spontaneous process because it increases the entropy of the system. The opposite process, namely spontaneous de-mixing, will not occur.

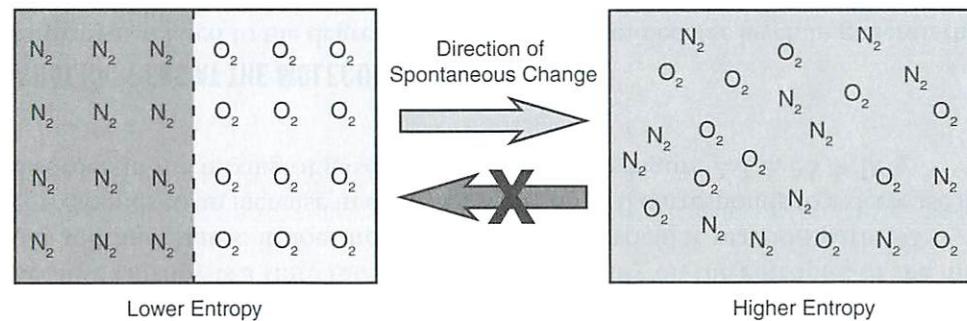


Figure 2.3.2 Mixing of gases is driven by entropy.

Note that processes that occur spontaneously are not necessarily fast. In fact, spontaneity and reaction rate are unrelated. For example, the detonation of an explosive and the corrosion of a piece of metal are both spontaneous processes, but they occur at vastly different rates.

Entropy, S , is a state function. ΔS is the entropy change for a given process:

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

For a chemical reaction, S_{final} and S_{initial} are the entropies of all products and reactants, respectively.

Because entropy is a state function, ΔS depends only on the entropies of the initial and final states; it does not depend on the particular reaction path. $\Delta S > 0$ corresponds to an increase in disorder, while $\Delta S < 0$ corresponds to a decrease in disorder. In the mixing of gases example shown in Figure 2.3.2, $\Delta S > 0$.

WHAT HAPPENS AT THE MOLECULAR LEVEL?

Entropy is related to the degree of disorder at the molecular level. In general, the more random the distribution of molecules, the greater the entropy. States that are highly disordered are generally more probable in nature.

Figure 2.3.3 shows four noninteracting gas molecules (A, B, C, D) randomly moving about in a container. Below the figure is a chart showing the possible arrangements that result in 0, 1, 2, 3, or 4 molecules in the left half of the container. For example, there are four possible arrangements in which three molecules are located in the left half and one molecule in the right half. The situation in which there are two molecules in the left half of the container has the highest number of possible arrangements, six. The system with the largest number of possible arrangements is the most probable state of the system. The greater the number of possible arrangements, the greater the entropy.



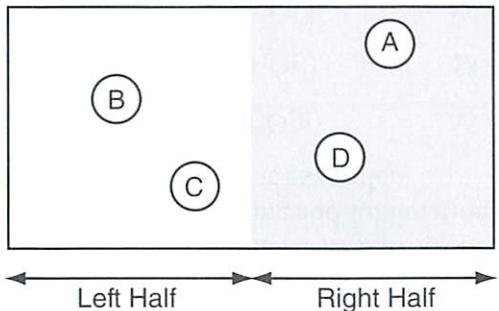


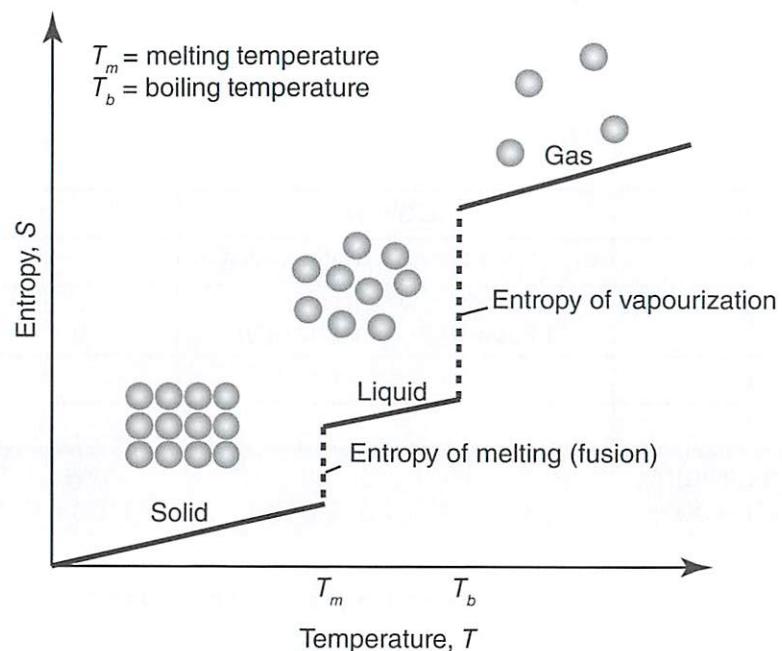
Figure 2.3.3 Random arrangement of four molecules.

# OF MOLECULES IN LEFT HALF	POSSIBLE MOLECULES IN LEFT HALF	# OF POSSIBLE ARRANGEMENTS
0	-	1
1	A or B or C or D	4
2	(A,B) or (A,C) or (A,D) or (B,C) or (B,D) or (C,D)	6
3	(A,B,C) or (A,B,D) or (A,C,D) or (B,C,D)	4
4	(A,B,C,D)	1

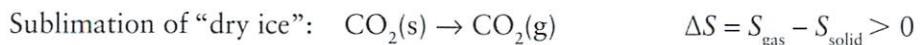
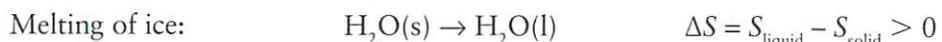
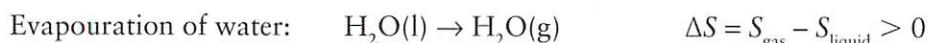
EFFECT OF HEAT AND CHEMICAL REACTIONS ON ENTROPY

Heat

The addition of heat, particularly when associated with a phase change, greatly affects entropy, as shown in the following diagram.



The vapourization of a liquid into a gas increases entropy because the gas is more disordered than the liquid. Similarly, melting and sublimation increase the entropy. For any substance, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$. For example:



Note that the change in entropy from a liquid to a gas is much larger than the change in entropy from a solid to a liquid.



Entropy increases with temperature, which is a measure of the kinetic energy of molecular motion in the system. This includes translational, vibrational, and rotational motions. Atoms and molecules can move in straight lines, and they can also vibrate and rotate. While increasing the temperature of a solid does not increase translational motion (the atoms are fixed in a lattice arrangement), there will be an increase in vibrational motion, hence an increase in entropy.

At a temperature of absolute zero, a substance has no translational or rotational motion, but the atoms are still vibrating due to a quantum effect known as *zero-point vibrational energy*. As it is warmed, the molecules in the solid begin to vibrate more. This vibrational motion results in a larger distribution of atomic or molecular positions, hence an increase in entropy.

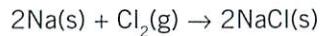
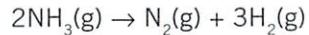
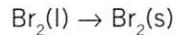
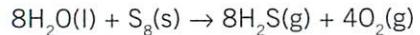
Chemical Reactions

Chemical reactions can greatly affect entropy if they involve one or more reactants or products in the gas phase. Increasing the number of molecules in the gas phase also increases the entropy because two moles of gas particles have more freedom of motion, and therefore more possible arrangements, than one mole of gas particles. For example, in the decomposition of N_2O_4 :



Example 2.3.1. Predicting the Sign of ΔS (In-Class Exercise)

Without any additional data, predict the sign of ΔS° for the following reactions:



THE SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics states that:

Every spontaneous process increases the entropy of the universe.

$$\Delta S_{\text{univ}} > 0$$

Because ΔS_{univ} has contributions from both the system and the surroundings, it can also be stated that for any spontaneous process:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

To determine if a process occurs spontaneously, one has to determine whether the process is associated with an overall increase of entropy to the universe.

It is possible for a spontaneous process to have $\Delta S_{\text{sys}} < 0$, provided that $\Delta S_{\text{surr}} > 0$ is so large that $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$.

For example, spontaneous condensation of water vapour reduces the entropy of the system but the heat released in this process increases the entropy of the surroundings by a larger amount. The overall entropy of the universe increases as a result.

Nature and the Second Law of Thermodynamics

The second law dictates an overall trend in nature towards high entropy, which is equivalent to molecular disorder and chaos. Yet, the world is full of highly ordered structures, such as buildings, streets, cars, plants, animals, people, etc. One might get the impression that the very existence of life contradicts the second law.

A simple explanation is that nature tolerates the creation of order in one part of the universe, as long as this is compensated by the formation of chaos somewhere else. Thus, the presence of highly ordered systems in our environment does not violate the second law. The human body can grow because it consumes enormous amounts of relatively ordered substances (sugars, proteins, fats) and turns them into heat, $\text{CO}_2(\text{g})$, and $\text{H}_2\text{O}(\text{g})$. The release of these gases leads to a tremendous increase in the entropy of the surroundings.



STANDARD MOLAR ENTROPIES

Earlier in this chapter, we mentioned that only the internal energy changes (ΔE) of a system could be determined, not the absolute internal energy. Likewise, with enthalpy, only the enthalpy changes (ΔH) are measurable, not the absolute enthalpy.

With respect to the entropy of solids, the third law of thermodynamics states:

The entropy of a perfectly ordered crystalline solid is defined to be zero at a temperature of absolute zero (0 K).

In the same way that sea level provides a means of determining absolute altitude, this definition of zero entropy allows absolute entropies to be determined.

Using the third law, one can assign a standard molar entropy (S°) to all elements and compounds. The S° values are typically reported in $J\ mol^{-1}\ K^{-1}$ (not $kJ\ mol^{-1}$) and refer to standard states, where all gases have partial pressures of 1 atm and all species in solution have a concentration of 1 M. Usually, the listed values are for a temperature of 298.15 K. Note that the S° values of all elements and compounds are always greater than zero because entropy increases as temperature increases, and $S^\circ = 0$ at 0 K. In contrast, ΔH_f° is zero for elements in their standard states. Standard entropies for selected compounds are shown in Table 2.3.1.

TABLE 2.3.1 STANDARD MOLAR ENTROPIES FOR SELECTED COMPOUNDS

COMPOUND	$S^\circ\ (J\ mol^{-1}\ K^{-1})$	COMPOUND	$S^\circ\ (J\ mol^{-1}\ K^{-1})$
CO(g)	197.7	$\text{CH}_3\text{CH}_2\text{OH(l)}$	160.7
$\text{CO}_2(\text{g})$	213.7	$\text{H}_2(\text{g})$	130.6
$\text{CH}_4(\text{g})$	186.2	$\text{H}_2\text{O(l)}$	69.9
$\text{C}_2\text{H}_4(\text{g})$	200.8	$\text{H}_2\text{O(g)}$	188.7
$\text{C}_2\text{H}_6(\text{g})$	219.5	$\text{N}_2(\text{g})$	191.6
$\text{C}_3\text{H}_8(\text{g})$	269.6	$\text{NH}_3(\text{g})$	111.3
$\text{CH}_3\text{OH(l)}$	126.8	$\text{O}_2(\text{g})$	205.1

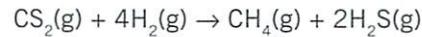
Based on tabulated S° values, the standard entropy change, ΔS° , can be determined for any reaction according to:

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

The equation above is analogous to Hess's law, which was used to find ΔH° from the tabulated ΔH_f° values earlier in the chapter.

Example 2.3.2. Determination of Standard Entropy Change

Determine the standard entropy change for the following reaction:



based on the following S° values in $\text{J mol}^{-1} \text{ K}^{-1}$:

$$\text{CS}_2(\text{g}): 151.0 \quad \text{H}_2(\text{g}): 130.6 \quad \text{CH}_4(\text{g}): 186.2 \quad \text{H}_2\text{S}(\text{g}): 205.6$$

Solution: As entropy is an extensive property, it is important that the equation is balanced. Once the equation is correct, then use the standard entropy change equation:

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(1 \text{ mol} \times 186.2 \text{ J mol}^{-1} \text{ K}^{-1}) + (2 \text{ mol} \times 205.6 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$- [(1 \text{ mol} \times 151.0 \text{ J mol}^{-1} \text{ K}^{-1}) + (4 \text{ mol} \times 130.6 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$\Delta S^\circ = -76.0 \text{ J K}^{-1}$$

The entropy change of this reaction is negative because the number of moles of gas has decreased from 5 to 3.



Section 2.3 Practice Problems

1. A box contains four coins. (a) Complete the table below to show the number of head (H) and tail (T) arrangements that correspond to all observable states of the coins. (b) If the box is shaken and then stopped, what is the most probable distribution of heads and tails in the box?

OBSERVABLE STATE	ARRANGEMENTS (MICROSCOPIC STATES)	NUMBER OF ARRANGEMENTS	PROBABILITY FOR AN OBSERVABLE STATE
4 heads, 0 tails	HHHH	1	
3 heads, 1 tail	HHHT, HHTH...		

2. A container is separated by a wall into two parts with volumes V_1 and V_2 , respectively. In V_1 there is a gas of mass M while V_2 is empty. The wall is removed and, as expected, the gas expands. This process is associated with a change in entropy ΔS_1 . Assume the same setup but instead of V_2 , the volume is $2 \times V_2$. The process is the same but now the gas expands in a larger volume. Is the change in entropy for the second process larger or smaller than the change in entropy in the former process?
3. Use the entropy data in Table 2.3.1 to calculate ΔS° for each of the following reactions:
- $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$
 - $4\text{NH}_3\text{(g)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{N}_2\text{(g)} + 6\text{H}_2\text{O(l)}$
 - $\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$

4. For the following pairs of substances, all under standard conditions, predict which one of each pair has the larger standard entropy and explain why:
 - a. 2 moles of NO_2 and 1 mole of N_2O_4
 - b. Hg and Au
 - c. 1 mole of each of He(g) and $\text{H}_2\text{O(g)}$
 - d. 1 mole of each of S_6 and S_8
5. One mole of ice at 0.0°C is heated to 100°C and then is cooled back into ice at 0.0°C . The pressure of the initial and final state of the system is the same.
 - a. Is the change in the entropy of the system positive, negative, or zero?
 - b. Does the rapid or slow way that the process may take place affect the answer in (a)?
6. A container holds 1 mole of liquid water at 25°C , which is subsequently heated to 50°C at constant pressure. Is the change in entropy of the system positive, negative, or zero?
7. Consider the same system in Problem 6, but instead of heating, work is performed on the system by shaking the container or stirring the water. Can one achieve the same change in entropy as Problem 6 by performing work on the system instead of transferring heat? Justify your answer.
8. What is the entropy change when two moles of water at 0°C turn into ice at 0°C ? The ΔH_{fusion} of water is 6.01 kJ mol^{-1} .



■ 2.4 Free Energy

OBJECTIVES

After studying this topic, you should be able to:

- Describe and use the Gibbs free energy relationship to determine the spontaneity of a reaction.
- Explain whether a reaction is enthalpically or entropically driven, or both.
- Apply the Gibbs relationship in the determination of phase change temperatures.

FREE ENERGY

The second law of thermodynamics states that every spontaneous process increases the entropy of the universe.

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad (2.4.1)$$

Because the universe is an isolated system itself, the second law can also be stated as follows: A process in an *isolated* system is spontaneous if

$$\Delta S_{\text{sys}} > 0 \quad (2.4.2)$$

The case of an isolated system is of limited interest in chemistry where one often deals with *closed* systems at *constant temperature and pressure*. It would be useful to have a criterion of spontaneity that would apply to systems under constant T and P . Fortunately such a criterion exists, as we will now show.

When a process occurs at *constant pressure and temperature*, the heat change associated with the surroundings is given by ΔH_{surr} . One can show that, under these conditions, the entropy change of the surroundings is:

$$\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T}$$

In any given process, the amount of heat flowing out of a system and into the surroundings, and vice versa, must be equal in magnitude but opposite in sign. That is, $\Delta H_{\text{surr}} = -\Delta H_{\text{sys}}$ and so, at constant T and P ,

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad (2.4.3)$$

After substituting Equation 2.4.1 into Equation 2.4.3, we obtain:

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \quad (2.4.4)$$

For processes occurring at constant temperature and pressure, Equation 2.4.4 is equivalent to Equation 2.4.1, but involves only the properties of the system. In the next few expressions, the subscript “sys” will be dropped and it will be assumed that all thermodynamics properties are those of the system.

After multiplying both sides of Equation 2.4.4 by $(-T)$, the equation for any spontaneous change becomes:

$$\Delta H - T\Delta S < 0 \quad (2.4.5)$$

Equation 2.4.5 helps introduce a new thermodynamic quantity, the *Gibbs free energy*, G , which is expressed as:

$$G = H - TS \quad (2.4.6)$$

The Gibbs free energy, named after American scientist J. W. Gibbs, is the amount of energy that is available (or “free”) to enable spontaneous change to occur at constant temperature and pressure. The Gibbs free energy is a state function, and every chemical reaction is associated with a free energy change given by:

$$\Delta G = \sum G_{\text{products}} - \sum G_{\text{reactants}}$$

Combined with Equation 2.4.6, this free energy change can also be expressed as:

$$\Delta G = \Delta H - T\Delta S \quad (2.4.7)$$

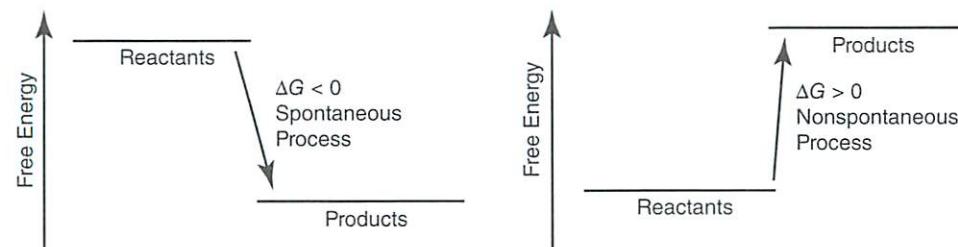
This relationship, known as the Gibbs equation, is one of the most important relationships in thermodynamics. With Equations 2.4.7 and 2.4.5, the second law of thermodynamics can be described as “for every process spontaneous at constant temperature and pressure, $\Delta G < 0$.”



Thus, the criteria of spontaneity of a process at constant temperature and pressure are as follows:

- $\Delta G < 0$ The reaction will proceed spontaneously as written.
- $\Delta G = 0$ The system is at equilibrium. The numbers of moles of reactants and products do not change over time.
- $\Delta G > 0$ The reaction will not proceed spontaneously as written; instead, the reverse process will proceed spontaneously.

A negative value for ΔG does not necessarily indicate that the reaction proceeds to completion. When $\Delta G < 0$, the reaction *favours* the formation of the products. Similarly, a positive value for ΔG does not necessarily indicate there are no products formed. When $\Delta G > 0$, the reaction *favours* the reactants, with little or no products formed. The extent of the reaction is determined by the sign and magnitude of ΔG .



WHAT DRIVES A PROCESS?

The sign of $\Delta G = \Delta H - T\Delta S$ is determined by the signs of ΔH and ΔS . The four possible sign combinations are summarized in Table 2.4.1.

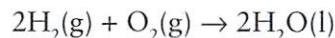
TABLE 2.4.1 IMPACT OF SIGNS ON ΔG

ΔH	ΔS	ΔG	COMMENTS
-	+	-	Enthalpically and entropically driven
+	-	+	
-	-	+ or - *	Enthalpically driven, if spontaneous
+	+	+ or - *	Entropically driven, if spontaneous

* The sign may change with temperature.

Enthalpically Driven Processes

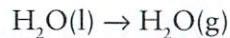
Most strongly exothermic reactions ($\Delta H \ll 0$) are spontaneous regardless of the sign of ΔS because the large negative magnitude of ΔH tends to make ΔG negative. For example, consider the reaction:



which has $\Delta H \ll 0$. Although this process is associated with an entropy decrease ($\Delta S < 0$, which is unfavourable), $\Delta G = (\Delta H - T\Delta S) < 0$. The free energy change of this spontaneous process can be harnessed by hydrogen fuel cells in the form of electricity. Spontaneous processes with $\Delta H < 0$ and $\Delta S < 0$ are said to be *enthalpically driven*.

Entropically Driven Processes

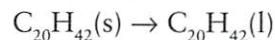
Endothermic reactions ($\Delta H > 0$) can only be spontaneous if they are associated with a large entropy increase ($\Delta S \gg 0$) such that $\Delta G = (\Delta H - T\Delta S) < 0$. These processes are said to be *entropically driven*. One example is the evaporation of water:



Water that evaporates from the palm of a human hand makes it feel cold because the process absorbs heat from the skin. For the same reason, the production of sweat is an effective way to reduce body temperature.

It is not a bad approximation to assume that ΔH and ΔS are independent of temperature. Then Equation 2.4.7 provides a simple means to predict how changes in temperature will affect the spontaneity of chemical reactions.

For example, why does candle wax melt at an elevated temperature? Candle wax is mainly composed of a long-chain alkane, $\text{C}_{20}\text{H}_{42}$. The phase change is:



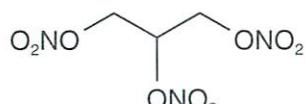
The individual alkane chains in the solid are held together by intermolecular forces. Breaking these interactions requires energy, so $\Delta H > 0$. Furthermore, it is known that $\Delta S > 0$, as it is for any solid-to-liquid phase transition. At room temperature, $T\Delta S$ is small, so $\Delta G = (\Delta H - T\Delta S) > 0$ and the candle wax remains in the solid state. As temperature increases, the magnitude of $T\Delta S$ increases, eventually causing ΔG to become negative. Melting is therefore entropically driven.



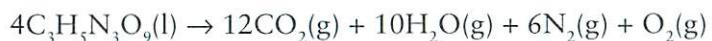
There is a point where the temperature gives a ΔG of zero. This temperature is the melting point temperature (T_m), and at this temperature, $\Delta G = 0$, so $\Delta H_{\text{fus}} = T_m \Delta S_{\text{fus}}$. Analogously, for a liquid-to-gas transition, the boiling temperature (T_b) is defined as $\Delta H_{\text{evap}} = T_b \Delta S_{\text{evap}}$.

Enthalpically and Entropically Driven Processes

Some processes are spontaneous because they are associated with favourable enthalpy and entropy changes ($\Delta H < 0$ and $\Delta S > 0$). For example, the decomposition of an explosive, such as nitroglycerin:



nitroglycerin



is highly exothermic ($\Delta H \ll 0$) and produces an increase of entropy ($\Delta S \gg 0$) such that $\Delta G = (\Delta H - T\Delta S) < 0$. Reactions of this type are said to be both *enthalpically and entropically driven*.

STANDARD FREE ENERGY CHANGE

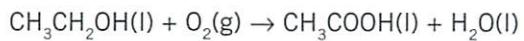
Like ΔH , the sign and magnitude of ΔG is affected by temperature, pressure, and the concentrations of reactants and products. It is often useful to focus on standard conditions, where all gases are present at a partial pressure of 1 atm, all species in solution have a concentration of 1 M, and the system temperature is 298.15 K. The free energy change under standard conditions is denoted as ΔG° . Equation 2.4.7 becomes:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2.4.8)$$

where ΔS° is the standard entropy change and ΔH° is the standard enthalpy change, both of which were discussed in previous topics.

Example 2.4.1. Spontaneity of a Reaction (In-Class Exercise)

Use the data below to determine if the oxidation of ethanol to acetic acid is spontaneous under standard conditions at 25 °C.



ΔH°_f (kJ mol ⁻¹)	-288.3	0	-485.8	-285.8
S° (J mol ⁻¹ K ⁻¹)	148.5	205.0	178.7	69.9

Is this process enthalpically or entropically driven, or both?

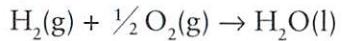
STANDARD FREE ENERGY OF FORMATION

As with enthalpy, the absolute free energy of a substance cannot be determined. ΔG°_f , the *standard free energy of formation*, is the standard free energy change that occurs when 1 mol of a compound is made from elements in their standard states. This definition is analogous to that of ΔH°_f .

Likewise, the ΔG°_f of any element in its standard state is defined as zero:

$$\Delta G^\circ_f(\text{element in standard state}) = 0$$

For example, the reaction:



has a ΔG° of -237.2 kJ mol⁻¹. Thus, the ΔG°_f of $\text{H}_2\text{O(l)}$ is -237.2 kJ mol⁻¹, because $\text{H}_2\text{(g)}$ and $\text{O}_2\text{(g)}$ are elements and are defined as having with $\Delta G^\circ_f = 0$.

Because free energy is a state function it can be stated that:

$$\Delta G^\circ = \sum \Delta G^\circ_f(\text{products}) - \sum \Delta G^\circ_f(\text{reactants}) \quad (2.4.9)$$

Equation 2.4.9 is analogous to Hess's law. Therefore, ΔG° for any reaction can be determined based on tabulated data that lists the standard free energy of formation (ΔG°_f) of the reactants and products.



Example 2.4.2. Determination of Standard Free Energy

Determine ΔG° for the following reaction:



based on the following ΔG_f° (kJ mol⁻¹):

$\text{KClO}_3(\text{s})$: -296.3 $\text{KClO}_4(\text{s})$: -303.2 $\text{KCl}(\text{s})$: -409.2

Using Equation 2.4.9:

$$\begin{aligned}\Delta G^\circ &= [(3 \text{ mol } \text{KClO}_4 \times -303.2 \text{ kJ mol}^{-1}) + (1 \text{ mol } \text{KCl} \times -409.2 \text{ kJ mol}^{-1})] \\ &\quad - [(4 \text{ mol } \text{KClO}_3 \times -296.3 \text{ kJ mol}^{-1})] \\ &= -133.6 \text{ kJ}\end{aligned}$$

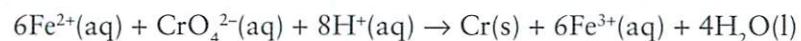
Section 2.4 Practice Problems

1. Determine ΔG° for the reaction: $N_2(g) + O_2(g) \rightarrow 2NO(g)$ at 25 °C based on the following data:

	$N_2(g)$	$O_2(g)$	$NO(g)$
ΔH_f° (kJ mol ⁻¹)	0	0	90.2
S° (J mol ⁻¹ K ⁻¹)	191.5	205.0	210.7

Will this reaction occur spontaneously?

2. Determine ΔG° for the reaction:



Data: ΔG_f° (kJ mol⁻¹): $Fe^{2+}(aq) = -78.9$; $CrO_4^{2-}(aq) = -727.8$; $H^+(aq) = 0$; $Fe^{3+}(aq) = -4.7$; $H_2O(l) = -228.6$

3. The oxidation of ethanol releases energy. Does the oxidation of 1 g of ethanol, C_2H_5OH , produce more or less Gibbs free energy than the oxidation of 1 g of glucose, $C_6H_{12}O_6$? Write a balanced equation for each reaction. Based on the results, which reaction occurs faster?

Data: ΔG_f° (kJ mol⁻¹): $C_2H_5OH(l) = -174.8$; $C_6H_{12}O_6(s) = -917.2$; $H_2O(l) = -120.4$; $CO_2(g) = -394.4$

4. Consider a reaction where $\Delta H^\circ = 150$ kJ and $\Delta S^\circ = 400$ J K⁻¹.

- Will this reaction occur spontaneously at 25 °C?
- What is the minimum temperature at which the reaction will occur spontaneously?

5. Estimate the boiling point of Br_2 based on the following data:

$$S^\circ Br_2(l) = 152.2 \text{ J mol}^{-1} \text{ K}^{-1} \quad S^\circ Br_2(g) = 245.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H_f^\circ Br_2(g) = 30.91 \text{ kJ mol}^{-1}$$



6. Organ pipes in unheated churches develop “tin disease,” in which white tin is converted to grey tin. What is the minimum temperature at which the church must be maintained in order to prevent the reaction from occurring?

	White Sn	Grey Sn
ΔH_f° (kJ mol ⁻¹)	0	-2.09
S° (J mol ⁻¹ K ⁻¹)	51.55	44.14

7. Which of the following is/are true?
- A formation reaction is one in which one mole of compound is made from its constituents in their most stable thermodynamic state, at 25 °C, 1 atm.
 - Entropy and energy are equivalent.
 - Under standard conditions, ΔG° for a reaction can be used as a criterion for spontaneity.

