Faculty of Science

Unit 5:
Thermodynamics

CHEM 1523
Principles of Chemistry

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Overview

The science of thermodynamics (*thermo*, heat, and *dynamics*, change) was developed during the mid-nineteenth century in response to questions raised by the technology of the Industrial Revolution—in particular, to attempts to make the steam engine more efficient. It was soon apparent that there is a definite upper limit on the amount of work that such an engine can do for a given energy input. No conceivable mechanical or technological advancement would ever raise this limit. Mathematical relationships limit the efficiency of engines. Thermodynamics can be thought of as the science of the possible—or of the impossible.

How is thermodynamics related to chemistry? A large part chemical science has to do with changes of one kind or another: chemical change (change in composition), changes in physical state, and so forth. Sometimes these changes take place in one direction and sometimes in another. For example, below a certain temperature an equimolar mixture of H_2 and O_2 has a tendency to change into water. Above this temperature, the reverse process, the decomposition of H_2O, occurs. Thermodynamics predicts the conditions for this kind of change *on the basis of certain observable properties of the reactants and products*. As you can imagine, such a prediction tool saves the chemist a great deal of work. With thermodynamics, every possible chemical reaction does not have to be studied experimentally. One of the crucial questions of chemistry is, "Will some change tend to occur?" If the thermodynamic answer is "no," then the chemical system is said to be at **equilibrium**. If the answer is "yes," then the substances present are not at equilibrium and they will tend to react or change until equilibrium is achieved.

Thermodynamics answers the question, "Does a particular reaction occur?" In many cases, the answer to this question is obvious. The cartoon in Figure 5.1, below, illustrates this point. The humour in the situation of a rock slide crashing uphill is that you know very well from your everyday experience that this does not happen, and you can probably predict with confidence that it is unlikely to ever happen. All your past experience should tell you that the opposite is what will happen. A boulder will roll down a hill, converting potential energy into kinetic energy as it rolls. The kinetic energy will be dispersed. To get boulders to behave as those in the cartoon, dispersed kinetic energy would have to become concentrated in the boulders and roll them back up the hill. Experience tells you that this is improbable enough to be able to call such an event impossible. A study of thermodynamics gives you a mathematical basis for labelling certain physical events or chemical reactions as impossible.

A reaction that is thermodynamically possible is known as a **spontaneous reaction**. Thermodynamics does not deal with the concept of time. All thermodynamics addresses are whether or not the reaction "goes." How long the reaction takes is immaterial to thermodynamics (Unit 2 of this course, on kinetics, dealt with such questions of time). To be able to make predictions on the spontaneity of a particular reaction, you first will be introduced to the concept of **entropy**, the degree of disorder. Entropy can be a puzzling notion to students. You may think that there is no way to measure entropy since you cannot put it in a volumetric flask, or weigh it, or measure it with a thermometer. But entropy is not a vague philosophical idea. It can be measured, although not with an "entropy meter." As you work through this unit you will find that you already have an understanding of entropy even though you may have never called it by this name.

Figure 5.1: Thermodynamics in action!

The subject of thermodynamics is quite independent of the atomic theory since you do not need to invoke atoms or molecules to apply the laws of thermodynamics. This means that thermodynamics can be used to answer a wider variety of questions than those we might deal with in a chemistry course.

Are perpetual motion machines possible? How do refrigerators work? Why do boulders not roll uphill by themselves? Will you get more heat from a neatly laid fire than from a randomly laid fire? Can you build a 100% efficient machine? Is an energy crisis inevitable? By the end of this unit, you will be able to apply thermodynamics to the consideration of such questions.

Learning Outcomes

Once you have finished this unit, you should be able to:

- Explain the physical meaning and consequences of the first law of thermodynamics.
- Define system, surroundings, reversible process, internal energy, enthalpy, heat, and work.
- Calculate the heat of a reaction from tables of standard enthalpies of formation (Hess's law calculations).
- Calculate ΔE of a specified reaction from the ΔH of the reaction, and vice versa.
- Explain the concept of entropy and its relationship to the second and third laws of thermodynamics.
- Calculate and/or estimate $\Delta S°$ for phase changes and chemical reactions.
- Describe the physical significance of free energy and of the free energy change, ΔG.
- Use tables of standard ΔG of formation to determine whether a given reaction will take place spontaneously at a specified temperature.
- Calculate equilibrium constants from $\Delta G°$ values, and vice versa.

Thermochemistry

When chemical substances react to produce products, there is almost always a loss or gain of potential energy. These differences are mainly due to the differences in energies of the chemical bonds in the reactants and in the products. When the products are more strongly bonded (lower potential energy) than the reactants, the excess energy is usually given off as heat. Occasionally the reverse situation applies, and the reactants absorb heat from the surroundings when forming products. Virtually all chemical changes are accompanied by the emission or absorption of heat, and the study of these heat changes is known as **thermochemistry**.

Study Sections 6.1, 6.2, and 6.3 in your textbook. You should know the terms **endothermic** and **exothermic reactions**. Note particularly that just because many reactions occurring at room temperature give out heat (are exothermic), that does not mean *all* reactions occurring at room temperature are exothermic.

However, most reactions at room temperature or below are exothermic. At higher temperature, endothermic reactions are often favoured. Later in this unit, we will examine the concept of thermodynamic spontaneity, that is, the conditions that allow a reaction to "go." You will then see that whether or not a reaction is exothermic is just part, although usually a large part, of the driving force behind a reaction.

The change in **enthalpy** of a reaction (given the symbol ΔH) is the heat liberated or absorbed when the reaction is carried out at constant pressure. This is a commonly used thermochemical value. Most reactions are at a constant pressure of 1.00 atm, but why a value of 1.00 atm? The answer is simply because this is the generally found atmospheric pressure. It is important to realize that you cannot measure H, the enthalpy of a single substance, but only ΔH, the overall change in enthalpy between the reactants and the products of a reaction. For convenience, the enthalpy of an element at 25°C and 1.00 atm is arbitrarily defined as zero. If two such compounds combine to form a compound and heat is given off, then the enthalpy of the compound is known. Of course, this is really the enthalpy difference between the reactants and the products. That is why the enthalpy values of compounds are given as ΔH instead of H.

Pay particular attention to the guidelines explained in Section 6.3 of the textbook. These statements provide you with working rules on the use of ΔH and thermochemical equations. Work through Example 6.1 and its practice exercise.

Calorimetry

Study Section 6.5 in your textbook. **Calorimetry** is the process of measuring the heat flow between system and surroundings. The temperature change when heat flows from a system to a **calorimeter** is used to measure this heat flow. To relate temperature change (usually an increase) of the calorimeter to the heat flow, you must know the definition of heat capacity.

$$\text{heat capacity} = \frac{\text{heat absorbed}}{\Delta t}$$

Heat capacities of substances are given as **specific heat capacity**, or as **molar heat capacity**. The specific heat capacity refers to the heat required to raise the temperature of one gram of a substance by 1°C. The molar heat capacity is that amount of heat necessary to raise the temperature of one mole of a substance by 1°C. This means that

molar heat capacity = specific heat capacity × molar mass

You are not required to memorize specific or molar heat capacities; they would be given to you if needed.

The heat capacity of a substance is an important property because it relates the temperature change to the amount of heat entering or leaving the substance. If the heat capacity is high, as is the case for water, then the temperature is less affected by changes in heat content. This is why large bodies of water tend to have a moderating influence on coastal climates. Metals, in contrast, have very low heat capacities, so their temperatures change greatly when heat flows to or from them.

The SI metric unit of heat energy is the joule ($kg\, m^2\, s^{-2}$) and the standard value of a joule is not taken as a direct measurement of heat. Heat capacities of substances differ with temperature. This difference is usually small and is neglected over the temperature ranges normally found in the laboratory.
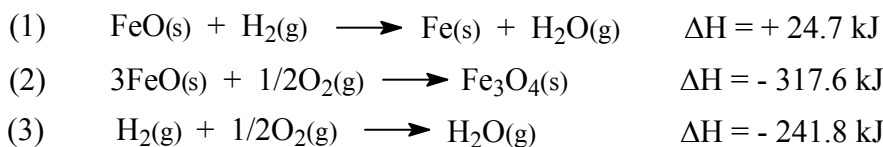
Work through Example 6.5 in the textbook and its practice exercise. Then go over Example 6.6, which involves a bomb calorimeter. In this case, the heat capacity refers to the total heat capacity of everything inside the bomb calorimeter; that is, the water, the reaction chamber, the thermometer, and so on. The heat capacity for a particular calorimeter remains constant provided you always use the same amount of water. The heat capacity of the chemicals inside the reaction chamber is usually small compared to the heat capacity of the calorimeter and thus is often disregarded. Try the practice exercise with Example 6.6 to make sure you understand these concepts.

Example 6.7 and its practice exercise involve the use of a constant pressure calorimeter. These are most often used when the reaction does not involve gases.
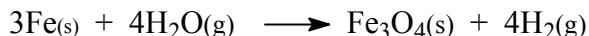
Hess's Law

Study Section 6.6 of your textbook. **Hess's law** says that the overall ΔH of a reaction is the sum of the ΔH's of the steps of the reaction. In other words, enthalpies are additive. Study this material carefully and work through Example 6.9 and its practice exercise. In addition, go over the Hess's law calculation in the Chemistry in Action box in this section. Hess's law calculations are not as complicated as they might appear at first glance. All you are doing is manipulating the equations by reversing or multiplying them. Then you make parallel manipulations to the given ΔH values before adding them.
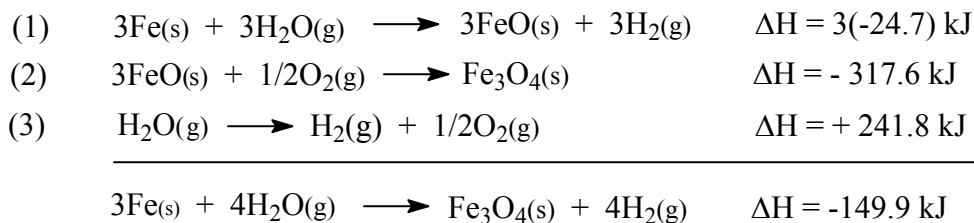
Problem: Given

(1) $FeO_{(s)} + H_{2(g)} \longrightarrow Fe_{(s)} + H_2O_{(g)}$ $\Delta H = + 24.7\ kJ$

(2) $3FeO_{(s)} + 1/2O_{2(g)} \longrightarrow Fe_3O_{4(s)}$ $\Delta H = - 317.6\ kJ$

(3) $H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H = - 241.8\ kJ$

calculate the ΔH for the reaction

$$3Fe_{(s)} + 4H_2O_{(g)} \longrightarrow Fe_3O_{4(s)} + 4H_{2(g)}$$

Solution: You need to rearrange equations (1), (2), and (3) so that you can cancel out compounds and elements not found in the final equation. Start by arranging the equations so that species you want as reactants are on the left-hand side of the equation and species you want as products are on the right-hand side of the equation. For this example, the manipulation is

(1) $3Fe_{(s)} + 3H_2O_{(g)} \longrightarrow 3FeO_{(s)} + 3H_{2(g)}$ $\Delta H = 3(-24.7)$ kJ

(2) $3FeO_{(s)} + 1/2O_{2(g)} \longrightarrow Fe_3O_{4(s)}$ $\Delta H = -317.6$ kJ

(3) $H_2O_{(g)} \longrightarrow H_{2(g)} + 1/2O_{2(g)}$ $\Delta H = +241.8$ kJ

_____

$3Fe_{(s)} + 4H_2O_{(g)} \longrightarrow Fe_3O_{4(s)} + 4H_{2(g)}$ $\Delta H = -149.9$ kJ

Note that the $\frac{1}{2}O_{2(g)}$ on the left-hand side cancels out with the $\frac{1}{2}O_{2(g)}$ on the right-hand side. Similarly, $3FeO_{(s)}$ vanishes from the total equation. Equation (1) is reversed and multiplied by 3. Equation (2) remains the same. Equation (3) is reversed. The ΔH value for equation (1) is reversed and multiplied by 3, ΔH for equation (2) remains the same, and ΔH for equation (3) is reversed. Summation of these ΔH values gives

$$3(-24.7) + (-317.6 + 241.8) = -149.9 \text{ kJ}$$

as shown above.

Hess's law can be applied to the making and breaking of bonds in a chemical reaction. Chemical bonds form when electrons and nuclei arrange themselves in a configuration of low potential energy. The energy lost is given off as heat. Thus, bond-making reactions are always exothermic. Similarly, to break a chemical bond, electrons must be pulled away from nuclei. This requires energy to be put into the system. Bond-breaking reactions are thus endothermic. Chemical reactions involve *rearrangements* of atoms—that is, bond breaking and bond making. Whether the overall process is endothermic or exothermic depends on whether more heat is released during bond making than is absorbed during bond breaking. Table 9.4 in Chapter 9 of your textbook lists bond energies for various bonds—remember, these values are positive if the bond is breaking and negative if the bond is forming.

The Born-Haber cycle is another example of an application of Hess's law.

## Standard Enthalpies of Formation and Reaction

A particular common enthalpy change is enthalpy (or heat) of formation, usually quoted at standard conditions of 1 atmosphere and 25°C.

The degree sign in ΔH°_f or ΔH°_{form} denotes standard state. The standard heat of formation is defined as the heat released or absorbed when a compound is formed from its elements in their standard state.

Thus, if you are given a ΔH°_f of a compound, you can write an equation for the reaction of formation. For example

$$\Delta H^\circ_f (H_2SO_4, \ell) = -814 \text{ kJ/mol}$$

means that the reaction

$$H_2(g) + S(s) + 2O_2(g) \longrightarrow H_2SO_4(\ell)$$
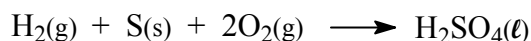
has a $\Delta H^\circ_{reaction}$ of –814 kJ / mol H_2SO_4. H_2SO_4 is not formed in one reaction as this equation might lead you to believe. But the series of steps that leads to the formation of H_2SO_4 from its elements is, overall, exothermic, releasing 814 kJ of heat per mole of $H_2SO_4(\ell)$ formed.

$\Delta H^\circ_f (NH_4Br, s) = -270$ kJ/mol means

$$\tfrac{1}{2}N_2(g) + 2H_2(g) + \tfrac{1}{2}Br_2(\ell) \rightarrow NH_4Br(s)$$
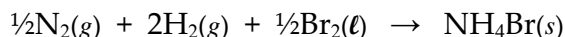
has a $\Delta H^\circ_{reaction}$ of –270 kJ/mol.

A list of ΔH°_f values is given in Appendix 3 and in Table 6.4 of your textbook. You do not need to memorize these values. If necessary, they would be given to you in an examination.

If you are supplied with ΔH°_f values for the species involved, a simplified approach to Hess's law calculations uses the general statement that

$$\Delta H^\circ_{reaction} = \Sigma\, \Delta H^\circ_f(\text{products}) - \Sigma\, \Delta H^\circ_f(\text{reactants})$$

where Σ means *the sum of*. In the previous example,

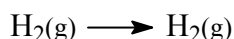$$3Fe(s) + 4H_2O(g) \longrightarrow Fe_3O_4(s) + 4H_2(g)$$
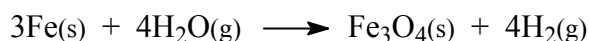
The value of $\Delta H^\circ_{reaction}$ is

$$\Delta H^\circ_f (Fe_3O_4, s) - 4[\Delta H^\circ_f (H_2O, g)]$$

Using the values of ΔH°_f found in Appendix 3 and the ΔH°_f value of $Fe_3O_4(s)$ of –1118 kJ mol^{-1},

$$\Delta H^\circ_{reaction} = (-1118) - 4(-242) = -150 \text{ kJ}$$

Note that if you are not told otherwise, you can assume that the reaction occurs under standard conditions. Also note that the ΔH°_f for an element is zero. That is, for the reaction

$$H_2(g) \longrightarrow H_2(g)$$

there is no enthalpy change—and neither is there a reaction when you form an element in its standard state from itself in its standard state.

In addition to $\Delta H°_{reaction}$ (also written as $\Delta H°_{rxn}$), you may also encounter the symbols for standard enthalpy change of phase transition. These are $\Delta H°_{vap}$, $\Delta H°_{sub}$, and $\Delta H°_{fus}$.

Now read about heat of solution and dilution in Section 6.7 of the textbook.

Thermodynamic Definitions

Review Section 6.3 in your textbook to be sure that you understand the difference between **system** and **surroundings**. In most chemical reactions this difference is clear-cut, but you can define the system as you see fit. Normally we consider everything inside a container as part of the system, and the surroundings as what lies outside of the container. This means that the container is the **boundary** between the system and the surroundings. However, if you choose, you can include the room with the container to be part of the system. The surroundings will then be everything outside the room. Defining the limits of the system (by specifying a well-defined boundary) is up to you. Once you define the system, you must be consistent in dealing with it.

An **isolated** system is one where there is no energy or mass transfer across the boundary between system and surroundings. The only example of a *true* isolated system is the universe, but many chemical and physical systems act for all intents and purposes as if they were isolated. Hot coffee inside a Thermos flask is considered an isolated system. Of course, once you open the Thermos and pour out the coffee, then both energy and mass are transferred and the system is no longer isolated. Even if you do not open it, no insulated flask can retain its heat forever; no Thermos is a true isolated system.

State functions are path independent. Think of a system consisting of a block of aluminum. If this piece of aluminum is in a definite *state* (defined by its volume, its temperature, and the pressure on it), then every other property of the aluminum is defined. The variables *V*, *T*, and *P* are sufficient to fix the values of all other properties, such as density, number of moles, and so on. If the block of aluminum at 25°C is heated to 100°C, cooled to 50°C, and then heated to 150°C, the final state of the aluminum will be the same as if it had been heated to 150°C directly. This is what is meant by a **path-independent state function**. The volume of the aluminum at 150°C does not depend on how the aluminum reached the temperature. This may seem trivially obvious, but it is important that you can distinguish path-independent state functions.

This unit concentrates on four state functions: internal energy (*E*), enthalpy (*H*), entropy (*S*), and free energy (*G*). It is usually not possible to determine the absolute value of these state functions, rather, the change in the function is measured.

The change in the internal energy of a system, ΔE, is measured in joules. You may sometimes come across the non-metric unit of energy, the calorie (the relative conversion factor is 1 cal = 4.184 J). Calories are still used in nutritional analysis, although the nutritional calorie unit is actually a kilocalorie! The calorie count of an apple at 85 calories does not seem very large but, converted to its SI metric equivalent, 85 nutritional calories is really 85,000 calories times 4.184 J/cal, or 355,640 joules. The psychological effect of this would probably have dieters forsaking their diets! The second Chemistry in Action box in Chapter 6 of the textbook discusses nutrition.

Work and Heat

Work and heat are given lower-case letter symbols, *w* and *q*. The lower-case letter symbol denotes that they are path-dependent quantities. They are not state functions. They represent processes. Suppose you take a container of water and stir it vigorously. The mechanical work you do on the system (the water) may raise its temperature by a few degrees. You could achieve the same effect by placing the container of water on a stove for a few minutes. The final state of the water is defined by its change in temperature and is independent of how it reached this temperature. One method of raising the temperature will not give the water more "heat," and the other method will not give the water more "work." Work and heat are processes that raise the temperature of the water.

In this unit, the term *work* refers to simple mechanical work. Work also has the energy unit, the joule. If the system does work, the sign of w is negative. This can be explained by saying that the total energy of the system decreases. Some of this energy is transformed and used as work. It is lost to the system. If work is done on the system, then the total energy of the system increases, so work done on the system is positive. The mechanical work considered in thermodynamics is generally work of expansion or contraction of gaseous systems. Work is defined as

$$w = -P_{external}\Delta V$$

where $\Delta V = V_{final} - V_{initial}$. For an expansion, $V_{final} > V_{initial}$ and ΔV is positive. Thus, work of expansion is negative (the system is doing the work). For a contraction, $V_{final} < V_{initial}$ and ΔV is negative. Thus, work of contraction is positive (as you would expect when the surroundings do work on the system and it contracts).

Units of pressure are N / m^2, pressure is force per unit area, and units of volume are m^3. On substitution

$$\text{Unit of work} = -N \times m^{-2} \times m^{3} = -N\,m$$

$$= -J \text{ (a newton metre is a joule)}$$

The conversion from litre atmosphere to joules is 1 L atm = 101.3 J.

If heat is absorbed by the system, the total energy of the system increases; q is positive. If the system loses heat, then the total energy of the system is reduced and q is negative. The SI unit of heat is the joule. If you are given this in calories, it can be converted by using the equation 1 calorie = 4.184 joules. Students sometimes think that a reaction that gives out heat should not have a negative value, probably because they can feel an increase in the temperature of the surroundings. Remember that you are part of the *surroundings* and that the sign of q tells you what is happening to the *system*. It is worth repeating this convention for the signs of heat and work. Memorize the following:

$$\text{heat absorbed by the system} = +q$$
$$\text{heat released by the system} = -q$$
$$\text{work done on the system} = +w$$
$$\text{work done by the system} = -w$$

The First Law of Thermodynamics

Study Section 6.4 of your textbook. Sections 6.3 and 6.4 provide a good description of the first law and of the thermodynamic basis for being able to eliminate the possibility of a perpetual motion machine. You should memorize the mathematical statement of the first law:

$$\Delta E = q + w$$

where the signs of q and w are as summarized above. You should also be able to explain what the **first law of thermodynamics** means. It simply says that there are only two ways the internal energy of the system can be changed; the system can do work or have work done on it, and heat may pass in either direction across the boundary. This really amounts to a statement of the law of conservation of energy. As an example, think of an engine that produces 1000 J of work. It will need to be supplied with at least 1000 J of heat (through combustion of an equivalent amount of fuel). If less heat than necessary is supplied, the rest of the work would have to be supplied at the expense of the internal energy of the engine. This would lower the engine's temperature and eventually it would freeze! Implicit in this is the concept of an isothermal process, where the temperature of the system remains unchanged. If the system does work on the surroundings and its temperature remains constant, then its internal energy, ΔE, remains constant. This means that heat must flow into the system to replace the energy lost as work.

Similarly, if the system absorbs heat isothermally (its temperature remains constant), then it must do work on the surroundings to rid itself of the excess energy.

Work through Example 6.2 and its practice exercise in your textbook, then try the following calculations.

Problem: During an isothermal reaction, the system absorbed 11.4 J of heat. Calculate the work done on or by the system.

Solution: $\Delta E = q + w$. For a constant temperature process, $\Delta E = 0$, and since $q = +11.4$, $\Delta E = 0 = +11.4 + w$, we have $w = -11.4$ J. This tells you that work is done by the system. Since heat is absorbed, the system must have a means of using up this extra energy to keep its internal energy unchanged ($\Delta E = 0$). Therefore, the system uses up this energy by doing work.

Problem: Calculate ΔE when the system absorbs 34 J of heat and has 16 J of work performed on it.

Solution:

$$q = +34 \text{ J} \qquad w = +16 \text{ J}$$

Therefore, $\qquad \Delta E = q + w = (+34) + (+16) = +50$ J

Problem: Calculate ΔE when the system releases 67 J of heat and does 42 J of work.

Solution:

$$q = -67 \text{ J} \qquad w = -42 \text{ J}$$

Therefore, $\qquad \Delta E = q + w = (-67) + (-42) = -109$ J

Problem: Calculate ΔE when the system releases 67 J of heat and has 16 J of work performed on it.

Solution:

$$q = -67 \text{ J} \qquad w = +16 \text{ J}$$

Therefore, $\qquad \Delta E = q + w = (-67) + (+16) = -51$ J

These examples show how important it is to make sure you specify the correct sign for heat and work.

In constant volume reactions, $\Delta V = 0$, so $P \Delta V = 0$ and work = 0. That is, when there is no expansion or contraction, no mechanical work is involved. In this case, $\Delta E = q$, or $\Delta E = q_v$, where the subscript v indicates a constant volume. Another important type of process is one where no heat flows across the boundary. In such an **adiabatic** process, no heat is exchanged, $q = 0$, and $\Delta E = w$.

This means that any work done by the system must decrease the system's internal energy and thus its temperature. Conversely, if you do work on the system adiabatically, the temperature will rise.

Problem: Calculate ΔE for the constant volume process where 23 J of heat is lost from the system.

Solution:

$$w = 0 \text{ (since } P\,\Delta V = 0) \qquad q = -23 \text{ J}$$

Therefore, $\Delta E = q + w = (-23) + (0) = -23$ J

Problem: Calculate ΔE for an adiabatic process that has 45 J of work performed on it.

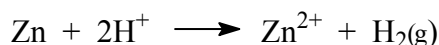**Solution:**

$$q = 0 \text{ (an adiabatic process)} \qquad w = +45 \text{ J}$$

Therefore, $\Delta E = q + w = (0) + (+45) = +45$ J

Enthalpy

Generally, chemical reactions are carried out at constant pressure. Suppose you drop some zinc metal into a solution of hydrochloric acid, in an attempt to measure the decrease in internal energy, ΔE, associated with the reaction

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_{2(g)}$$

In this reaction the volume of the system increases greatly because one of the products, H_2, is a gas. So the system must "push" away a volume of air equal to the volume of H_2 produced. The system does work against a constant pressure of 1 atm. This expansion work means there is less energy available to be given off by the reaction. The amount of heat released (ΔH) will be the change in internal energy (ΔE), less the amount of work done ($-P\,\Delta V$). The change in the thermodynamic state function enthalpy (ΔH) measures the heat change in a constant pressure reaction.

$$\Delta E = q + w$$

$$= q_p + (-P\,\Delta V)$$

where the subscript p indicates a constant pressure.

The thermodynamic definition of enthalpy is $\Delta H = q_p$.

So $\Delta E = \Delta H - P\Delta V$

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

This last relationship is often written as

$$\Delta H = \Delta E + RT\Delta n$$

using the gas law relationship $P\Delta V = RT\Delta n$. The difference between ΔH and ΔE is due to expansion or contraction during the reaction.
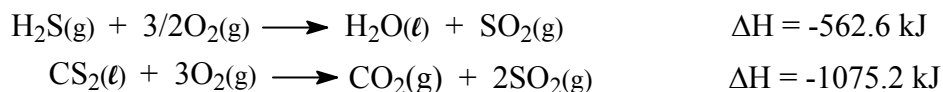
If there is no difference between the number of moles of gas on either side of the equation, there is no expansion or contraction. In that case the values of ΔH and ΔE are the same. Changes in volume of liquids and solids are too small to affect ΔV in any appreciable manner. So, for reactions that involve only liquids and solids, ΔH and ΔE can usually be considered identical.

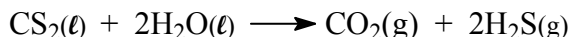In summary, the three important mathematical expressions involved are as follows:

$$\Delta E = q + w$$
$$w = -P\Delta V$$
$$\Delta H = \Delta E + P\Delta V \quad (= \Delta E + RT\Delta n)$$

The following problem involves Hess's law (itself an expression of the law of conservation of energy) and a ΔE calculation.
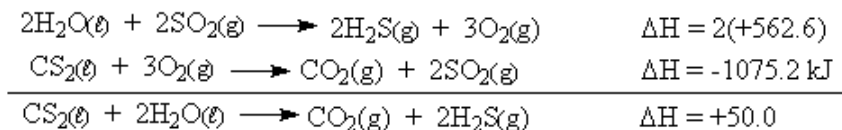
Problem: Given

$$H_2S(g) + 3/2 O_2(g) \longrightarrow H_2O(\ell) + SO_2(g) \qquad \Delta H = \text{-562.6 kJ}$$
$$CS_2(\ell) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) \qquad \Delta H = \text{-1075.2 kJ}$$

calculate ΔH and ΔE for the reaction

$$CS_2(\ell) + 2H_2O(\ell) \longrightarrow CO_2(g) + 2H_2S(g)$$

(Assume a temperature of 25°C.)

Solution: Arrange the two given equations as

$$2H_2O(\ell) + 2SO_2(g) \longrightarrow 2H_2S(g) + 3O_2(g) \qquad \Delta H = 2(+562.6)$$
$$CS_2(\ell) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) \qquad \Delta H = \text{-1075.2 kJ}$$
$$\overline{CS_2(\ell) + 2H_2O(\ell) \longrightarrow CO_2(g) + 2H_2S(g) \qquad \Delta H = +50.0}$$

The first equation given had to be reversed and multiplied by 2. ΔH for the overall reaction is therefore +50.0 kJ. Using

$$\Delta E = \Delta H - P\Delta V = \Delta H - RT\Delta n$$

where Δn = final number of moles of gas – initial moles of gas = 3 – 0 = 3,

we find
$$\Delta E = +50.0 \text{ kJ} - 8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1} \times 298 \text{ K} \times 3 \text{ mol}$$
$$= +50.0 \text{ kJ} - 7.43 \text{ kJ}$$
$$= +42.6 \text{ kJ}$$

(At constant volume there is no work of expansion, so the system would not have to absorb the extra 7.43 kJ of heat energy necessary for the work of expansion.)

Entropy and the Second Law of Thermodynamics

Study Sections 17.1, 17.2, 17.3, and 17.5 in your textbook. Your textbook discusses the second law of thermodynamics and introduces a new state function, entropy, *S*. You are already aware of the second law of thermodynamics, although you do not know it by that name. At this point, you can consider entropy to be the *amount of disorder in the system*.

One way of stating the **second law of thermodynamics** is to say that heat always flows from a hot body to a cold body. You do not need a course in chemistry to tell you that if you put a hot body next to a cold body, then the hot body would not get hotter and the cold body would not get colder. That is an observation from everyday life that you have no doubt known since you were very young, so you are already aware that there is a directional flow of heat. As an aside, you may have heard the recording "At the Drop of Another Hat" by Flanders and Swann. It contains a song entitled "The First and Second Law," with the refrain:

> *Heat won't pass from a cooler to a hotter;*
>
> *You can try it if you like but you far better notter[1]*

Students have no trouble remembering the second law in this format!

That there is a directional component to an irreversible process is what the second law is all about. Below are a few more examples from everyday life, which should help you see that you are actually very familiar with the second law and that you automatically assume the second law is working. In the examples are scenarios of what would happen if the second law were reversed. The results are obviously ludicrous!

You are sailing on Lake Okanagan on a perfect summer's day in July. Suddenly you find that your sailboat is held fast in ice for a metre in every direction, and yet other sailboats nearby are racing through the warm lake water. Unlikely? Impossible? It is the reverse process that you would expect to occur. If you dropped a large iceberg into Lake Okanagan on a hot July day, the ice would melt.

You are swimming off Kitsilano Beach in Vancouver. Suddenly you find that all the Na^+ ions and all the Cl^- ions in the sea water in Vancouver harbour have associated and precipitated out underneath you. You end up stranded on top of an enormous salt crystal. Unlikely? Impossible? The reverse process is more logical.

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[1] Reproduced by permission of the estate of Michael Flanders and Donald Swann.

A large crystal of NaCl put into the water at Kitsilano Beach will dissolve and the ions will disperse throughout the harbour (and eventually the Pacific Ocean).

You should be able to think of a number of equally absurd examples of reversals of the second law of thermodynamics. A movie run backwards is usually full of lovely irreversible processes being reversed. This technique is often used effectively in TV advertising. All of this should convince you that these processes have a preferred direction. We will return to the two specific examples (Lake Okanagan and Kitsilano Beach) when we discuss the meaning of entropy.

The above examples of the second law seem very obvious, but the natural direction of many chemical processes is not always apparent from simple examination of the system. A chemist will also want to know how factors such as changes in temperature and pressure will affect the direction of a reaction.

The second law is also important because it allows an understanding of why some processes that might otherwise be observed never actually occur. For example, why cannot thermal energy present in sea water be extracted in order to drive a ship across the ocean, leaving icebergs in its wake? There is nothing to this idea that violates the first law; some of the internal energy of the sea water would simply be converted to work. Or, since gas molecules are moving randomly, what is to keep them from suddenly all "randomly" moving into one half of the room, leaving you in a vacuum? The answer to the second question is *nothing except pure chance*—we will examine this idea of chance later in this unit.

As for the ship, the second law states that in order to convert heat into work, the heat must flow from a higher to a lower temperature. This is what happens in an engine, where heat is produced at a high temperature in the combustion chamber and flows to the lower temperature of the environment. The greater this difference in temperature, the more of the heat the engine can capture and convert into work. The trouble with the ship propulsion scheme is that there is no lower temperature region in the sea water to which the heat can flow. For an engine to convert *all* of its fuel (heat) input into work, either the combustion temperature would have to be infinitely high (hard on the engine!), or the outside temperature would have to be absolute zero. Neither of these is possible, of course, so no engine can convert all its heat to work.

Practical power plants operate at the highest possible temperatures in order to recover the maximum amount of work from the heat provided by the fuel. A modern gas turbine using high-temperature ceramic parts can convert as much as 55% of the heat into work. Ordinary steam turbines and internal combustion engines are limited to about 25% efficiency. You should see that these limitations are imposed by the second law, not the mechanical design of the engine.

To understand the second law, you must also understand that the word *spontaneous* has a different meaning in thermodynamics than in everyday life. Normally, you would interpret the word *spontaneous* as involving time. If the audience breaks into spontaneous applause, you understand that there is an immediate gesture on the part of the audience. If you make a spontaneous announcement, then you did not wait for three weeks before speaking—you spoke out then and there. Thermodynamically, however, spontaneous means that the reaction occurs. There is no relationship to time. The weathering of rocks is considered to be spontaneous. It does happen. It might take millions of years, but the fact that it does happen, means it is considered thermodynamically spontaneous. Whenever the word *spontaneous* is used in this unit or later in the course, it will have no connotation of time. It will mean that the process does occur.

Your textbook refers to the second law of thermodynamics as: "The entropy of the universe is constantly increasing." There are many other ways of saying this. At first glance, the following statements may not appear to be saying the same thing but, in fact, they are:

- There is a natural tendency for a system to become more disordered.
- In any spontaneous process there is always an increase in the entropy of the universe.
- It is impossible to transfer heat from a cold to a hot reservoir without, at the same time, converting a certain amount of work into heat (think of a refrigerator).
- Entropy is time's arrow.

This last statement of the second law (by physicist Sir Arthur Eddington) can be understood if you think of the example of running a movie. You can easily detect if the movie is running forwards or backwards by knowing, through experience, which processes are irreversible. You cannot "uneat" a banana; spilled milk will not lift itself off the floor and back into a glass; a diver cannot dive out of a pool feet first back onto a springboard. You are using the irreversibility of the process to detect the running direction of the movie.

Entropy and Probability

So far, we have discussed entropy in terms of the degree of disorder in the system, but it is also worthwhile to relate entropy and probability. An understanding of this relationship should help you comprehend the second law.

The mathematical relationship between entropy and probability is

$$S = k \ln \Omega$$

$$= 2.303 \, k \log \Omega$$

where k is a constant known as the **Boltzmann constant** and Ω (omega) is the thermodynamic probability. Ω is simply the number of equivalent ways of arranging the various atoms, molecules, or species in the system under consideration. The equation $S = k \ln \Omega$ relating probability to entropy, is due to Ludwig Boltzmann (it is written on his tombstone!). You do not have to memorize or even use this formula in this course, however, it will help you to see that as the probability, Ω, increases, then so does the entropy. The greater the probability, the more disorder there is in the system. Below are a number of examples to help you understand this point.
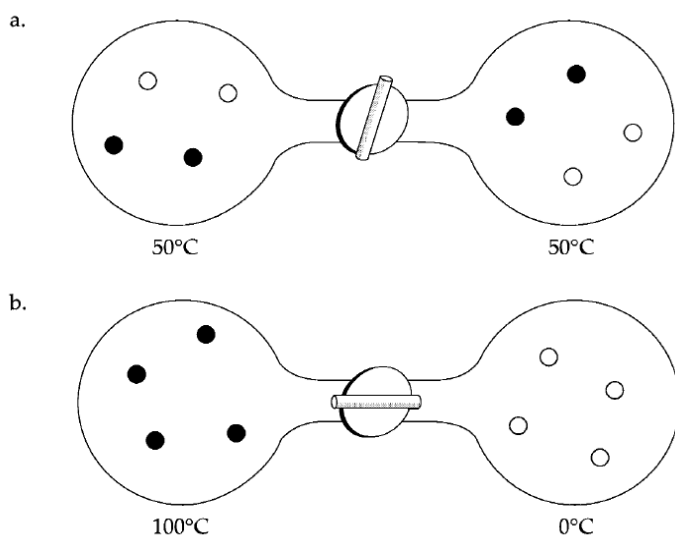
Figure 5.2: a. Stopcock closed. **b.** Stopcock open, allowing the gas molecules to mix. The faster-moving molecules are represented by a black spot, the slower molecules by a circle.

Figure 5.2(a) in this unit shows an imaginary experimental setup where there are four molecules of gas in each of two containers. These two containers are connected by a short passage controlled by a stopcock. In each container there are two molecules of gas at 100°C and two molecules at 0°C. (You can now see why this is an imaginary experiment. Temperature is a bulk property of a gas, not a property of an individual molecule. But, for the sake of this explanation, we'll assume that the speed of an individual molecule could be related to an individual temperature.) The average temperature of each container is 50°C. If the stopcock is turned and the contents of the two containers are allowed to mix, it is not unreasonable to suppose that the two faster-moving (100°C) molecules in the right-hand container may move to the left-hand container.

At the same time, the two slower-moving (0°C) molecules from the left-hand container may move into the right-hand one. The result would be the arrangement shown in Figure 5.2(b). This is not an unlikely result. It is one of a small number of possible arrangements of four molecules in each container. But the average temperature on the left would now be 100°C, and the one on the right, 0°C. This is of course a violation of the second law of thermodynamics. The two containers were initially at the same temperature and spontaneously one became hotter and the other became colder.

Now consider a similar setup, but with an increase in the number of molecules as shown in Figure 5.3. Both containers are initially at the same temperature. It now becomes much less likely that all the faster-moving molecules just happen to move into the container on the left and all the slow molecules just happen to move to the container on the right. The more molecules you start with, the less likely you are to get such an ordered arrangement.

When you consider that even in one gram of hydrogen gas there are over 10^{23} molecules, the chance of a spontaneously ordered arrangement becomes incredibly small. This is the basis of the relationship of entropy and probability. As the number of molecules increases, the chance of a disordered arrangement is far greater than the chance of an ordered arrangement. As the probability of a disordered arrangement increases, the entropy increases. In a real experiment the number of molecules is so large that the probability of an ordered arrangement is small enough to ignore.
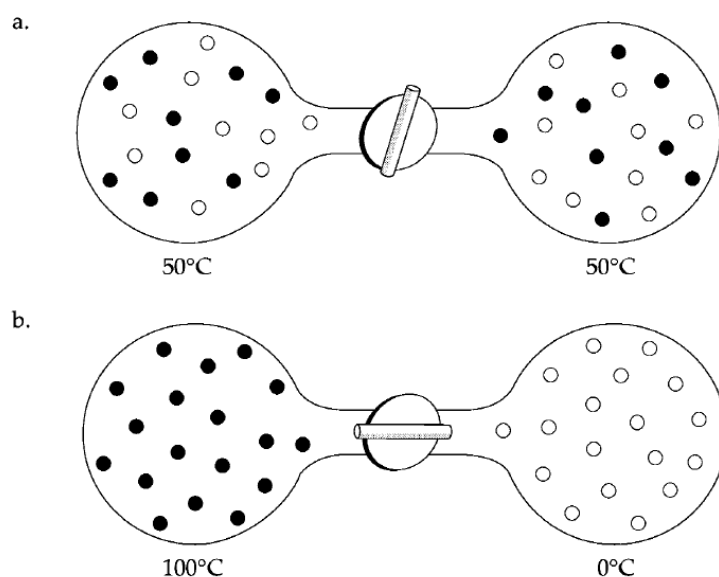
Figure 5.3: a. Stopcock closed. **b.** Stopcock open, allowing the gas molecules to mix.

The second law of thermodynamics is based on probability. When you deal with large numbers of molecules, as you do in reality, the chance of the second law being contravened becomes vanishingly small. If you were sailing on Lake Okanagan on that July day, it is possible that all the very slow moving (and hence cold) water molecules could just happen to be in the vicinity of your sailboat. Under these circumstances you could find yourself trapped in ice. But the chance of this happening is *extremely* small. In fact, it is extremely improbable anytime in the next 10 billion years or so before the sun burns out. Nor do you have to worry about being marooned on top of a giant sodium chloride crystal while swimming at Kitsilano. There is a probability that all the Na^+ and Cl^- ions in the Vancouver harbour could just happen to precipitate out of solution underneath you, but that possibility is so small that it can be safely ignored.

The concept of entropy, its relationship to probability, and the idea of the entropy of the universe increasing are not restricted to the realm of chemistry. Your chance of being dealt a disordered hand of cards in poker is much higher than your chance of being dealt an ordered flush. There are many different arrangements of cards that are not a flush. This is sometimes referred to as *poker entropy*.

You might remember that CHEM 1503 mentioned the relationships between escaping tendency and disordered arrangements in a discussion about the colligative properties of solutions. You may hear the second law invoked in discussions of economics, sociology, and history, although it is not normally used in this manner. The second law does not say that an ordered system cannot exist. It says that if the entropy of a system decreases, then the entropy of the surroundings increases to more than offset the decrease.

Many times you can predict whether the entropy of a chemical or physical reaction is increasing or decreasing. If there is an expansion, then there is more space available for different arrangements of a gas. Entropy increases. Entropy decreases when a gas is condensed to a liquid or a liquid cools to a solid. (Unit 1 of CHEM 1503 deals with the difference in the degree of order in gases, liquids, and solids.) If the number of particles (molecules, ions, atoms) increases during a reaction, then the disorder increases and so does the entropy of the system.

Try the following examples.

Problem: Predict whether there is an increase or decrease in the entropy of the substance undergoing each of the following changes.

    a.   Water freezes
    b.   Ether evaporates
    c. $CO_2(s)$ sublimes
    d. $NaCl(s)$ dissolves in water
    e. H_2 and O_2 gases are mixed
    f.   Water and alcohol are mixed

Solution:

   a.   Entropy decreases. Ice is a much more ordered structure than liquid water, where the molecules are in constant random motion.

   b.   Entropy increases. When a liquid becomes a gas, the molecules have more space in which to move and can arrange themselves in many more ways.

   c.   Entropy increases. Carbon dioxide molecules occupy lattice points in a regular manner in the solid state. There are no such restrictions in the gaseous state.

   d.   Entropy increases. The orderly arrangement found in the solid sodium chloride lattice is broken down in water and the Na^+ ions and the Cl^- ions are free to move in a random manner throughout the water.

   e.   Entropy increases. A mixture means there are more possible ways of arranging the molecules involved.

   f.   Entropy increases. A mixture means there are more possible ways of arranging the molecules involved.

Problem: Predict the sign of ΔS for each of the following reactions.

   a. $CO_{(g)} + 2H_{2(g)} \longrightarrow CH_3OH_{(\ell)}$
   b. $Mg_{(s)} + H_2O_{(\ell)} \longrightarrow MgO_{(s)} + H_{2(g)}$
   c. $C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(g)}$
   d. $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$

Solution:

   a. ΔS is negative. There is a decrease in the disorder of the system as you go from 3 moles of gas to 1 mole of liquid.

   b. ΔS is positive. The reaction goes from 1 mole of solid and 1 mole of liquid to 1 mole of solid and 1 mole of gas. Disorder increases.

   c. ΔS is positive. Six moles of gas go to 7 moles of gas, so disorder increases.

   d.   It is not possible to predict the sign of ΔS in this case. Three moles of gas go to 3 moles of gas.

Work through Examples 17.1 and 17.3 in the textbook and their practice exercises.

Entropy Changes in Chemical Reactions

In this unit, we have seen that energies can only be found on a relative basis, defined according to some arbitrary zero level. This is why standard enthalpies of formation of elements are defined as zero.

Entropy, however, is different because there is a well-defined zero of entropy, based on the **third law of thermodynamics** (there are only three laws of thermodynamics!). The third law of thermodynamics says that *the entropy of a perfect crystalline substance at absolute zero of temperature is zero*. There is no such thing as a perfect crystal (all solids have some microscopic defect and/or a minute amount of impurity), and it is impossible to reach the absolute zero of temperature. Thus, zero entropy is a theoretical concept, but having a zero entropy point gives a convenient way to find an entropy value of a substance at a particular temperature. Appendix 3 in your textbook lists absolute entropy values for a number of substances. Absolute entropy is given the symbol S°. The ° means "at the standard state of 1 atmosphere pressure and 25°C." S° is the difference between the entropy of the substance at 25°C and the entropy of the substance at –273°C.

$$\Delta S = S_{\text{stand temp}} - S_{\text{absol zero}}$$

But entropy at absolute zero is always zero, so here

$$\Delta S = S°$$

Take a look at the values given in Appendix 3. Notice that the $S°$ values for gases are higher than those for liquids. Elemental solids have simple, ordered arrangements and their $S°$ values are comparatively low.

Example 17.2 in your textbook shows how absolute entropy values can be used to calculate $\Delta S°$ for a given reaction. Make sure you understand this method and then try the practice exercise and the following example.

Problem: In the previous problem it was not possible to predict the sign of ΔS for the reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$
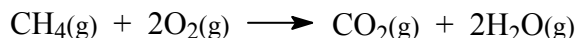
Using the values of $S°$ in Appendix 3 and given $S°$ for $CH_4(g)$ is 186 J K^{-1} mol^{-1}, calculate ΔS for the reaction at 25°C (i.e., $\Delta S°$).

Solution:

$$\Delta S° = S°_{\text{products}} - S°_{\text{reactants}}$$

$$= (214 + 2 \times 189) - (186 + 2 \times 205) \text{ J K}^{-1}$$

$$= -4 \text{ J K}^{-1}$$

This is a very small negative entropy change. You could not have predicted its sign. Note that units of entropy are joules per Kelvin (J K^{-1}), whereas units of enthalpy and energy are usually quoted as kilojoules. This tells you that entropy changes in a reaction at 25°C are usually in the order of 1/1000 of the corresponding enthalpy changes. This is an important point and we will discuss it in more detail under the next heading.

Gibbs Free Energy

Study Section 17.5 in your textbook. This section introduces a new thermodynamic function, Gibbs free energy. According to the definition of ΔG in Equation 17.10, there are two factors to be considered when you are trying to determine whether or not a reaction is spontaneous. These factors are the enthalpy change (ΔH) of the reaction and the entropy change (ΔS) of the reaction. A negative ΔH contributes to the spontaneity of a reaction. A positive ΔS also contributes to the spontaneity of the reaction. In other words, if a reaction is exothermic and has increasing entropy, then both terms work towards spontaneity. Because many chemical reactions have $-\Delta H$, students often assume that only enthalpy governs spontaneity. Enthalpy is usually about 1000 times greater than the entropy term. This means that you are often unaware of the contribution of ΔS to the spontaneity of the reaction.

You can think of free energy as a measure of the tendency of a system to undergo a change at a given temperature. As a change occurs, there is less capacity for further change—free energy is "lost." A decrease in free energy is indicated by a negative value of ΔG. The more negative ΔG is for a given process, the greater the possible free energy loss and the greater the capacity for spontaneous change.

The Gibbs equation defines the state function, **Gibbs free energy**, G.

$$G = H - TS$$

A change in the free energy is given as

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

Be sure to memorize this important equation. It shows how the factors of enthalpy and entropy relate in predicting whether or not a reaction is spontaneous. Also memorize the information in the following box, because you should know that where

$\Delta G < 0,$	the reaction is spontaneous;
$\Delta G = 0,$	the reaction is in equilibrium;
$\Delta G > 0,$	the reaction is *not* spontaneous.

Now convince yourself, using the Gibbs equation, that a reaction with ΔH negative and ΔS positive will always occur.

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = (-) - T(+) \quad < 0$$

Temperature, in degrees Kelvin, is always positive. In this case, irrespective of the numerical value of ΔH, ΔS, and T, the result will always be a negative ΔG.

This is saying mathematically that any reaction which is exothermic and has increasing entropy always "goes."

The opposite set of circumstances is where the reaction is endothermic and the entropy is decreasing. Neither of these two factors favours the reaction. You should predict that such a reaction would never be spontaneous. If you substitute these signs in the Gibbs equation,

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

$$\Delta G = (+) - T(-),$$

the result will always be $\Delta G > 0$, irrespective of the numerical value of ΔH, ΔS, and T. By definition, ΔG positive means the reaction never "goes." (Of course, a negative value of T could give an overall negative value of ΔG; but the temperature is on the Kelvin scale, and you cannot get negative values since these would be below absolute zero.)

If the reaction is exothermic, then ΔH favours the reaction. If, at the same time, the entropy of the reaction is decreasing, then ΔS is working against spontaneity. In a case like this, whether or not the reaction "goes" depends on the numerical values of ΔH, ΔS, and T.

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

$$\Delta G = (-) - T(-)$$

Remember that the value of ΔS is usually a lot less than that of ΔH. Consequently, the reaction is spontaneous until a certain temperature. Above this temperature the $T\Delta S$ term is sufficient to overcome the driving force of the negative ΔH and the reaction ceases to be spontaneous. Under these circumstances the reverse reaction is favoured. A famous example of this is the synthesis of ammonia from its elements:

$$N_2 + 3H_2 \longrightarrow 2NH_3.$$
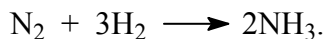
This reaction is the basis of the synthetic fertilizer industry and it is of great economic importance. At low temperatures, the reaction is very slow. At high temperatures, the decreasing entropy of the reaction (and hence a large $T\Delta S$ term) favours the reverse reaction. The German chemist, Fritz Haber, won a Nobel Prize for working out the optimum conditions for carrying out this reaction on an industrial scale.

Most chemical reactions of the decomposition type involve enthalpy changes that work against the reaction and entropy changes favouring the reaction. Such a reaction has ΔH positive and ΔS positive.
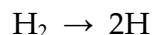
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (+) - T(+)$$

You should be able to see mathematically that, in this case, ΔG would be negative when the $T\Delta S$ term is numerically greater than the ΔH term.

There will be a temperature above which the reaction "goes." At high temperatures, the entropy term overcomes the unfavourable enthalpy term. Typical examples are:

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2$$

and
$$H_2 \rightarrow 2H$$

In these cases, the overall positive ΔH is due to there being more energy required to break chemical bonds than is evolved when (or if) new chemical bonds are formed. When a large molecule breaks into smaller parts, there is an increase in entropy due to more "randomness." Thermodynamics therefore predicts that *any stable molecule will decompose into its elements at high temperatures*.

For a chemical reaction where reactants are changing into products, there comes a point where the free energy is as low as it can possibly get—no more can be lost and so no further change can occur. Such a reaction is at *equilibrium*. The conditions that constitute equilibrium for a chemical reaction are a very important characteristic of that reaction.

Since both ΔH and $T\Delta S$ contribute to the free energy change of a process, you can expect that there will be some processes where one or the other of these terms dominates to the extent that the other is considered negligible. Such processes are said to be **enthalpy driven** or **entropy driven**. The spontaneous expansion of a gas as it becomes more randomized within a larger volume is the entire driving force, since the entropy of the surroundings remains largely unchanged in the absence of any significant flow of heat. Extraction of a metal from its oxide ore by reaction with charcoal (an ancient form of smelting) can be considered to be entropy driven. For example,

$$CuO + C \longrightarrow Cu + CO_{(g)}$$
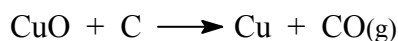
You can predict a large increase in entropy in this type of reaction because one of the products is a gas. Moreover, this reaction is carried out at a high temperature, so $T\Delta S$ will be large. The previous decomposition reaction examples given (H_2O and H_2) are also entropy driven.

It is harder to think of a chemical reaction that is purely enthalpy driven. Even if ΔS is small, it gets multiplied by the absolute temperature and so can become important at high temperatures.

A combustion reaction such as

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$$
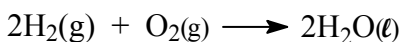
is essentially enthalpy driven. Consider that in any combustion reaction a lot of heat is given off, so ΔH is negative and large.

Since the entropy is decreasing in this reaction (gases becoming liquid), the entropy term works against this reaction. It is the large enthalpy term that drives this reaction.

There is a simple entropy-driven process that you can study at home. Find a rubber band, the larger the better. Stretch the rubber band and hold it, still stretched, to your top lip or forehead. (For this experiment, a wider rubber band gives a more obvious result.) Now let the rubber ban return to its unstretched state and again hold it to your lip or forehead. Do you feel any temperature change? The unstretched rubber band should feel cool in comparison to when it is stretched. Holding it against your lip or forehead is recommended since these areas of your body are very sensitive to temperature change. Assuming you do agree that the unstretched rubber band feels cooler than the stretched rubber band, how can you interpret these results?

Is the reaction

$$\text{rubber band}_{\text{stretched}} \rightarrow \text{rubber band}_{\text{unstretched}}$$
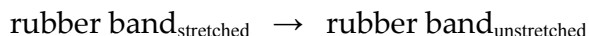
spontaneous? Yes? Then ΔG for this reaction is negative. Because the rubber band felt cooler to your skin, the reaction must be taking heat from your skin. The reaction of stretched to unstretched must be an endothermic one, so for this reaction ΔH is positive. And, since temperature (in Kelvin) is always positive, upon substituting into

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

we obtain

$$(-) = (+) - T(\Delta S)$$

The only way that ΔG can be negative is if ΔS is positive and the $T\Delta S$ term is numerically larger than the positive ΔH term. (If you have difficulty seeing this, try putting a negative value in for ΔS. Then you get $(+) - (-)$ and that will be overall positive, since two negatives make a positive. This cannot be correct, since ΔG is not positive. The reaction from stretched to unstretched definitely does occur.) Thus, the reaction of a stretched rubber band going to an unstretched rubber band is entropy driven. As a child, you may have had a toy car where the windup mechanism was a rubber band, or you may have made one yourself with thread spools and nails, so that the car would move as the rubber band unwound itself. Your car was entropy driven, although you had to supply the original energy by winding it up.

Figure 5.4 in this unit explains this process by showing the molecular structure of the rubber in the rubber band.

When the rubber band is not stretched, the long molecules of the rubber polymer lie in a randomly tangled state.

When the rubber band is stretched, as illustrated in Figure 5.4 (b), the molecules are held in a more ordered, parallel arrangement. Obviously, there is more disorder in the unstretched state, so entropy increases as the rubber band goes from stretched to unstretched. In the stretched state the molecules align in such a way that more intermolecular attractions between molecules are possible. These attractions are broken when the molecules revert to the tangled, unstretched arrangement. New intermolecular attractions form in the unstretched state, however, not as many are possible as in the stretched state. Consequently, more energy is required to break the intermolecular attractions than is released when new intermolecular attractions are made. Overall, ΔH is positive.

a.

Intermolecular
attractions

b.

Intermolecular
attractions
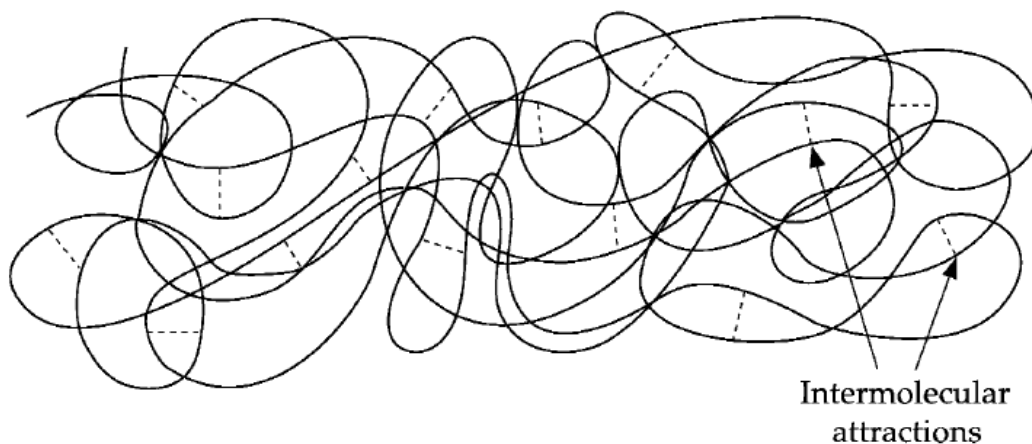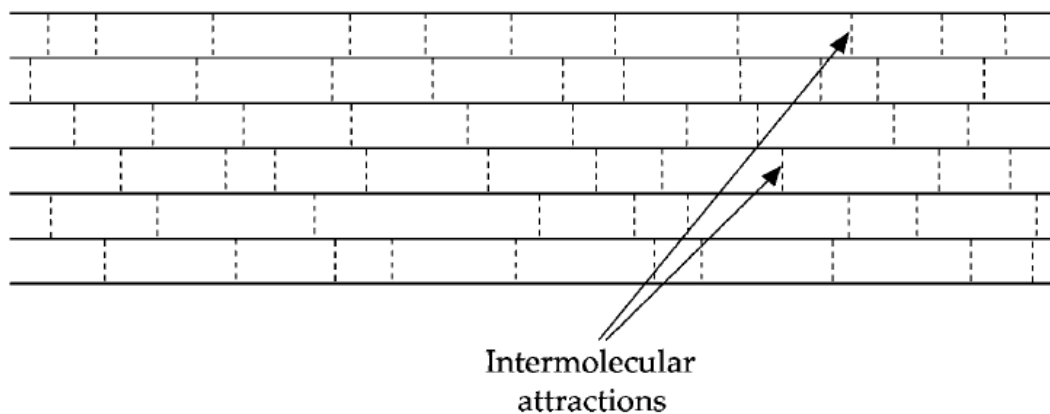
Figure 5.4: a. The unstretched state of a rubber band. The diagram shows a tangled disordered arrangement of long chains of molecules with intermolecular attractions between them (dotted).

b. The stretched state where the molecules align in an orderly fashion. A greater number of intermolecular attractions are possible in this arrangement.

Table 17.3 in your textbook summarizes the relationship between spontaneity, which we just discussed. This table is important.

You should be able to see that if ΔH is negative and ΔS is positive, then the reaction always "goes"; that if ΔH is negative and ΔS is negative, then the reaction only "goes" below a certain temperature, and so on. You should not just memorize this table. You should be able to reproduce such a table because you *understand* these relationships.

Free Energy Calculations for Chemical Reactions

There are two methods of calculating ΔG for any particular reaction. Appendix 3 of your textbook gives $\Delta G°_{formation}$ ($\Delta G°_f$) values for a number of substances. These values can be treated in exactly the same way that you used $\Delta H°_{formation}$ values. That is,

$$\Delta G°_{reaction} = \Sigma \Delta G°_f(\text{products}) - \Sigma \Delta G°_f(\text{reactants})$$

This is used in Example 17.4 and its practice exercise in your textbook. Also, if you know ΔH for the reaction and ΔS for the reaction, you can calculate ΔG for the reaction by using the Gibbs equation,

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

Problem: Calculate $\Delta G°$ for the reaction

$$C_2H_4(g) \ + \ 3O_2(g) \longrightarrow 2CO_2(g) \ + \ 2H_2O(\ell)$$
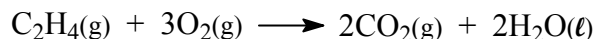
using the values in Appendix 3 of your textbook and the following values for C_2H_4.

$$\Delta H°_f = +52 \text{ kJ mol}^{-1}$$

$$S° = 220 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G°_f = 68 \text{ kJ mol}^{-1}$$

Solution: There are two methods of doing this calculation. First use the $\Delta G°_f$ of the substances involved.

$$\Delta G° = \Sigma \Delta G°_f(\text{products}) - \Sigma \Delta G°_f(\text{reactants})$$

so

$$\Delta G° = [2 \times (-394.4) + 2 \times (-237)] - (+68) \text{ kJ}$$
$$= -1330.8 \text{ kJ} = -1331 \text{ kJ}$$

Note that, by definition, the $\Delta G°_f$ of an element in its standard state is 0.

The second method involves calculating ΔH and ΔS for the reaction.

$$\Delta H° = \Sigma \Delta H°_f(\text{products}) - \Sigma \Delta H°_f(\text{reactants})$$

so

$$\Delta H° = [2 × (–393.5) + 2 × (–286)] – (+52) \text{ kJ}$$

$$= –1411 \text{ kJ}$$

and

$$\Delta S° = S°_{\text{products}} – S°_{\text{reactants}}$$

so

$$= (2 × 213.7 + 2 × 70) – (220 + 3 × 205) \text{ J K}^{-1}$$

$$= –267.6 \text{ J K}^{-1}$$

Now, using the Gibbs equation $\Delta G° = \Delta H° – T\Delta S°$,

$$\Delta G° = –1411 \text{ kJ} – 298 \text{ K} × (–0.2676 \text{ kJ K}^{-1})$$

$$= –1411 + 79.74$$

$$= –1331.26 \text{ kJ} = –1331 \text{ kJ}$$

The superscript ° tells you the pressure is 1 atmosphere. If you are not told a temperature, you would normally assume that it is 25°C.

The temperature at which a reaction stops being spontaneous and starts to be nonspontaneous is where ΔG changes from negative to positive. This is the $\Delta G = 0$ point and is the free energy definition of *equilibrium*. If

$$\Delta G = 0,$$

then $$\Delta G = 0 = \Delta H – T\Delta S$$

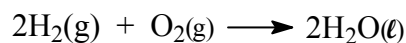so $$\Delta H = T\Delta S$$

and $$T = \frac{\Delta H}{\Delta S}$$

This relationship can be used to find the temperature where the reaction ceases or begins.

Problem: At what temperature is the following reaction possible?

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$$

For this reaction, $\Delta H = –571.7$ kJ and $\Delta S = –326.4$ J K^{-1}.

Solution: You should first decide that this reaction is enthalpy driven, with the decreasing entropy working against it at higher temperatures. Consult Table 17.3 in your textbook to check this out.

$$T = \frac{\Delta H}{\Delta S} = \frac{-571.7 \; kJ}{-326.4 \; x \; 10^{-3} \; kJ \; K^{-1}}$$

$$T = 1752 \; K = 1479°C$$

The reaction will occur at any temperature below 1479°C. Above this temperature, the decreasing entropy component cancels out the exothermic ΔH component of the free energy.

Phase Transitions

For a phase change, where the temperature remains constant, a useful mathematical definition of the entropy of this reversible process is

$$\Delta S = \frac{q_{reversible}}{T}$$

This formula can be used to find the entropy change occurring in a change of state.

Problem: Calculate the entropy change when 10.0 g of solid gold melts. The melting point of gold is 1063°C and the heat of fusion of gold is 12.36 kJ mol^{-1}.

Solution: ΔH_{fusion} for gold is $+12.36$ kJ mol^{-1}. This value is positive since heat is absorbed by the system when a solid changes to a liquid. For 10.0 g of gold,

$$\Delta H = q_{rev} = \frac{+12.36 \; kJ \; mol^{-1} \; x \; 10.0 \; g}{197 \; g \; mol^{-1}}$$

$$q_{rev} = 627 \; J$$

so
$$\Delta S = \frac{q_{rev}}{T} = \frac{627 \; J}{(1063 + 273) \; K} = 4.69 \; x \; 10^{-1} \; J \; K^{-1}$$

The entropy change for melting 10.0 g of gold is positive. This is expected since the degree of disorder increases when the regular structure of solid gold breaks down and the more random arrangement of a liquid results. The units of entropy are J K^{-1}.

Free Energy and Equilibrium

Study Section 17.6 in your textbook, about the relationship between ΔG and the equilibrium constant. That is

$$\Delta G^o = -RT \ln K \quad (or \; \Delta G^o = -2.303 \; RT \log K)$$

Note that for a reaction in solution the equilibrium constant is K_c and that for a gaseous reaction the K used in the expression is K_p. Table 18.4 summarizes the relationship between $\Delta G°$ and K. Consider the simple reaction Y → Z at 298K where $K_c = 25.0$. There are many values of ΔG for this reaction because there are many concentrations of Y and Z. There is only one standard concentration (1.00 M), so there is only one $\Delta G°$ value. Graphed below in Figure 5.5 are ΔG values against ln Q (Q is the reaction quotient). Remember that there are many values of Q, only one of which is $Q = K_c$. On the graph, at the point ln $Q = 3.219$ (i.e., $Q = 25.0$), the value of ΔG is zero, and at that point the system is at equilibrium. If $\Delta G < 0$ (and thus $Q < K_c$), then the reaction Y → Z is favoured. If $\Delta G > 0$ ($Q > K_c$), the reverse reaction Z → Y is spontaneous. Ln Q values to the right of 3.219 represent the situation where Z → Y has negative free energy. For this reaction, when all concentrations are 1.00 M, $Q = 1$ and ln $Q = 0$. At this point, $\Delta G = \Delta G° = –7.98$ kJ.

When you calculate the standard Gibbs free energy change, $\Delta G°$, for a reaction such as

$$Y → Z,$$
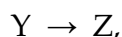
you are finding the "driving force" for conversion of one mole of Y into one mole of Z. If $\Delta G°$ is negative, then you know that one mole of Z is more stable than a mole of Y.
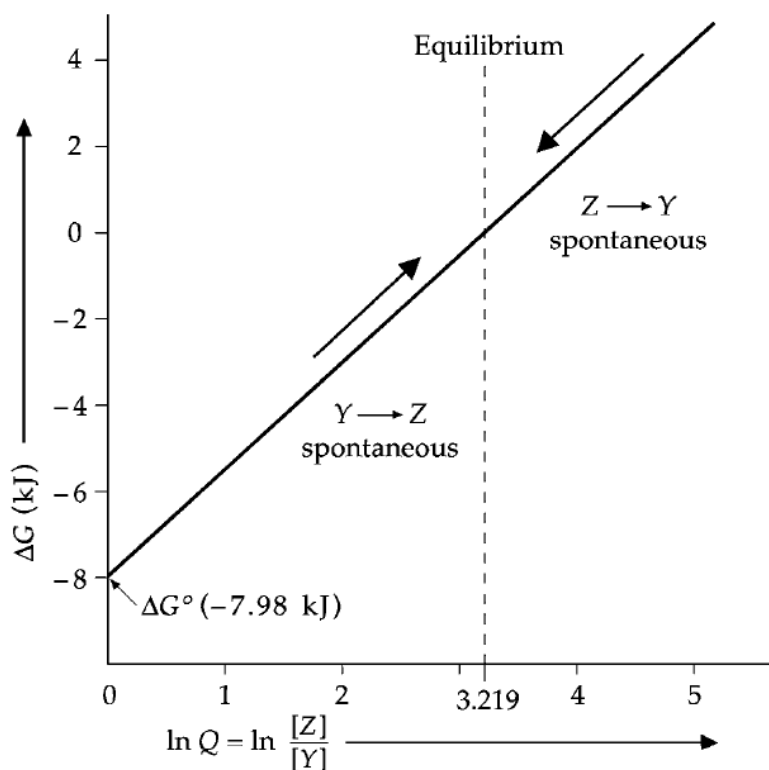
Figure 5.5: The free energy change, ΔG, calculated as a function of ln Q for the reaction Y → Z.
At $\Delta G = 0$, $K_c = 25$.

The reaction will tend to "go" in the direction written. A larger negative $\Delta G°$ does not mean that the reaction will go faster (thermodynamics does not predict rates of reaction) but that the reaction will go further. The more negative the $\Delta G°$, the more completely will the reactants be transformed into products.

The basic idea is that if $\Delta G°$ is highly negative, the position of the equilibrium is strongly "to the right"; the amount of Y present at equilibrium will be insignificant and the reaction is considered to be "complete." If $\Delta G°$ is highly positive, then the position of the equilibrium is strongly "to the left"; the amount of Z will be negligible. This is the same as saying that the reaction "does not take place." It is also equivalent to saying that the reverse reaction will take place; that is,

$$Z \rightarrow Y$$
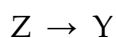
What if $\Delta G°$ is neither highly positive nor highly negative? Then substantial amounts of all substances will be present at equilibrium. Such a reaction is "incomplete" and always results in a mixture. An incomplete reaction is said to be *reversible*. Since $\Delta G°$ is always affected by the temperature, the relative amounts of products and reactants present at equilibrium vary with the temperature. The greater the magnitude of the entropy change, the more will the equilibrium composition change with temperature.

Work through Examples 17.6, 17.7, and 17.8 in the textbook. You may also want to read about thermodynamics in living systems (Section 17.7 in your textbook), especially if you are taking courses in biology. Use the summary at the end of this chapter to review the important concepts in thermodynamics.

Self-Assessment

Having reached the end of Unit 5, you should be able to:

- Explain the physical meaning and consequences of the first law of thermodynamics.
- Define system, surroundings, reversible process, internal energy, enthalpy, heat, and work.
- Calculate the heat of a reaction from tables of standard enthalpies of formation (Hess's law calculations).
- Calculate ΔE of a specified reaction from the ΔH of the reaction, and vice versa.
- Explain the concept of entropy and its relationship to the second and third laws of thermodynamics.
- Calculate and / or estimate $\Delta S°$ for phase changes and chemical reactions.

- Describe the physical significance of free energy and of the free energy change, ΔG.
- Use tables of standard ΔG of formation to determine whether a given reaction will take place spontaneously at a specified temperature.
- Calculate equilibrium constants from $\Delta G°$ values, and vice versa.

Practice Exercise 5

Finish working through Unit 5 before starting this practice exercise which is found listed under the Practice Exercises section of course. The material in this unit is integrated throughout the practice exercises. The solutions to these problems will be provided once you have completed this practice exercise. You may first want to try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can begin the practice exercise immediately. If you have no difficulties with this practice exercise, begin Assignment 5. If you feel that you need more practice, go to the Suggested Supplementary Exercises.

You should make a serious attempt to solve the practice exercise problems by yourself, using as a guide similar exercises from the textbook and from this unit. If your attempt is serious, you will learn a lot from the worked solutions in the Solutions to Practice Exercise 5 section of the Course Units.
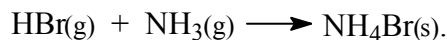
1. Calculate the ΔH for the reactions

$$2P_{(s)} + 2SO_{2(g)} + 5Cl_{2(g)} \longrightarrow 2SOCl_{2(\ell)} + 2POCl_{3(\ell)}$$
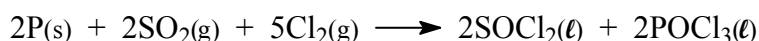
given the following.

a. $SOCl_{2(\ell)} + H_2O_{(\ell)} \longrightarrow SO_{2(g)} + 2HCl_{(g)}$ $\Delta H = +10.3$ kJ
b. $PCl_{3(\ell)} + 1/2O_{2(g)} \longrightarrow POCl_{3(\ell)}$ $\Delta H = -325.1$ kJ
c. $P_{(s)} + 3/2Cl_{2(g)} \longrightarrow PCl_{3(\ell)}$ $\Delta H = -306.7$ kJ
d. $4HCl_{(g)} + O_{2(g)} \longrightarrow 2Cl_{2(g)} + 2H_2O_{(\ell)}$ $\Delta H = -206.2$ kJ

2. Two moles of an ideal gas at 25.0°C and a pressure of 4.00 atm are allowed to expand against a constant outside pressure of 1.00 atm until the volume increases by a factor of 3.00. The expansion occurs at constant temperature. Calculate the following.

a. ΔV b. w

c. ΔE d. q

3. Using the average bond energies for the Br–Br and F–F bonds given in Table 9.4 of your textbook and the $\Delta H°_f$ of $BrF_3(g)$, given as –256 kJ mol^{-1}, calculate the average bond energy of the Br–F bond in $BrF_3(g)$.

4. a. Using the values of $\Delta H°_f$ given in Appendix 3 and given that $\Delta H°_f$ of $NH_4Br(s)$ is –270 kJ, calculate $\Delta H°$ for the reaction

$$HBr(g) + NH_3(g) \longrightarrow NH_4Br(s).$$

   b. Also calculate $\Delta E°$ for this reaction.

5. Calculate the $\Delta S°$ value for each of the following reactions using the absolute entropy values given in Appendix 3 of your textbook as well as the following $S°$ values:

$$C_2H_4(g) \ 220, \quad P_4(g) \ 280, \quad PCl_3(g) \ 217 \ (J \ K^{-1} \ mol^{-1})$$

   a. $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(\ell)$
   b. $P_4(g) + 6Cl_2(g) \longrightarrow 4PCl_3(g)$
   c. $CaCO_3(s) \longrightarrow CaO(s) + C_2(g)$

6. Ethane gas, C_2H_6, burns in excess oxygen to form carbon dioxide and water. Calculate $\Delta G°_{combustion}$ of ethane in kJ per mol as follows:

   a. Using $\Delta G°_f$ values given in Appendix 3 of your textbook and $\Delta G°_f(C_2H_6, g) = –33$ kJ mol^{-1}.

   b. Using the Gibbs equation and appropriate values from Appendix 3 as well as $\Delta H°_f(C_2H_6, g) = –85$ kJ and $S° = 230$ J K^{-1} mol^{-1}.

7. Calculate the normal boiling point of ammonia, given that for ammonia
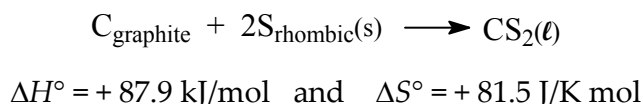
$$\Delta H_{vaporization} = +23.3 \ kJ \ mol^{-1} \quad and \quad \Delta S = +97.2 \ J \ K^{-1} \ mol^{-1}.$$

8. The enzyme triose phosphate isomerase catalyzes the interconversion of glyceraldehydes 3-phosphate (G 3-P) and dihydroxyacetone phosphate (DHAP),

$$G \ 3\text{-}P \ \rightarrow \ DHAP$$
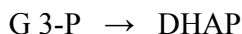
   If the thermodynamic equilibrium constant, K, in the direction written is 22.0 at 298K, calculate $\Delta G°$ for this reaction. (Don't be put off by the biochemical terms in this problem. You can calculate $\Delta G°$ here even if you have no knowledge of biology. This does show that thermodynamic calculations are not restricted to chemistry.)

9.   A 1.45 g sample of acetic acid, $C_2H_4O_2$, was burned in excess oxygen in a calorimeter. The calorimeter contained 750 g of water and had a heat capacity of 2.67 kJ/°C. The temperature of the calorimeter and its contents increased from 24.32°C to 27.95°C. Calculate the molar $\Delta H°_{combustion}$ of acetic acid. The specific heat capacity of water is 4.184 J/°C/g. (You can neglect the heat capacity of the small amount of acetic acid and its combustion products.)

10. For the reaction

$$C_{graphite} \; + \; 2S_{rhombic}(s) \; \longrightarrow \; CS_2(\ell)$$

$$\Delta H° = +87.9 \text{ kJ/mol} \quad \text{and} \quad \Delta S° = +81.5 \text{ J/K mol}$$

a.   Is this reaction spontaneous at 25°C?

b.   Assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature, calculate the temperature at which the reaction will occur.

Suggested Supplementary Exercises

At the end of each chapter in your textbook are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved in the concepts discussed. Fully worked solutions for most of the following exercises are given in the *Student Solutions Manual*. Most selected exercises at the ends of the chapters have their answers in the back of the textbook, or a solution method is described in the *Student Solutions Manual*.

You should make a serious attempt to solve a problem by yourself before looking at a worked solution.

From Chapter 6:

6.17, 6.18, 6.20, 6.21, 6.22, 6.29, 6.32, 6.34, 6.37, 6.38, 6.40, 6.43, 6.46, 6.47, 6.58, 6.60, 6.66, 6.72, 6.76, 6.84, 6.100, 6.110

From Chapter 17:

17.10, 17.11, 17.13, 17.18, 17.20, 17.23, 17.24, 17.25, 17.27, 17.29, 17.30, 17.31

Assignment 5

Now refer to your *Assignments* and complete Assignment 5. Consult your Course Guide for the week this assignment is due. Send the assignment to your Open Learning Faculty Member. If you are sending it by mail, remember to include a Marked Assignment (MA) form. Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.