

Thermodynamics

CHAPTER 12

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ESSENTIAL DEFINITIONS

In the discussion of thermodynamics precise terminology is used to avoid confusion and to ensure that experimental results may be compared from one laboratory to another. Some of the important terms defined in this chapter are *system*, *state function*, *standard state*, and the *exo-* and *endo-* prefixes.

System

A **system** is that part of the universe that is under study. Everything else in the universe is called the **surroundings**. When hydrogen and oxygen are placed in a bomb calorimeter to study the formation of water, all of the hydrogen and oxygen atoms and the calorimeter are the system. The surrounding laboratory, the building, the city, and so on are parts of the surroundings.

There are several types of systems. An **open system** can transfer both energy and matter to and from the surroundings. An open bottle of perfume is an example of an open system. A **closed system** is one where energy can be transferred to the surroundings but matter cannot. A well-stoppered bottle of perfume is a closed system. In an **isolated system** there is no transfer of energy or matter to or from the surroundings. A thermos bottle is a close approximation of an isolated system since it minimizes heat transfer to the surroundings. Calorimeters are designed to be as close as possible to a closed system.

State Function

In this chapter we will encounter enthalpy change, ΔH ; entropy change, ΔS ; free-energy change, ΔG ; and energy change, ΔE . The numerical values and mathemati-

cal signs of these **state functions** depend only on the difference between the final state and the initial state of the system.

The state of a system is defined by the mass and phase (solid, liquid, or gas) of the matter in the system, as well as the temperature and pressure of the system. For the melting of 1 mole of ice, the initial state is described as 18 g $\text{H}_2\text{O}(\text{s})$ at 1.00 atm pressure and 273 K, and the final state as 18 g $\text{H}_2\text{O}(\ell)$ at 1.00 atm pressure and 273 K. With this precise description all scientists should, within experimental error, obtain identical values of ΔH , ΔS , ΔG , and ΔE for the melting of ice.

Two quantities that are *not* state functions are heat (q) and work (w). The values for these quantities depend on the sequence of steps used to transform matter from the initial state to the final state.

Standard State

The thermodynamic quantities ΔH , ΔS , ΔG , and ΔE are **extensive properties** of matter, meaning that they change as the amount of sample changes. To make these quantities **intensive properties** of matter, we must define precisely the temperature, pressure, mass, and physical state of the substance. A system is in the **standard state** when the pressure is 1 atmosphere, the temperature is 25°C, and 1 mole of compound is present. When the thermodynamic quantities are determined at standard state, they are intensive properties and a superscript 0 is added to their symbols: as ΔH° , ΔS° , ΔG° and ΔE° . For a chemical reaction, the standard state involves the number of moles designated by the stoichiometric coefficients in the simplest balanced chemical equation.

Exo- and Endo- Prefixes and Sign Conventions

The prefix *exo-*, as in *exothermic*, indicates that energy is being lost from the system to the surroundings. Mathematically, the prefix *exo-* corresponds to a negative sign for numerical thermodynamic quantities. For an exothermic reaction the heat of reaction, ΔH , is a negative number.

The prefix *endo-* indicates that energy is gained from the surroundings. An *endothermic* reaction absorbs heat energy and appears to cool as it progresses. For an endothermic reaction the heat of reaction, ΔH , is a positive number.

TYPES OF ENERGY

Energy takes many forms. Heat and light, along with chemical, nuclear, electrical, and mechanical energy, are some of the common types. Any one of these forms of energy can be converted into any of the other forms. In addition, the **law of conservation of energy** states that energy is never created or destroyed. As a result of these properties, all forms of energy can be converted into heat energy, which we can measure in a calorimeter as described below.

Energy can also be categorized as either kinetic energy, KE, or potential energy, PE. **Kinetic energy** is the energy that matter possesses because of its motion. There is one equation to describe kinetic energy:

$$\text{KE} = \frac{1}{2}mv^2 \quad (12.1)$$

When the mass, m , is expressed in kilograms and the velocity, v , in meters per second, the energy units are joules.

Potential energy is stored energy, which may be released under the appropriate conditions, as in a nuclear reaction. There are several forms of potential energy, such as **gravitational energy** and the energy of **electrostatic attraction** between oppositely charged ions. Each form of potential energy is described by its own equation, but these equations are similar to each other. They all have the forms

$$\text{PE}_{\text{grav}} = K_{\text{grav}} \left(\frac{m_1 m_2}{r} \right) \quad \text{and} \quad \text{PE}_{\text{elect}} = K_{\text{elect}} \left(\frac{q_1 q_2}{r} \right) \quad (12.2)$$

The two masses, m , in gravitational attraction and the two charges, q , in electrostatic attraction are separated by a distance, r . K is a proportionality constant that is different for each type of potential energy.

The total energy of a substance is the sum of its kinetic and potential energies.

$$\text{Energy (E)} = \text{potential energy (PE)} + \text{kinetic energy (KE)} \quad (12.3)$$

In chemical substances, the kinetic energy is the motion of the molecules. The potential energy of a chemical is the sum of all attractions, including all the covalent bonds, ionic bonds, or electrostatic attractions in the substance.

MEASUREMENT OF ENERGY

Heat is often called the “lowest form” of energy. In this form it is easily measurable by determining temperature changes caused by the release or absorption of heat in a chemical process.

Specific Heat

Heat energy was originally defined in terms of the calorie, which is the amount of heat needed to raise the temperature of 1 gram of pure water from 14.5 to 15.5°C. The joule is the metric unit for energy; 1 calorie is equal to exactly 4.184 joules. By virtue of these definitions, 4.184 joules of energy is needed to raise the temperature of 1 gram of water by 1 degree Celsius. This quantity is known as the **specific heat** of water:

$$\text{Specific heat of water} = 4.184 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1} \quad (12.4)$$

Once the specific heat of water is defined, the specific heat of any other substance can be determined. One method is to immerse a hot object in a known quantity of water and then measure the temperature change that occurs. This method is illustrated in Exercise 12.1.

As an interesting sidelight, in 1818 Pierre Dulong and A.T. Petit discovered that for most metals the specific heat multiplied by the atomic mass of the metal was equal to a constant. The **Dulong and Petit law** is as follows:

$$\text{Specific heat} \times \text{molar mass} = 25 \text{ J mol}^{-1} \text{ } ^\circ\text{C}^{-1} \quad (12.5)$$

This law helped confirm the molar masses of the elements when disagreements occurred. In addition, specific heat is an intensive physical property of all elements and compounds and can be used to identify substances.

Equation 12.6 enables chemists to determine the heat energy of any process by measuring the change in temperature of a known mass of water. The equation is as follows:

$$\text{Heat energy} = (\text{Specific heat}) (\text{Mass}) (\text{Temperature change})$$

$$q = \text{sp. ht.} \times \text{g} \times \Delta T \quad (12.6)$$

In this equation q , the heat energy, is expressed in joules. The temperature change is always determined as the final temperature minus the initial temperature ($^{\circ}\text{C}_{\text{final}} - ^{\circ}\text{C}_{\text{initial}}$). Equation 12.6 is applicable to any substance, not just water.

There is a distinct difference between heat energy and temperature, as Equation 12.6 indicates. Temperature is a measure of the average kinetic energy of a group of atoms, and a temperature change is a change in the average kinetic energy. Heat energy is produced when both the kinetic energy and the energy of attractions between the atoms in the group change in a chemical or physical process.

EXERCISE 12.1

An insulated cup contains 75.0 g of water at 24.00°C . A 26.00-g sample of a metal at 85.25°C is added. The final temperature of the water and metal is 28.34°C .

- What is the specific heat of the metal?
- According to the law of Dulong and Petit, what is the approximate molar mass, MM , of the metal?
- What is the apparent identity of the metal?

Solution

- The law of conservation of energy requires that the heat energy gained by the water be exactly equal to the heat energy lost by the metal as it cools in the water. Mathematically this is written as

$$+q_{\text{water}} = -q_{\text{metal}}$$

Using Equation 12.6, we expand this equation:

$$(\text{sp. heat}_{\text{H}_2\text{O}})(g_{\text{H}_2\text{O}})(\Delta T_{\text{water}}) = -(\text{sp. heat}_{\text{metal}})(g_{\text{metal}})(\Delta T_{\text{metal}})$$

Entering the data yields

$$4.184 \text{ J g}^{-1} ^{\circ}\text{C}^{-1}(75.0 \text{ g})(4.34 ^{\circ}\text{C}) = -(\text{sp. heat}_{\text{metal}})(26.00 \text{ g})(-56.91^{\circ}\text{C})$$

$$1362 \text{ J} = 1480 \text{ g } ^{\circ}\text{C}(\text{sp. heat}_{\text{metal}})$$

$$\text{sp. heat}_{\text{metal}} = 0.920 \text{ J g}^{-1} ^{\circ}\text{C}^{-1}$$

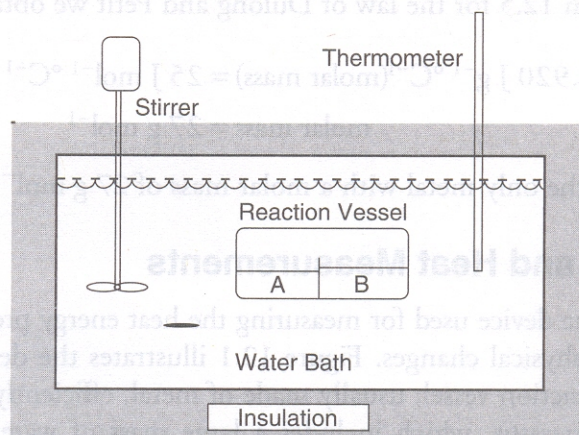


FIGURE 12.1. Diagram of a calorimeter and its essential components. Reactants A and B may be mixed by rotating the reaction vessel. In a bomb calorimeter the reaction vessel is filled with reactant and O_2 , which are then ignited with an electric spark.

EXERCISE 12.2

A calorimeter has a heat capacity of $1265 \text{ J } ^\circ\text{C}^{-1}$. A reaction causes the temperature of the calorimeter to change from 22.34°C to 25.12°C . How many joules of heat were released in this process?

Solution

The heat released in a calorimeter is given in Equation 12.8. We calculate ΔT as $25.12 - 22.34 = +2.78^\circ\text{C}$. Entering these data into the equation gives

$$\begin{aligned} q &= 1265 \text{ J } ^\circ\text{C}^{-1} (2.78^\circ\text{C}) \\ &= 3517 \text{ J of heat energy is released} \end{aligned}$$

FIRST LAW OF THERMODYNAMICS

The **first law of thermodynamics** states that energy is always conserved. In chemistry this law means that the measurable quantities heat (q) and work (w) must add up to the total energy change in a system:

$$\Delta E = q + w \quad (12.9)$$

The value of q has a positive sign if heat is added to the system. The value of w is positive if work is done on the system. Similarly, q is a negative value if heat is released from the system, and w is a negative value if work is done by the system.

If the system cools, q has a positive sign and the process is said to be endothermic. If the system heats up, it is exothermic and q has a negative sign. As we will see later, work is equal to the pressure times the change in volume, $P\Delta V$. If the volume increases, work is done by the system and w has a negative sign. When work is done on the system, the volume decreases and w has a positive sign.

(b) Using Equation 12.5 for the law of Dulong and Petit we obtain

$$0.920 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}(\text{molar mass}) = 25 \text{ J mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$$

$$\text{molar mass} = 27 \text{ g mol}^{-1}$$

(c) Aluminum is the only metal with a molar mass of 27 g mol^{-1} .

Calorimeters and Heat Measurements

A **calorimeter** is the device used for measuring the heat energy produced by chemical reactions and physical changes. Figure 12.1 illustrates the design features of a calorimeter. The reaction vessel, usually made of metal, efficiently transfers heat to the rest of the apparatus, which includes a large mass of water in an insulated container that prevents heat from being lost to the surroundings. Also included are a stirrer and a very accurate thermometer. All parts of the calorimeter heat up or cool down as heat is released or absorbed in the chemical process. Water is the major part of the system; however, for the most accurate measurements the specific heats and masses of the reaction vessel, the thermometer, the stirrer, and the container itself must be included in the calculation.

The total **heat capacity**, C , of the calorimeter, sometimes called the calorimeter constant, is defined as the sum of the products of the specific heat and the mass of all components of the calorimeter:

$$C (\text{J } ^{\circ}\text{C}^{-1}) = (\text{sp. ht.})_1(\text{mass})_1 + (\text{sp. ht.})_2(\text{mass})_2 + (\text{sp. ht.})_3(\text{mass})_3 + \cdots \quad (12.7)$$

The heat energy produced in the calorimeter is then calculated as

$$q = C(^{\circ}\text{C}_{\text{final}} - ^{\circ}\text{C}_{\text{initial}}) \quad (12.8)$$

where C replaces the $(\text{sp. ht.} \times \text{g})$ terms in Equation 12.6.

The most convenient method for determining the heat capacity, C , of a calorimeter is to calibrate the device, using a reaction that will produce a known amount of heat, and then calculate C from the observed temperature change using Equation 12.8.

The change in energy of a system, at constant temperature, is also the difference in potential energy between the final and initial states of the system:

$$\Delta E = PE_{\text{final}} - PE_{\text{initial}} \quad (12.10)$$

As we will see later, ΔE is mainly heat energy. Therefore a system that increases its potential energy is often said to be endothermic, while a decrease in potential energy indicates an exothermic process.

Work

In Equation 12.9 the energy change is the sum of the heat and the work. Heat is measured using a calorimeter, and work is also easily measured. **Work** is defined as the force applied to an object as it moves a certain distance:

$$\text{Work} = \text{Force} \times \text{Distance moved} \quad (12.11)$$

Force can be defined as the pressure exerted over a given area, so

$$\text{Work} = \text{Pressure} \times \text{Area} \times \text{Distance moved}$$

Multiplying the area by the distance results in volume units or an overall volume change:

$$\text{Work} = \text{Pressure} \times \text{Volume change} \quad (12.12)$$

$$w = P\Delta V$$

Work is the product of the pressure and the change in volume that occurs during a chemical reaction.

EXERCISE 12.3

Demonstrate that work is not a state function by calculating the work involved in expanding a gas from an initial state of 1.00 L and 10.0 atm of pressure to (a) 10.0 L and 1.0 atm pressure, (b) 5.00 L and 2.00 atm and then to 10.0 L and 1.00 atm pressure.

Solution

$$\begin{aligned} \text{(a) } w &= -P\Delta V = -(1.00 \text{ atm})(10.0 \text{ L} - 5.00 \text{ L}) \\ &= -9.00 \text{ L atm} \end{aligned}$$

$$\begin{aligned} \text{(b) } w &= -P\Delta V = -(2.00 \text{ atm})(5.0 \text{ L} - 1.00 \text{ L}) - (1.00 \text{ atm})(10.0 \text{ L} - 5.00 \text{ L}) \\ &= -13.0 \text{ L atm} \end{aligned}$$

In both parts of this exercise the sample starts at the same state (1.00 L and 10.0 atm) and ends in the same state (10.0 L and 1.00 atm). However, the work in units of liter atmospheres is different. This can occur only if w is not a state function.

Use of R for the Conversion of Energy Units

We have different energy units—calories, joules, and the newly introduced liter-atmosphere. They are all conveniently related through the universal gas law constant, R . To make these conversions let us see how to convert L-atm to joules for the last problem.

$$? \text{joules} = -13.0 \text{ L-atm}$$

We will divide by the R that has units of L-atm and multiply by the R that has units of joules as follows:

$$? \text{joules} = -13.0 \text{ L-atm} \left(\frac{\text{mol K}}{0.0821 \text{ L-atm}} \right) \left(\frac{8.31 \text{ J}}{\text{mol K}} \right)$$

After canceling units we end up with the desired joules and -13.0 L-atm becomes $-1.32 \times 10^3 \text{ J}$. Similar conversions may be made between electronvolts (EV) and calories.

Definition of q_p , q_v , ΔE , and ΔH

The first law of thermodynamics may be rewritten as

$$\Delta E = q_p - P\Delta V \quad (12.13)$$

The minus sign enters this equation because an increase in volume means that the system does work on the surroundings, and such work has been defined as a negative quantity. The heat term, q , is given the subscript p indicate that the pressure must be constant.

When the heat energy is measured in a calorimeter that does not allow the volume to change, $P\Delta V$ must be zero. As a result $\Delta E = q_v$, where the subscript v indicates that the volume is held constant. Calorimeters that do not allow the volume to change are called **bomb calorimeters**, a name derived from the heavy stainless steel reaction vessel, which was known to explode if not used correctly.

For most real reactions chemists are interested in the heat generated at constant pressure, q_p . This variable is called the enthalpy change and is given the symbol ΔH . **Enthalpy**, H , is the heat content of a chemical, and ΔH is the difference in heat content of the products and reactants:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \quad (12.14)$$

Using Equations 12.9 and 12.12, we can write the relationship between ΔE and ΔH is

$$\Delta E = \Delta H - P\Delta V \quad (12.15)$$

For many reactions, the value of ΔH is very large and the value of $P\Delta V$ is relatively small, so that ΔE and ΔH are approximately equal.

Standard Enthalpy Changes and the Standard Heat of Reaction, ΔH°

The heat energy or enthalpy change, ΔH , produced by a chemical reaction is an **extensive property**, since reacting a larger amount of chemicals produces a larger amount of heat. For example, when propane is burned according to the equation



more heat is generated as more propane is burned. To make the heat produced by a reaction an **intensive property**, the amount of chemical that reacts must be specified. The standard heat of a reaction, ΔH° , is generally defined as the heat produced when the number of moles specified in the balanced chemical equation reacts. For the reaction of propane the heat of reaction, $\Delta H^\circ_{\text{react}}$, equals -2044 kJ when 1 mole of propane reacts with 5 moles of oxygen as shown in Equation 12.16. The negative sign indicates that a large amount of heat is released in this reaction, making propane an excellent fuel for cooking.

Hess's Law

Hess's law states that, whatever mathematical operations are performed on a chemical reaction, the same mathematical operations are applied also to the heat of reaction. Hess's law is summarized as follows:

1. If the coefficients of a chemical reaction are all multiplied by a constant, the $\Delta H^\circ_{\text{react}}$ is multiplied by that same constant.
2. If two or more reactions are added together to obtain an overall reaction, the heats of these reactions are also added to give the heat of the overall reaction.

Hess's law allows the chemist to measure $\Delta H^\circ_{\text{react}}$ for several reactions and then to combine the reactions and their heats to obtain $\Delta H^\circ_{\text{react}}$ for a completely different reaction.

For example, we saw above that the burning of propane produces a large amount of heat. The reaction in Equation 12.16 is easy to perform by igniting propane in the presence of oxygen. The reverse reaction for the synthesis of 1 mole of propane from carbon dioxide and water is impossible to perform, but it may be written as



Since reversing a reaction is the same as multiplying it by -1 , the heat needed for this reaction is $+2044 \text{ kJ}$. The change from a negative to positive value is explained on the basis that ΔH° , which is a state function, depends only on the final and initial states of the system. Synthesis of 1 mole of propane has the same final and initial states as the combustion of 1 mole of propane. The only difference is the direction of the process. We must reach the conclusion that ΔH° has the same magnitude for these two reactions, but they have different signs because they go in opposite directions. Figure 12.2 illustrates this process.

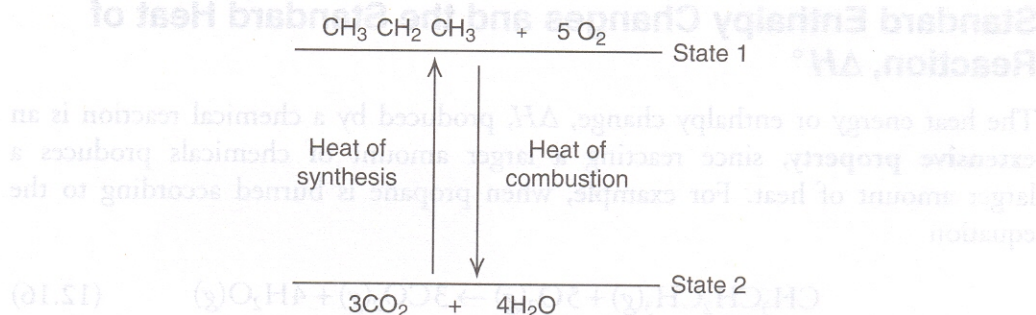


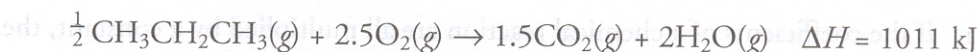
FIGURE 12.2. Diagram illustrating that the heat of a reaction has the same magnitude whether the reaction is run in the forward or reverse direction. The sign of the heat of reaction, however, is positive in one direction and negative in the other.

The general principle that $\Delta H^\circ_{\text{forward react}} = -\Delta H^\circ_{\text{reverse react}}$ is an essential part of Hess's law.

For the combustion of propane, Hess's first rule (see above) tells us that multiplying the reaction by 2 will result in ΔH° also being multiplied by 2:



If the reaction is multiplied by $1/2$, the ΔH° will also be multiplied by $1/2$:



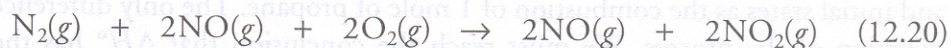
If the reaction is multiplied by 6, the ΔH° will also be multiplied by 6:



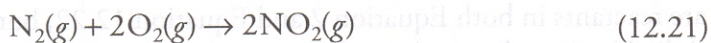
Once ΔH° is multiplied by any coefficient, the system is no longer in standard state and the superscript zero is dropped as shown.

The second of Hess's rules concerns the addition of chemical reactions. To repeat, when chemical reactions are added, all of the reactants are written as reactants of the overall reaction. All of the products are combined as products of the overall reaction. The last step in adding reactions is the cancellation of any identical reactants and products in the overall reaction.

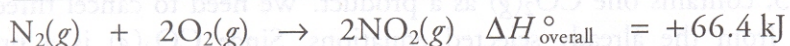
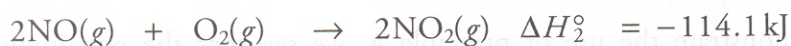
To add the two reactions below, the reactants and products in Equations 12.18 and 12.19 are combined in an overall reaction, Equation 12.20:



Two molecules of $\text{NO}(g)$ are canceled from both the reactant and product sides of Equation 12.20 to obtain the overall reaction:

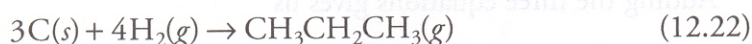


Since the two reactions were added, their heats of reaction are also added:

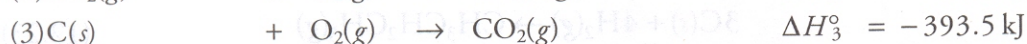
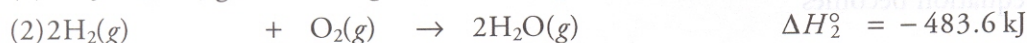


In this example $\Delta H_1^\circ + \Delta H_2^\circ = \Delta H_{\text{overall}}^\circ$.

The heats of many reactions can be determined if the heats of combustion are known for each of the reactants and products. To illustrate this more complex combination of reactions, we can determine the heat of reaction for the synthesis of propane from carbon and hydrogen:



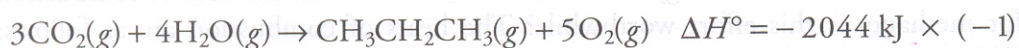
from the combustion reactions of propane, hydrogen, and carbon. These reactions, along with their ΔH° values, are as follows:



If it is not immediately obvious how these three equations should be combined, some general principles on how to approach the problem logically are helpful. In the list below, the first three principles tell us how to find which equation to start with. Once Equation 1 is established, the same principles are used to select and manipulate the remaining reactions. If needed, the fourth principle may be used.

1. Focus on the most complex molecules first.
2. Focus only on atoms and molecules that occur in just one reaction.
3. Focus on atoms and molecules that are in the overall equation.
4. Focus on finding atoms and molecules to cancel unneeded ones from already selected equations.

Using principles 1–3, we see that the combustion of propane in Equation 1 should be considered first. This equation contains 1 mole of propane and so does the overall equation, Equation 12.22. However, in the combustion reaction, Equation 1, propane is a reactant, and in Equation 12.22 it is a product. Consequently, Equation 1 must be reversed by multiplying it by -1 . This reverses the equation and at the same time changes the sign of ΔH° :

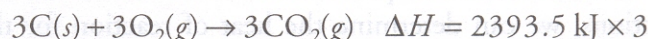


Using principle 3, we now focus on the reaction in Equation 2 and note that it includes $2\text{H}_2(\text{g})$ and that we need $4\text{H}_2(\text{g})$ in our overall equation. The hydrogens

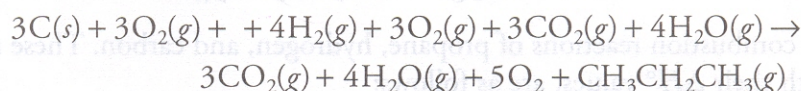
are reactants in both Equation 2 and Equation 12.22, but Equation 2 must be multiplied by 2 so that we have the correct number of H_2 in the final reaction. We will also have to multiply ΔH° by 2:



To demonstrate the use of principle 4, we see that the remaining reaction, Equation 3, contains one $\text{CO}_2(\text{g})$ as a product. We need to cancel three $\text{CO}_2(\text{g})$ molecules from the already selected equations. Since $\text{CO}_2(\text{g})$ is a product in Equation 3 and a reactant in the rearranged Equation 3, the CO_2 's will cancel when the reactions are added. However, Equation 3 must be multiplied by 3 so that all three $\text{CO}_2(\text{g})$ molecules will cancel:



Adding the three equations gives us



After canceling the three $\text{CO}_2(\text{g})$, four $\text{H}_2\text{O}(\text{g})$ and five $\text{O}_2(\text{g})$ molecules, the equation becomes



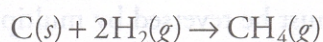
The heat of reaction is the sum of the three ΔH° values multiplied by the operations performed:

$$\begin{aligned} \Delta H_{\text{overall}}^\circ &= \Delta H_1^\circ \times 3(-1) + \Delta H_2^\circ \times 2 + \Delta H_3^\circ \times 3 \\ &= -2044 \text{ kJ} \times (-1) + -483.6 \text{ kJ} \times 2 + -393.5 \text{ kJ} \times 3 \\ &= +2044 \text{ kJ} - 967.2 \text{ kJ} - 1180.5 \text{ kJ} \\ &= -103.7 \text{ kJ} \end{aligned}$$

The advantage of being able to perform some simple experiments to obtain data for complex, even impossible reactions was recognized very quickly. During the energy crisis of the 1970s, the feasibility of producing alternative fuels was determined from thermochemical calculations.

EXERCISE 12.4

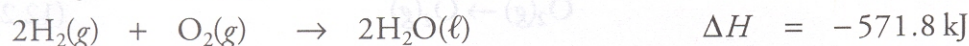
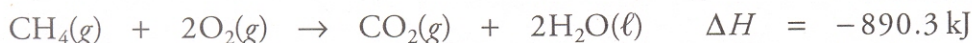
We may wish to synthesize methane from carbon and hydrogen:



In terms of the heat energy needed for this reaction and the heat of combustion for methane, is this effort worthwhile? The heats of combustion are as follows: $\text{CH}_4 = -890.3 \text{ kJ}$; $\text{H}_2 = -571.8 \text{ kJ}$, and $\text{C} = -393.5 \text{ kJ}$.

Solution

The three combustion reactions are written as



To obtain the desired reaction we need to reverse the combustion of methane and add it to the remaining reactions. The heat of this reaction is

$$\begin{aligned} \Delta H_{\text{react}}^{\circ} &= -890.3 \text{ kJ}(-1) + -571.8 \text{ kJ} + -393.5 \text{ kJ} \\ &= -75.0 \text{ kJ} \end{aligned}$$

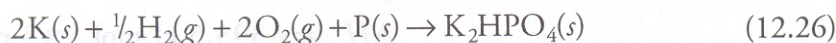
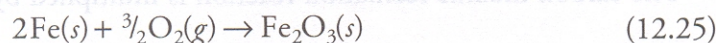
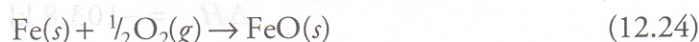
Ignoring all other factors, we see that the formation of CH_4 produces heat and its combustion produces a much greater amount of heat. On this basis, the synthesis of CH_4 is a feasible process. If, however, the energy required to make $\text{H}_2(g)$ from water is included in the calculation, the energy gain is very small and the investment in such a project may be suspect.

In this reaction, methane is formed from the elements carbon and hydrogen. This is known as a formation reaction, and we have determined the heat of formation.

Formation Reactions and Heats of Formation

In the preceding section we saw that the heats of many chemical reactions can be determined if the heats of combustion of all reactants and products are known. For other types of reactions the heat of combustion can also be tabulated. Such a table would be very long and complex, however, and finding the appropriate reactions to combine would be a monumental task. **Heats of formation** allow chemists to tabulate thermochemical data in a short, easy-to-use format.

A **formation reaction** is defined as one in which the reactants are elements in their standard state at 25°C and 1 atmosphere of pressure, and there is only 1 mole of product. Here are some examples of formation reactions:



Fractional coefficients may be used in formation reactions. Since there is always 1 mole of product, the standard heats of formation, ΔH_f° , are tabulated as the heat produced per mole of product.

Since the reaction can easily be deduced if the product is known, a table of data need contain only the name or formula of the product and its corresponding ΔH_f° . A tabulation of some heats of formation is given in Appendix 3.

Heats of formation of the elements are always zero, whether they are molecules or atoms. The reason is that the formation reaction for an element such as oxygen is defined as

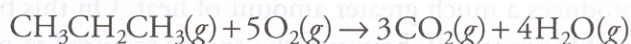


Since the oxygen is at 25°C and 1.00 atmosphere pressure as both the product and the reactant, the initial and final states of the oxygen in Equation 12.27 are the same, and their difference must be zero:

$$\Delta H_f^\circ \text{ (any element)} = 0 \quad (12.28)$$

Heats of formation can be calculated from heats of combustion, as was shown in Exercise 12.4.

For the combustion of propane (Equation 12.16):

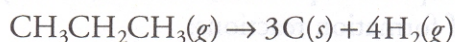


ΔH° can be calculated using the formation reactions and the tabulated heats of formation. Again, we will need a formation reaction for each of the reactants and products. Elements are excluded, however, since their heats of formation are always zero. In this example, the formation reactions for propane, carbon dioxide, and water are needed:



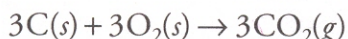
The following operations are performed on these reactions so that they can be combined to yield the combustion reaction:

The propane formation reaction is reversed.



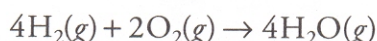
$$\Delta H = -103.8 \text{ kJ mol}^{-1} \times (-1 \text{ mol})$$

The carbon dioxide formation reaction is multiplied by 3.



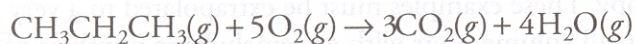
$$\Delta H = -393.5 \text{ kJ mol}^{-1} \times 3 \text{ mol}$$

The $\text{H}_2\text{O}(\text{g})$ formation reaction is multiplied by 4.



$$\Delta H = -241.8 \text{ kJ mol}^{-1} \times 4 \text{ mol}$$

After these three operations, adding the three reactions yields the combustion reaction:



The corresponding sum of the heats is the heat of reaction:

$$\begin{aligned}\Delta H^\circ &= (-103.8 \text{ kJ mol}^{-1})(-1 \text{ mol}) + (-393.5 \text{ kJ mol}^{-1})(3 \text{ mol}) \\ &\quad + (-241.8 \text{ kJ mol}^{-1})(4 \text{ mol}) \\ &= -2044 \text{ kJ}\end{aligned}$$

After several calculations using heats of formation have been made, a pattern appears. The heat of any reaction will be the sum of $(\Delta H_f^\circ \times \text{mol}_{\text{product}})$ for all the products minus the sum of $(\Delta H_f^\circ \times \text{mol}_{\text{reactant}})$ for all the reactants. The $\text{mol}_{\text{product}}$ and $\text{mol}_{\text{reactant}}$ terms refer to the stoichiometric coefficients in the balanced equation for the reaction:

$$\Delta H^\circ = \sum(\Delta H_f^\circ \times \text{coeff})_{\text{products}} - \sum(\Delta H_f^\circ \times \text{coeff})_{\text{reactants}} \quad (12.29)$$

TIP

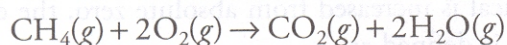
Equation 12.29 is given on the AP Exam.

EXERCISE 12.5

Calculate the heat of combustion of CH_4 . The heats of formation are as follows: $\Delta H_f^\circ(\text{CH}_4(g)) = -74.8 \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(\text{CO}_2(g)) = -110.5 \text{ kJ mol}^{-1}$, and $\Delta H_f^\circ(\text{H}_2\text{O}(g)) = -241.8 \text{ kJ mol}^{-1}$.

Solution

For the combustion of CH_4 the equation is



The heat of this reaction is calculated as

$$\begin{aligned}\Delta H_{\text{react}}^\circ &= [(-110.5 \text{ kJ mol}^{-1}) + (-241.8 \text{ kJ mol}^{-1})(2 \text{ mol})] \\ &\quad - [(-74.8 \text{ kJ mol}^{-1})(1) + (0.00 \text{ kJ mol}^{-1})(2 \text{ mol})] \\ &= -519.3 \text{ kJ}\end{aligned}$$

The value of 0.00 kJ mol^{-1} in this calculation represents the heat of formation of $\text{O}_2(g)$, which, by definition, is zero.