

## Review of Thermodynamics Calculations

The value of  $\Delta H$  for a reaction in one direction is equal in magnitude, but opposite in sign, to  $\Delta H$  for the reaction in the opposite direction, and  $\Delta H$  is directly proportional to the quantity of reactants and products. The standard enthalpy of formation,  $\Delta H_f^\circ$ , is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar and 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps. Gibbs free energy ( $G$ ) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A number of approaches to the computation of free energy changes are possible.

### 18.1 Standard Enthalpy of Formation

#### Learning Objectives

By the end of this section, you will be able to:

- Define standard enthalpy of formation
- Explain Hess's law and use it to compute reaction enthalpies

A standard enthalpy of formation

$$\Delta H_f^\circ$$

is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

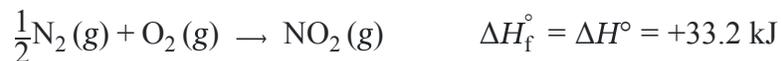


starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of  $\text{CO}_2$ , also at 1 atm and 25 °C. For nitrogen dioxide,

$\text{NO}_2(g)$ ,

$\Delta H_f^\circ$

is 33.2 kJ/mol. This is the enthalpy change for the reaction:



A reaction equation with

$\frac{1}{2}$

mole of  $\text{N}_2$  and 1 mole of  $\text{O}_2$  is correct in this case because the standard enthalpy of formation always refers to 1 mole of product,  $\text{NO}_2(g)$ .

You will find a table of standard enthalpies of formation of many common substances in [Appendix G](#). These values indicate that formation reactions range from highly exothermic (such as  $-2984 \text{ kJ/mol}$  for the formation of  $\text{P}_4\text{O}_{10}$ ) to strongly endothermic (such as  $+226.7 \text{ kJ/mol}$  for the formation of acetylene,  $\text{C}_2\text{H}_2$ ). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

## EXAMPLE 18.1.1

### Evaluating an Enthalpy of Formation

Ozone,  $\text{O}_3(g)$ , forms from oxygen,  $\text{O}_2(g)$ , by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation,

$$\Delta H_f^\circ$$

of ozone from the following information:



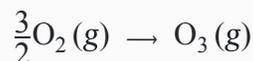
### Solution

$$\Delta H_f^\circ$$

is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus,

$$\Delta H_f^\circ$$

for  $\text{O}_3(g)$  is the enthalpy change for the reaction:



For the formation of 2 mol of  $\text{O}_3(g)$ ,

$$\Delta H^\circ = +286 \text{ kJ}.$$

This ratio,

$$\left(\frac{286 \text{ kJ}}{2 \text{ mol O}_3}\right),$$

can be used as a conversion factor to find the heat produced when 1 mole of  $\text{O}_3(g)$  is formed, which is the enthalpy of formation for  $\text{O}_3(g)$ :

$$\Delta H^\circ \text{ for 1 mole of O}_3(g) = 1 \text{ mol O}_3 \times \frac{286 \text{ kJ}}{2 \text{ mol O}_3} = 143 \text{ kJ}$$

Therefore,

$$\Delta H_f^\circ[\text{O}_3(g)] = +143 \text{ kJ/mol}.$$

## Check Your Learning

Hydrogen gas,  $\text{H}_2$ , reacts explosively with gaseous chlorine,  $\text{Cl}_2$ , to form hydrogen chloride,  $\text{HCl}(g)$ . What is the enthalpy change for the reaction of 1 mole of  $\text{H}_2(g)$  with 1 mole of  $\text{Cl}_2(g)$  if both the reactants and products are at standard state conditions? The standard enthalpy of formation of  $\text{HCl}(g)$  is  $-92.3 \text{ kJ/mol}$ .

### ✓ Answer

For the reaction

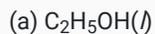


## EXAMPLE 18.1.2

### Writing Reaction Equations for

$$\Delta H_f^\circ$$

Write the heat of formation reaction equations for:



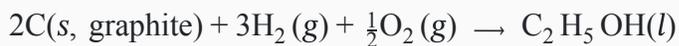
### Solution

Remembering that

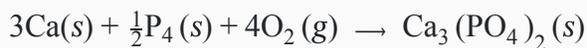
$$\Delta H_f^\circ$$

reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

(a)



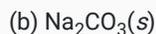
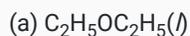
(b)



Note: The standard state of carbon is graphite, and phosphorus exists as  $\text{P}_4$ .

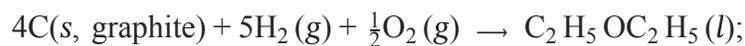
### Check Your Learning

Write the heat of formation reaction equations for:

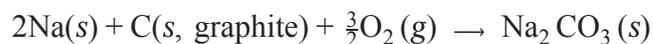


### ✓ Answer

(a)



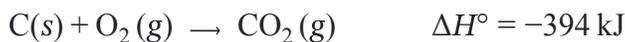
(b)



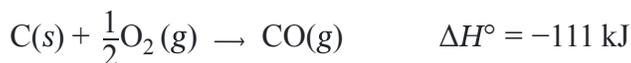
## 18.2 Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

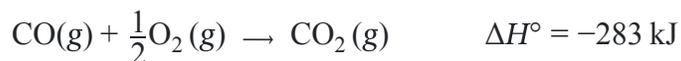
This type of calculation usually involves the use of Hess's law, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.* Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:



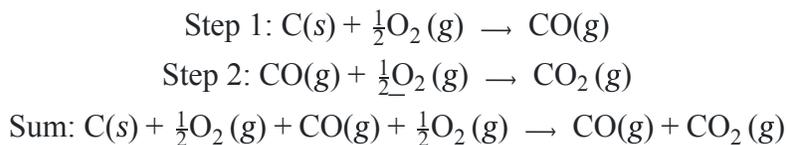
In the two-step process, first carbon monoxide is formed:



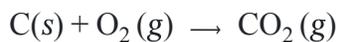
Then, carbon monoxide reacts further to form carbon dioxide:



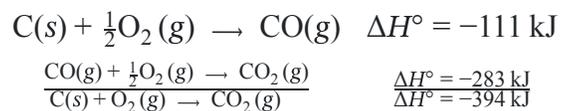
The equation describing the overall reaction is the sum of these two chemical changes:



Because the CO produced in Step 1 is consumed in Step 2, the net change is:



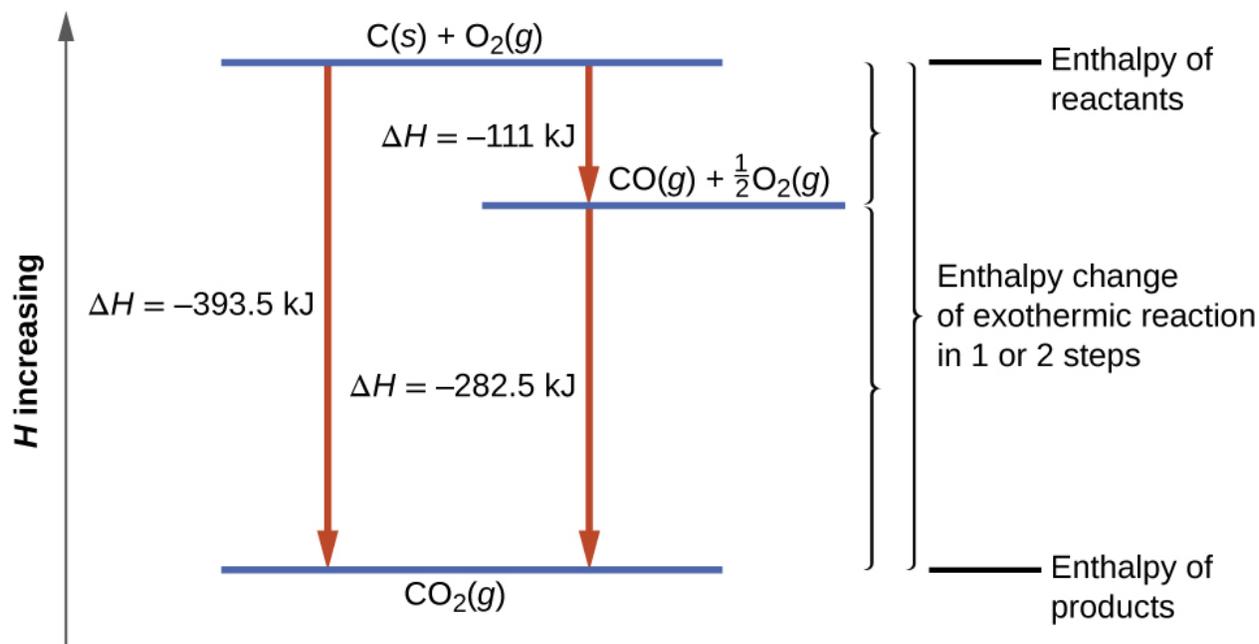
According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps.



The result is shown in [Figure 18.1](#). We see that  $\Delta H$  of the overall reaction is the same whether it occurs in one step or two. This finding (overall  $\Delta H$  for the reaction = sum of  $\Delta H$  values for reaction “steps” in the overall reaction) is true in general for chemical and physical processes.

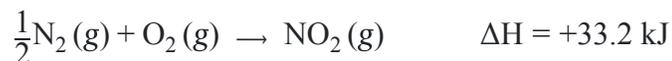
**Figure 18.1**

The formation of  $\text{CO}_2(\text{g})$  from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess’s law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

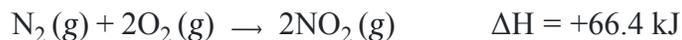


Before we further practice using Hess’s law, let us recall two important features of  $\Delta H$ .

1.  $\Delta H$  is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of  $\text{NO}_2(g)$  is +33.2 kJ:



When 2 moles of  $\text{NO}_2$  (twice as much) are formed, the  $\Delta H$  will be twice as large:

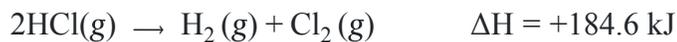


In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2.  $\Delta H$  for a reaction in one direction is equal in magnitude and opposite in sign to  $\Delta H$  for the reaction in the reverse direction. For example, given that:



Then, for the "reverse" reaction, the enthalpy change is also "reversed":



## EXAMPLE 18.2.1

### Stepwise Calculation of

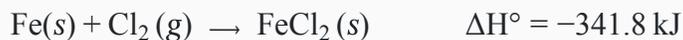
$$\Delta H_f^\circ$$

### Using Hess's Law

Determine the enthalpy of formation,

$$\Delta H_f^\circ,$$

of  $\text{FeCl}_3(s)$  from the enthalpy changes of the following two-step process that occurs under standard state conditions:

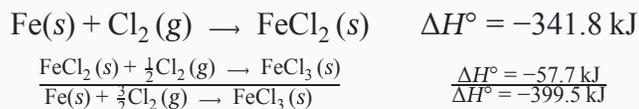


### Solution

We are trying to find the standard enthalpy of formation of  $\text{FeCl}_3(s)$ , which is equal to  $\Delta H_f^\circ$  for the reaction:



Looking at the reactions, we see that the reaction for which we want to find  $\Delta H_f^\circ$  is the sum of the two reactions with known  $\Delta H$  values, so we must sum their  $\Delta H$ s:



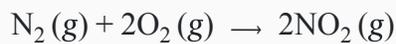
The enthalpy of formation,

$$\Delta H_f^\circ,$$

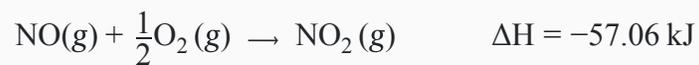
of  $\text{FeCl}_3(s)$  is  $-399.5 \text{ kJ/mol}$ .

### Check Your Learning

Calculate  $\Delta H$  for the process:



from the following information:



▼ Answer

66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of  $\Delta H$ ) if they are difficult to determine experimentally.

## EXAMPLE 18.2.2

### A More Challenging Problem Using Hess's Law

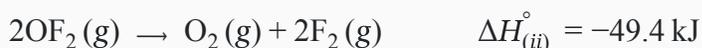
Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

(i)



Use the reactions here to determine the  $\Delta H^\circ$  for reaction (i):

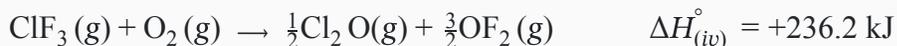
(ii)



(iii)



(iv)



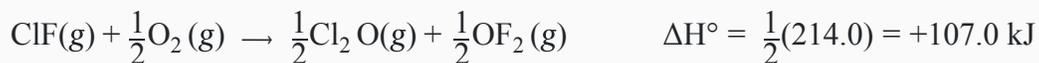
### Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that ClF(g) is needed as a reactant. This can be obtained by multiplying reaction (iii) by

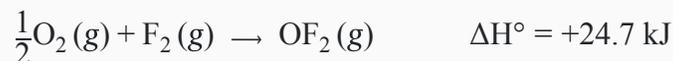
$$\frac{1}{2},$$

which means that the  $\Delta H^\circ$  change is also multiplied by

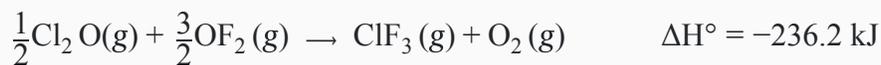
$$\frac{1}{2}:$$



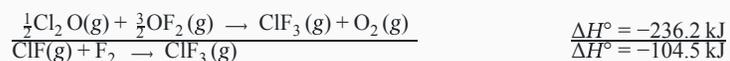
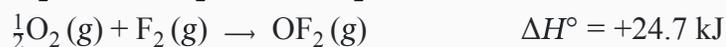
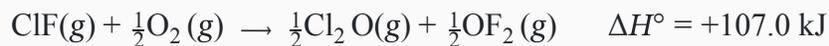
Next, we see that F<sub>2</sub> is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the  $\Delta H^\circ$  changes sign and is halved:



To get  $\text{ClF}_3$  as a product, reverse (iv), changing the sign of  $\Delta H^\circ$ :



Now check to make sure that these reactions add up to the reaction we want:



Reactants



and



cancel out product  $\text{O}_2$ ; product



cancels reactant



and reactant



is cancelled by products



and  $\text{OF}_2$ . This leaves only reactants  $\text{ClF}(g)$  and  $\text{F}_2(g)$  and product  $\text{ClF}_3(g)$ , which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified  $\Delta H^\circ$  values will give the desired  $\Delta H^\circ$ :

$$\Delta H^\circ = (+107.0 \text{ kJ}) + (24.7 \text{ kJ}) + (-236.2 \text{ kJ}) = -104.5 \text{ kJ}$$

## Check Your Learning

Aluminum chloride can be formed from its elements:

(i)

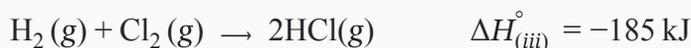


Use the reactions here to determine the  $\Delta H^\circ$  for reaction (i):

(ii)



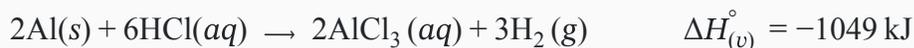
(iii)



(iv)



(v)



### ✓ Answer

-1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with  $\Sigma$  representing "the sum of" and  $n$  standing for the stoichiometric coefficients:

$$\Delta H_{\text{reaction}}^\circ = \Sigma n \times \Delta H_f^\circ(\text{products}) - \Sigma n \times \Delta H_f^\circ(\text{reactants})$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

## EXAMPLE 18.2.3

### Using Hess's Law

What is the standard enthalpy change for the reaction:



### Solution: Using the Equation

Use the special form of Hess's law given previously, and values from [Appendix G](#):

$$\begin{aligned}\Delta H_{\text{reaction}}^\circ &= \sum n \times \Delta H_{\text{f}}^\circ(\text{products}) - \sum n \times \Delta H_{\text{f}}^\circ(\text{reactants}) \\ &= [2 \text{ mol HNO}_3(\text{aq}) \times \frac{-207.4 \text{ kJ}}{\text{mol HNO}_3(\text{aq})} + 1 \text{ mol NO}(\text{g}) \times \frac{+90.2 \text{ kJ}}{\text{mol NO}(\text{g})}] \\ &\quad - [3 \text{ mol NO}_2(\text{g}) \times \frac{+33.2 \text{ kJ}}{\text{mol NO}_2(\text{g})} + 1 \text{ mol H}_2\text{O}(\text{l}) \times \frac{-285.8 \text{ kJ}}{\text{mol H}_2\text{O}(\text{l})}] \\ &= [2 \times (-206.64) + 90.25] - [3 \times 33.2 + -(-285.83)] \\ &= -323.03 + 186.23 \\ &= -136.80 \text{ kJ}\end{aligned}$$

### Solution: Supporting Why the General Equation Is Valid

Alternatively, we can write this reaction as the sum of the decompositions of  $3\text{NO}_2(\text{g})$  and  $1\text{H}_2\text{O}(\text{l})$  into their constituent elements, and the formation of  $2\text{HNO}_3(\text{aq})$  and  $1\text{NO}(\text{g})$  from their constituent elements. Writing out these reactions, and noting their relationships to the

$$\Delta H_{\text{f}}^\circ$$

values for these compounds (from [Appendix G](#)), we have:



Summing these reaction equations gives the reaction we are interested in:



Summing their enthalpy changes gives the value we want to determine:

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= \Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ} + \Delta H_4^{\circ} = (-99.6 \text{ kJ}) + (+285.8 \text{ kJ}) + (-414.8 \text{ kJ}) + (+90.2 \text{ kJ}) \\ &= -138.4 \text{ kJ}\end{aligned}$$

So the standard enthalpy change for this reaction is  $\Delta H^{\circ} = -138.4 \text{ kJ}$ .

Note that this result was obtained by (1) multiplying the

$$\Delta H_{\text{f}}^{\circ}$$

of each product by its stoichiometric coefficient and summing those values, (2) multiplying the

$$\Delta H_{\text{f}}^{\circ}$$

of each reactant by its stoichiometric coefficient and summing those values, and then (3) subtracting the result found in (2) from the result found in (1). This is also the procedure in using the general equation, as shown.

### Check Your Learning

Calculate the heat of combustion of 1 mole of ethanol,  $\text{C}_2\text{H}_5\text{OH}(l)$ , when  $\text{H}_2\text{O}(l)$  and  $\text{CO}_2(g)$  are formed. Use the following enthalpies of formation:  $\text{C}_2\text{H}_5\text{OH}(l)$ ,  $-278 \text{ kJ/mol}$ ;  $\text{H}_2\text{O}(l)$ ,  $-286 \text{ kJ/mol}$ ; and  $\text{CO}_2(g)$ ,  $-394 \text{ kJ/mol}$ .

#### ✓ Answer

$-1368 \text{ kJ/mol}$

## 18.3 Temperature Dependence of Spontaneity

### Learning Objectives

By the end of this section, you will be able to:

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Explain how temperature affects the spontaneity of some processes

As was previously demonstrated in the section on entropy in an earlier chapter, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction

or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

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

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since  $T$  is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both  $\Delta H$  and  $\Delta S$  are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case,  $\Delta G$  will be negative if the magnitude of the  $T\Delta S$  term is greater than  $\Delta H$ . If the  $T\Delta S$  term is less than  $\Delta H$ , the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures*.
2. **Both  $\Delta H$  and  $\Delta S$  are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case,  $\Delta G$  will be negative if the magnitude of the  $T\Delta S$  term is less than  $\Delta H$ . If the  $T\Delta S$  term's magnitude is greater than  $\Delta H$ , the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures*.
3.  **$\Delta H$  is positive and  $\Delta S$  is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case,  $\Delta G$  will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures*.
4.  **$\Delta H$  is negative and  $\Delta S$  is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case,  $\Delta G$  will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures*.

These four scenarios are summarized in [Figure 18.2](#).

**Figure 18.2**

*There are four possibilities regarding the signs of enthalpy and entropy changes.*

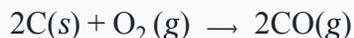
**Summary of the Four Scenarios for Enthalpy and Entropy Changes**

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature  Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

## EXAMPLE 18.3.1

### Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:



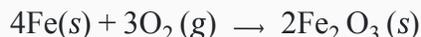
How does the spontaneity of this process depend upon temperature?

#### Solution

Combustion processes are exothermic ( $\Delta H < 0$ ). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas,  $\Delta S > 0$ ). The reaction is therefore spontaneous ( $\Delta G < 0$ ) at all temperatures.

#### Check Your Learning

Popular chemical hand warmers generate heat by the air-oxidation of iron:



How does the spontaneity of this process depend upon temperature?

#### ✓ Answer

$\Delta H$  and  $\Delta S$  are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in “spontaneity” (as reflected by its  $\Delta G$ ) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which  $\Delta G$  is plotted on the  $y$  axis versus  $T$  on the  $x$  axis:

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

$$y = b + mx$$

Such a plot is shown in [Figure 18.3](#). A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative  $\Delta G$ ) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the  $x$ -intercept of the line, that is, the value of  $T$  for which  $\Delta G$  is zero:

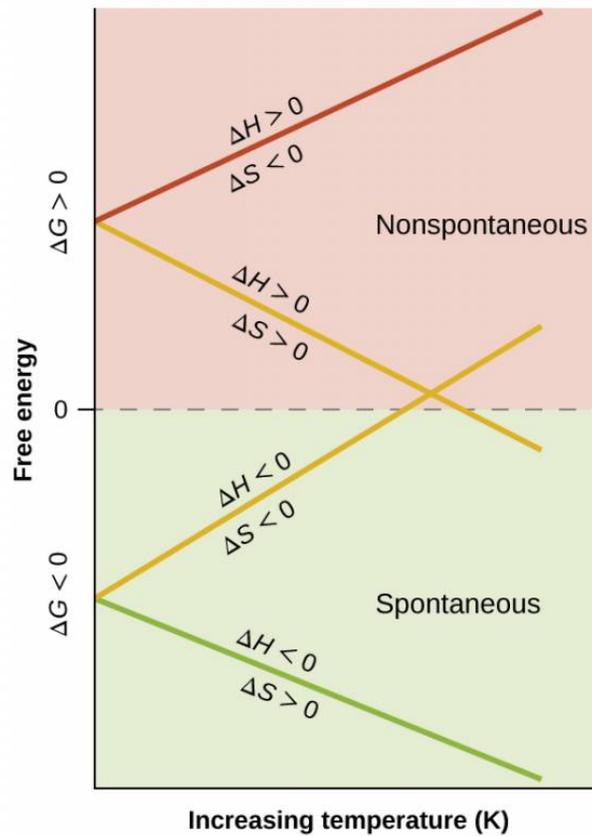
$$\Delta G = 0 = \Delta H - T\Delta S$$

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

So, saying a process is spontaneous at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which  $\Delta G$  for the process is zero. As noted earlier, the condition of  $\Delta G = 0$  describes a system at equilibrium.

**Figure 18.3**

*These plots show the variation in  $\Delta G$  with temperature for the four possible combinations of arithmetic sign for  $\Delta H$  and  $\Delta S$ .*



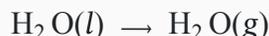
## EXAMPLE 18.3.2

### Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its liquid and gaseous phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in [Appendix G](#) to estimate the boiling point of water.

#### Solution

The process of interest is the following phase change:



When this process is at equilibrium,  $\Delta G = 0$ , so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \quad \text{or} \quad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from [Appendix G](#),

$$\begin{aligned}\Delta H^\circ &= 1 \text{ mol} \times \Delta H_f^\circ(\text{H}_2\text{O}(g)) - 1 \text{ mol} \times \Delta H_f^\circ(\text{H}_2\text{O}(l)) \\ &= (1 \text{ mol}) - 241.82 \text{ kJ/mol} - (1 \text{ mol})(-241.82 \text{ kJ/mol}) = 44.01 \text{ kJ} \\ \Delta S^\circ &= 1 \text{ mol} \times \Delta S^\circ(\text{H}_2\text{O}(g)) - 1 \text{ mol} \times \Delta S^\circ(\text{H}_2\text{O}(l)) \\ &= (1 \text{ mol})188.8 \text{ J/K}\cdot\text{mol} - (1 \text{ mol})70.0 \text{ J/K}\cdot\text{mol} = 118.8 \text{ J/K} \\ T &= \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3 \text{ J}}{118.8 \text{ J/K}} = 370.5 \text{ K} = 97.3 \text{ }^\circ\text{C}\end{aligned}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K ([Appendix G](#)). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

### Check Your Learning

Use the information in [Appendix G](#) to estimate the boiling point of CS<sub>2</sub>.

#### ✓ Answer

313 K (accepted value 319 K)

# Files

Open in Google Drive

## Previous Citation(s)

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