

## 16.14: The Free Energy

In the previous section, we were careful to differentiate between the entropy change occurring in the reaction system  $\Delta S_{\text{sys}}$ , on the one hand, and the entropy change occurring in the surroundings,  $\Delta S_{\text{surr}}$ , given by  $-\Delta H/T$ , on the other. By doing this we were able to get a real insight into what controls the direction of a reaction and why. In terms of calculations, though, it is a nuisance having to look up both entropy and enthalpy data in order to determine the direction of a reaction. For reasons of convenience, therefore, chemists usually combine the entropy and the enthalpy into a new function called the **Gibbs free energy**, or more simply the free energy, which is given the symbol  $G$ . If free-energy tables are available, they are all that is needed to predict the direction of a reaction at the temperature for which the tables apply.

In order to introduce free energy, let us start with the inequality

$$-\frac{\Delta H}{T} + \Delta S_{\text{sys}} > 0$$

This inequality must be true if a reaction occurring at constant pressure in surroundings at constant temperature is to be spontaneous. It is convenient to multiply this inequality by  $T$ ; it then becomes

$$-\Delta H + T\Delta S > 0$$

(From now on we will abandon the subscript "sys".) If  $-\Delta H + T\Delta S$  is greater than zero, it follows that multiplying it by  $-1$  produces a quantity which is *less* than zero, that is,

$$\Delta H - T\Delta S < 0 \quad (16.14.1)$$

This latest inequality can be expressed very neatly in terms of the free energy  $G$ , which is defined by the equation

$$G = H - TS$$

When a chemical reaction occurs at constant temperature, the free energy will change from an initial value of  $G$ , given by

$$G_1 = H_1 - TS_1$$

to a final value

$$G_2 = H_2 - TS_2$$

The change in free energy  $\Delta G$  will thus be

$$\Delta G = G_2 - G_1 = H_2 - H_1 - T(S_2 - S_1)$$

or

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

Feeding this result back into inequality 16.14.1 gives the result

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S < 0 \\ \Delta G &< 0 \end{aligned} \quad (16.14.2)$$

This very important and useful result tells us that when a spontaneous chemical reaction occurs (at constant temperature and pressure), the *free-energy change is negative*. In other words a *spontaneous change corresponds to a decrease in the free energy of the system*.

If we have available the necessary free-energy data in the form of tables, it is now quite easy to determine whether a reaction is spontaneous or not. We merely calculate  $\Delta G$  for the reaction using the tables. If  $\Delta G$  turns out to be positive, the reaction is nonspontaneous, but if it turns out to be negative, then by virtue of Eq. 16.14.2 we can conclude that it is spontaneous. Data on free energy are usually presented in the form of a table of values of **standard free energies of formation**. The standard free energy of formation of a substance is defined as the free-energy change which results when 1 mol of substance is prepared from its elements at the standard pressure of 1 atm and a given temperature, usually 298 K. It is given the symbol  $\Delta G_f^\circ$ . A table of values of  $\Delta G_f^\circ$  (298 K) for a limited number of substances is given in the following table.

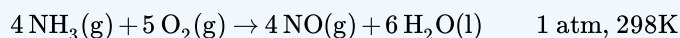
Table 16.14.1: Some Standard Free Energies of Formation at 298.15 K (25°C)

Compound	$\Delta G_f^\circ / \text{kJ mol}^{-1}$	Compound	$\Delta G_f^\circ / \text{kJ mol}^{-1}$
AgCl(s)	-109.789	H <sub>2</sub> O(g)	-228.572
AgN <sub>3</sub> (s)	591.0	H <sub>2</sub> O(l)	-237.129
Ag <sub>2</sub> O(s)	-11.2	H <sub>2</sub> O <sub>2</sub> (l)	-120.35
Al <sub>2</sub> O <sub>3</sub> (s)	-1582.3	H <sub>2</sub> S(g)	-33.56
Br <sub>2</sub> (l)	0.0	HgO(s)	-58.539
Br <sub>2</sub> (g)	3.110	I <sub>2</sub> (s)	0.0
CaO(s)	-604.03	I <sub>2</sub> (g)	19.327
CaCO <sub>3</sub> (s)	-1128.79	KCl(s)	-409.14
C--graphite	0.0	KBr(s)	-380.66
C--diamond	2.9	MgO(s)	-569.43
CH <sub>4</sub> (g)	-50.72	MgH <sub>2</sub> (s)	76.1
C <sub>2</sub> H <sub>2</sub> (g)	209.2	NH <sub>3</sub> (g)	-16.45
C <sub>2</sub> H <sub>4</sub> (g)	68.15	NO(g)	86.55
C <sub>2</sub> H <sub>6</sub> (g)	-32.82	NO <sub>2</sub> (g)	51.31
C <sub>6</sub> H <sub>6</sub> (l)	124.5	N <sub>2</sub> O <sub>4</sub> (g)	97.89
CO(g)	-137.168	NF <sub>3</sub> (g)	-83.2
CO <sub>2</sub> (g)	-394.359	NaCl(s)	-384.138
CuO(s)	-129.7	NaBr(s)	-348.983
Fe <sub>2</sub> O <sub>3</sub> (s)	-742.2	O <sub>3</sub> (g)	163.2
HBr(g)	-53.45	SO <sub>2</sub> (g)	-300.194
HCl(g)	-95.299	SO <sub>3</sub> (g)	-371.06
HI(g)	1.7	ZnO(s)	-318.3

This table is used in exactly the same way as a table of [standard enthalpies of formation](#). This type of table enables us to find  $\Delta G$  values for any reaction occurring at 298 K and 1 atm pressure, provided only that all the substances involved in the reaction appear in the table. The two following examples illustrate such usage.

#### ✓ Example 16.14.1: Spontaneous Reactions

Determine whether the following reaction is spontaneous or not:



#### Solution

Following exactly the same rules used for standard enthalpies of formation, we have

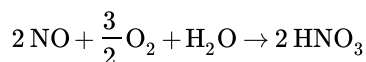
$$\begin{aligned} \Delta G_m^\circ &= \Sigma \Delta G_f^\circ (\text{products}) - \Sigma \Delta G_f^\circ (\text{reactants}) \\ &= 4 \Delta G_f^\circ (\text{NO}) + 6 \Delta G_f^\circ (\text{H}_2\text{O}) - 4 \Delta G_f^\circ (\text{NH}_3) - 5 \Delta G_f^\circ (\text{O}_2) \end{aligned}$$

Inserting values from the table of free energies of formation, we then find

$$\begin{aligned} \Delta G_m^\circ &= [4 \times 86.7 + 6 \times (-273.3) - 4 \times (-16.7) - 5 \times 0.0] \frac{\text{kJ}}{\text{mol}} \\ &= -1010 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

Since  $\Delta G_m^\circ$  is very negative, we conclude that this reaction is spontaneous.

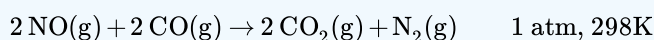
The reaction of  $\text{NH}_3$  with  $\text{O}_2$  is very slow, so that when  $\text{NH}_3$  is released into the air, no noticeable reaction occurs. In the presence of a catalyst, though,  $\text{NH}_3$  burns with a yellowish flame in  $\text{O}_2$ . This reaction is very important industrially, since the  $\text{NO}$  produced from it can be reacted further with  $\text{O}_2$  and  $\text{H}_2\text{O}$  to form  $\text{HNO}_3$ :



Nitric acid,  $\text{HNO}_3$  is used mainly in the manufacture of nitrate fertilizers but also in the manufacture of explosives.

#### ✓ Example 16.14.2: Spontaneous Reactions

Determine whether the following reaction is spontaneous or not:



**Solution** Following previous procedure we have

$$\begin{aligned} (\Delta G_m^\circ &= (-2 \times 394.4 + 0.0 - 2 \times 86.7 + 2 \times 137.3) \frac{\text{kJ}}{\text{mol}} \\ &= -687.6 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

The reaction is thus spontaneous.

This example is an excellent illustration of how useful thermodynamics can be. Since both  $\text{NO}$  and  $\text{CO}$  are air pollutants produced by the internal-combustion engine, this reaction provides a possible way of eliminating both of them in one reaction, killing two birds with one stone. A three-way catalytic converter is able to perform the equivalent of this reaction. The reduction step converts  $\text{NO}_x$  to  $\text{O}_2$  and  $\text{N}_2$ . Then, in the oxidation step,  $\text{CO}$  and  $\text{O}_2$  are converted to  $\text{CO}_2$ . If  $\Delta G_m^\circ$  had turned out to be  $+695 \text{ kJ mol}^{-1}$ , the reaction would be nonspontaneous and there would be no point at all in developing such a device.<sup>[1]</sup>

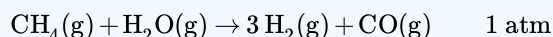
We quite often encounter situations in which we need to know the value of  $\Delta G_m^\circ$  for a reaction at a temperature other than 298 K. Although extensive thermodynamic tables covering a large range of temperatures are available, we can also obtain approximate values for  $\Delta G$  from the relationship

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ$$

If we assume, as we did previously, that neither  $\Delta H_m^\circ$  nor  $\Delta S_m^\circ$  varies much as the temperature changes from 298 K to the temperature in question, we can then use the values of  $\Delta H_m^\circ(298 \text{ K})$  obtained from the [Table of Some Standard Enthalpies of Formation at 25°C](#) and  $\Delta S_m^\circ(298 \text{ K})$  obtained from the [Table of Standard Molar Entropies](#) to calculate  $\Delta G_m^\circ$  for the temperature in question.

#### ✓ Example 16.14.3: Spontaneous at Different Temperatures

Using the [enthalpy values](#) and the [entropy values](#), calculate  $\Delta H_m^\circ$  and  $\Delta S_m^\circ$  for the reaction



Calculate an approximate value for  $\Delta G_m^\circ$  for this reaction at 600 and 1200 K and determine whether the reaction is spontaneous at either temperature.

**Solution** From the tables we find

$$\begin{aligned} \Delta H_m^\circ(298 \text{ K}) &= 3\Delta H_f^\circ(\text{H}_2) + \Delta H_f^\circ(\text{CO}) - \Delta H_f^\circ(\text{CH}_4) - \Delta H_f^\circ(\text{H}_2\text{O}) \\ &= (3 \times 0.0 - 110.6 + 74.8 + 241.8) \frac{\text{kJ}}{\text{mol}} = +206.1 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

and similarly

$$\Delta S_m^\circ(298 \text{ K}) = (3 \times 130.6 + 197.6 - 187.9 - 188.7) \frac{\text{J}}{\text{mol K}} = +212.8 \frac{\text{J}}{\text{mol K}}$$

At 600 K we estimate

$$\begin{aligned} \Delta G_m^\circ &= \Delta H^\circ(298 \text{ K}) - T\Delta S^\circ(298 \text{ K}) \\ &= 206.1 \frac{\text{kJ}}{\text{mol}} - 600 \times 212.8 \frac{\text{J}}{\text{mol}} \end{aligned}$$

$$= (206.1 - 127.7) \frac{\text{kJ}}{\text{mol}} = +78.4 \frac{\text{kJ}}{\text{mol}}$$

Since  $\Delta G$  is positive, the reaction is not spontaneous at this temperature

At 1200 K by contrast

$$\begin{aligned}\Delta G_m^\circ &= 206.1 \frac{\text{kJ}}{\text{mol}} - 1200 \times 212.8 \frac{\text{J}}{\text{mol}} \\ &= (206.1 - 255.4) \frac{\text{kJ}}{\text{mol}} = -49.3 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

At this higher temperature, therefore, the reaction is spontaneous.

From more extensive tables we find that accurate values of the free-energy change are  $\Delta G_m^\circ(600 \text{ K}) = +72.6 \frac{\text{kJ}}{\text{mol}}$  and  $\Delta G_m^\circ(1200 \text{ K}) = -77.7 \frac{\text{kJ}}{\text{mol}}$ . Our approximate value at 1200 K is thus about 50 percent in error. Nevertheless it predicts the right *sign* for  $\Delta G$ , a result which is adequate for most purposes.

1. Baird, C., Cann, M. Environmental Chemistry. 3<sup>rd</sup> edition. 2005. W. H. Freeman and Company. 83-85.

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