

“The energies of our system will decay, the glory of the sun will be dimmed, and the earth, tideless and inert, will no longer tolerate the race which has for a moment disturbed its solitude. Man will go down into the pit, and all his thoughts will perish.”

A.J. Balfour

Enthalpy, Entropy, and Free Energy Calculations

Can it be predicted if a reaction will occur? This is a question that can be answered by applying the principles of chemical thermodynamics, the study of the energy relationships associated with chemical reactions. The term used to label a reaction that proceeds without continual energy input is *spontaneous*. A spontaneous reaction is one that will occur all by itself, once it has been given a small amount of energy so that it can get started. The burning of paper, for example, is a spontaneous reaction. Once you add a little bit of energy, like the heat from a match, the paper continues to burn without any outside help, until there is no more paper to burn. In contrast, a *nonspontaneous* reaction is one that will not proceed unless an outside source of energy is used. An example of a nonspontaneous reaction is the decomposition of water into hydrogen and oxygen. If we add energy to water, the water may begin to decompose (if the amount of energy is great enough) but the decomposition will stop as soon as the energy source is cut off. In this unit we will focus on performing calculations that will allow us to predict the spontaneity of chemical reactions.

Free Energy

J. Willard Gibbs (1839–1903) can be considered as one of the founding fathers of the field of chemical thermodynamics. He introduced a quantity known as *Gibbs free energy*, G , that represents the amount of energy available in a chemical system that can do useful work. If we are to consider a chemical change, we are interested in the change of free energy, or ΔG . Thus ΔG is a measure of the amount of energy in a chemical change that is free to do work on another physical or chemical system.

The most notable aspect of the ΔG concept is that its sign allows us to predict the spontaneity of a chemical reaction that occurs at a constant temperature and pressure:

1. If ΔG is negative, the reaction is spontaneous.
2. If ΔG is positive, the reaction is nonspontaneous.
3. If ΔG is zero, the reacting system is at equilibrium, and there will be no change in the reaction on the macroscopic level.

Standard state values of ΔG , symbolized as ΔG° , are commonly found in tables of thermodynamic quantities. Recall that the thermodynamic standard state conditions are 25°C, 1 atm pressure for gases, and 1 M concentrations for solutions. Calculation of ΔG° for a reaction is given by

$$\Delta G^\circ = \sum n\Delta G_{\text{f}}^\circ \text{ products} - \sum n\Delta G_{\text{f}}^\circ \text{ reactants} \quad \text{(Eq.1)}$$

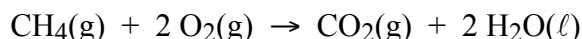
where ΔG_f° is the standard free energy of formation; that is, the free energy change that occurs when one mole of a compound is formed from elements in their standard states. Note the similarity of this equation to the equation used to calculate ΔH° for a reaction, which was introduced earlier in your study of chemistry.

EXAMPLE 1

Calculate the free energy change for the complete combustion of one mole of methane, $\text{CH}_4(\text{g})$, the main component of natural gas. Is this reaction spontaneous?

SOLUTION

Begin by writing the equation that represents this reaction. Recall that "complete combustion," or burning, is a reaction with oxygen from the atmosphere, forming carbon dioxide and water:



Now apply **Eq.1** and then consult a table of thermodynamic values:

$$\begin{aligned} \Delta G^\circ &= (1 \text{ mol})[\Delta G_f^\circ \text{ for } \text{CO}_2(\text{g})] + (2 \text{ mol})[\Delta G_f^\circ \text{ for } \text{H}_2\text{O}(\ell)] - \\ &(1 \text{ mol})[\Delta G_f^\circ \text{ for } \text{CH}_4(\text{g})] - (2 \text{ mol})[\Delta G_f^\circ \text{ for } \text{O}_2(\text{g})] = \\ &(1 \text{ mol})(-394.4 \text{ kJ/mol}) + (2 \text{ mol})(-237.0 \text{ kJ/mol}) - (1 \text{ mol})(-50.8 \text{ kJ/mol}) - \\ &(2 \text{ mol})(0) = -817.6 \text{ kJ} \end{aligned}$$

(Thermodynamic values are experimentally determined, so the values in your textbook may differ slightly from these.)

The negative value of ΔG° indicates that the reaction is spontaneous. This matches our experiences in everyday life, where we have seen that natural gas burns spontaneously.

Entropy

The standard state entropy change for a reaction, ΔS° , can be calculated from data in thermodynamic tables in a manner similar to changes in enthalpy and free energy. ΔS° for a chemical reaction is

$$\Delta S^\circ = \sum nS^\circ_{\text{products}} - \sum nS^\circ_{\text{reactants}} \quad \text{(Eq.2)}$$

A notable difference in ΔS° values is that we do not use "entropies of formation." This is a result of the Third Law of Thermodynamics, which defines a zero for entropy and thus allows us to calculate absolute entropy values.

EXAMPLE 2

Determine the standard entropy change for the decomposition of one mole of solid calcium carbonate, forming solid calcium oxide and carbon dioxide gas.

SOLUTION

This is a straight-forward application of Eq.2, followed by substitution of the appropriate values from a table.



$$\begin{aligned} \Delta S^\circ &= (1 \text{ mol})[\Delta S^\circ \text{ for CaO}(\text{s})] + (1 \text{ mol})[\Delta S^\circ \text{ for CO}_2(\text{g})] - \\ &(1 \text{ mol})[\Delta S^\circ \text{ for CaCO}_3(\text{s})] = \\ &(1 \text{ mol}) (39.8 \text{ J/mol K}) + (1 \text{ mol}) (213.7 \text{ J/mol K}) - (1 \text{ mol}) (92.9 \text{ J/mol K}) = \\ &160.6 \text{ J/K} \end{aligned}$$

Free Energy, Enthalpy, and Entropy

By definition, Gibbs free energy is

$$G \equiv H - TS \quad \text{(Eq.3)}$$

We are interested in the change of free energy associated with chemical reactions rather than absolute quantities, so we have

$$\Delta G = \Delta H - \Delta(TS) \quad \text{(Eq.4)}$$

and if we consider constant temperature processes,

$$\Delta G = \Delta H - T\Delta S \quad \text{(Eq.5)}$$

and, finally, adding in standard state conditions, we have

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{(Eq.6)}$$

Eq.6, the Gibbs–Helmholtz equation, tells us that the standard free energy change depends on both the change in enthalpy and the change in entropy. We will explore this idea further during the workshop activities; for now, let's see how ΔG° can be calculated from ΔH° and ΔS° values.

EXAMPLE 3

Calculate ΔG° for the reaction in Example 2, the decomposition of calcium carbonate, from ΔH° and ΔS° values.

SOLUTION

We have already calculated ΔS° for the reaction $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ as 160.6 J/K. We can find ΔH° for the reaction in a similar manner:

$$\begin{aligned} \Delta H^\circ &= (1 \text{ mol})[\Delta H^\circ \text{ for CaO}(\text{s})] + (1 \text{ mol})[\Delta H^\circ \text{ for CO}_2(\text{g})] - \\ &(1 \text{ mol})[\Delta H^\circ \text{ for CaCO}_3(\text{s})] = \\ &(1 \text{ mol}) (-635.3 \text{ kJ/mol}) + (1 \text{ mol}) (-393.5 \text{ kJ/mol}) - (1 \text{ mol}) (-1207.0 \text{ kJ/mol}) \\ &= 178.2 \text{ kJ} \end{aligned}$$

Now use Equation **Eq.6** to find the value of ΔG° :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 178.2 \text{ kJ} - 298.15 \text{ K} \times \frac{160.6 \text{ J}}{\text{K}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 130.3 \text{ kJ}$$

Notice that we used 298.15 K, or 25°C as the value of T. This is thermodynamic standard temperature. Also note how the ΔS° value was in joules per kelvin, while the ΔH° value was in kJ. The J \leftrightarrow kJ conversion must be accounted for in the calculation.

Nonstandard Conditions and Free Energy

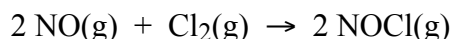
Up to this point, we have only considered thermodynamic changes under standard conditions. ΔG at any conditions can be determined by

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (\text{Eq.7})$$

where Q is the reaction quotient. This is the same quantity that was introduced while we were studying chemical equilibria.

EXAMPLE 4

Consider the reaction of nitrogen monoxide and chlorine to form nitrosyl chloride:



- Calculate ΔG° for the reaction.
- Calculate ΔG when $p_{\text{NO}} = 0.30 \text{ atm}$, $p_{\text{Cl}_2} = 0.10 \text{ atm}$, and $p_{\text{NOCl}} = 0.45 \text{ atm}$.

SOLUTION

- ΔG° is found by applying Eq.1:

$$\begin{aligned} \Delta G^\circ &= (2 \text{ mol})[\Delta G_f^\circ \text{ for NOCl(g)}] - (2 \text{ mol})[\Delta G_f^\circ \text{ for NO(g)}] - \\ &(1 \text{ mol})[\Delta G_f^\circ \text{ for Cl}_2\text{(g)}] = \\ &(2 \text{ mol})(66.2 \text{ kJ/mol}) - (2 \text{ mol})(86.6 \text{ kJ/mol}) - (1 \text{ mol})(0) = -40.8 \text{ kJ} \end{aligned}$$

- ΔG at nonstandard conditions (the pressures are not 1 atm in this case) is found by applying Eq.7: $\Delta G = \Delta G^\circ + RT \ln Q$. Begin by calculating Q:

$$Q = \frac{(p_{\text{NOCl}})^2}{(p_{\text{NO}})^2 (p_{\text{Cl}_2})} = \frac{(0.45)^2}{(0.30)^2 (0.10)} = 23$$

Now find ΔG :

$$\Delta G = \Delta G^\circ + RT \ln Q = -40.8 \text{ kJ} + \frac{8.314 \text{ J}}{\text{mol K}} \times 298.15 \text{ K} \times \ln 23 \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -33.0 \text{ kJ}$$

The Equilibrium Constant and Free Energy

Starting from Equation **Eq.7**,

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (\text{Eq.7})$$

and using the facts that at equilibrium, $Q = K$ and $\Delta G = 0$,

$$0 = \Delta G^\circ + RT \ln K \quad (\text{Eq.8})$$

and finally rearranging to isolate ΔG° ,

$$\Delta G^\circ = -RT \ln K \quad (\text{Eq.9})$$

we obtain the relationship between the change in free energy for a reaction and the equilibrium constant.

EXAMPLE 5

K_{sp} for the reaction $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ is 1.1×10^{-10} . Use thermodynamic data to determine ΔG° for this reaction, and then calculate K from **Eq.9**. How do the K values compare?

SOLUTION

ΔG° is found in the usual manner:

$$\begin{aligned} \Delta G^\circ &= (1 \text{ mol})[\Delta G_f^\circ \text{ for } \text{Ba}^{2+}(\text{aq})] + (1 \text{ mol})[\Delta G_f^\circ \text{ for } \text{SO}_4^{2-}(\text{aq})] - \\ &(1 \text{ mol})[\Delta G_f^\circ \text{ for } \text{BaSO}_4(\text{s})] = \\ &(1 \text{ mol})(-560.8 \text{ kJ/mol}) + (1 \text{ mol})(-744.5 \text{ kJ/mol}) - (1 \text{ mol})(-1362.3 \text{ kJ/mol}) = \\ &57.0 \text{ kJ} \end{aligned}$$

Now use **Eq.9** to find K :

$$\Delta G^\circ = -RT \ln K \quad \ln K = \frac{-\Delta G^\circ}{RT} \quad K = e^{(-\Delta G^\circ/RT)}$$

Let's get the coefficient of e first:

$$\frac{-\Delta G^\circ}{RT} = -57.0 \text{ kJ} \times \frac{K}{8.314 \text{ J}} \times \frac{1}{298.15 \text{ K}} \times \frac{1000 \text{ J}}{\text{kJ}} = -23.0$$

↑
assume molar quantities

$$K = e^{-23.0} = 1.0 \times 10^{-10}$$

The K calculated from ΔG_f° values agrees with the tabulated K_{sp} value to ± 1 in the doubtful digit.
