

## 18.9: Free Energy Changes for Nonstandard States: The Relationship between $\Delta G_{\text{rxn}}^{\circ}$ and $\Delta G_{\text{rxn}}$

In Section 18.8, we learned how to calculate the *standard* free energy change for a reaction ( $\Delta G_{\text{rxn}}^{\circ}$ ). However, the standard free energy change applies only to a very narrow set of conditions, namely, those conditions in which the reactants and products are in their standard states.

### Standard versus Nonstandard States

Consider the standard free energy change for the evaporation of liquid water to gaseous water:



The standard free energy change for this process is positive, so the process is nonspontaneous. But you know that if you spill water onto the floor under ordinary conditions, it spontaneously evaporates. Why? *Because under ordinary conditions the reactants and products are not in their standard states* and  $\Delta G_{\text{rxn}}^{\circ}$  applies only when the reactants and product are in their standard states, sometimes called *standard conditions*. For a gas (such as the water vapor in the reaction just given), the standard state is the pure gas at a partial pressure of 1 atmosphere. In a flask containing liquid water and water vapor in its standard state ( $P_{\text{H}_2\text{O}} = 1 \text{ atm}$ ) at 25 °C, the water does not vaporize. In fact, since  $\Delta G_{\text{rxn}}^{\circ}$  is negative for the reverse reaction, the reaction spontaneously occurs in reverse—water vapor condenses.

In open air under ordinary circumstances, the partial pressure of water vapor is much less than 1 atm. The state of the water vapor is not its standard state, and therefore the value of  $\Delta G_{\text{rxn}}^{\circ}$  does not apply. For the nonstandard state, we must calculate  $\Delta G_{\text{rxn}}$  (as opposed to  $\Delta G_{\text{rxn}}^{\circ}$ ) to predict spontaneity.



Spilled water spontaneously evaporates even though  $\Delta G^{\circ}$  for the vaporization of water is positive. Why?

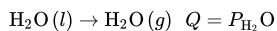
### The Free Energy Change of a Reaction under Nonstandard Conditions

We can calculate the **free energy change of a reaction under nonstandard conditions** ( $\Delta G_{\text{rxn}}$ ) from  $\Delta G_{\text{rxn}}^{\circ}$  using the relationship:

[18.13]

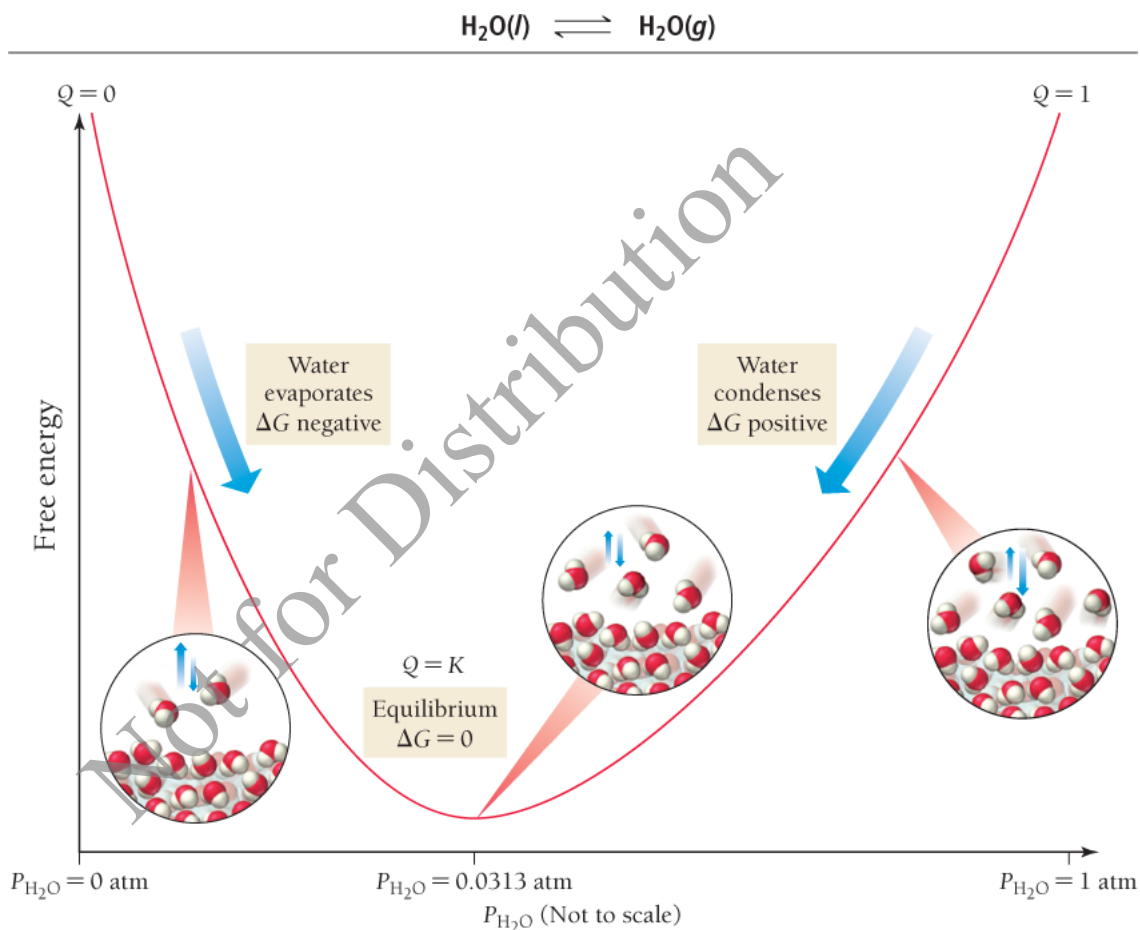
$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + RT \ln Q$$

where  $Q$  is the reaction quotient (defined in Section 15.7),  $T$  is the temperature in kelvins, and  $R$  is the gas constant in the appropriate units (8.314 J/mol · K). In Equation 18.13 and all subsequent thermodynamic equations, we use  $Q_p$  for reactions involving gases and  $Q_c$  for reactions involving substances dissolved in solution. We can demonstrate the use of this equation by applying it to the liquid–vapor water equilibrium under several different conditions, as shown in Figure 18.10. Note that by the law of mass action, for this equilibrium,  $Q = P_{\text{H}_2\text{O}}$  (where the pressure is expressed in atmospheres):



**Figure 18.10 Free Energy versus Pressure for Water**

The free energy change for the vaporization of water is a function of pressure.



## Standard Conditions

Under standard conditions,  $P_{\text{H}_2\text{O}} = 1 \text{ atm}$  and therefore  $Q = 1$ . Substituting, we get the expression:

$$\begin{aligned} \Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^{\circ} + RT \ln Q \\ &= +8.59 \text{ kJ/mol} + RT \ln(1) \\ &= +8.59 \text{ kJ/mol} \end{aligned}$$

Under standard conditions,  $Q$  is always equal to 1, and since  $\ln(1) = 0$ , the value of  $\Delta G_{\text{rxn}}$  is equal to  $\Delta G_{\text{rxn}}^{\circ}$ , as expected. For the liquid–vapor water equilibrium, because  $\Delta G_{\text{rxn}}^{\circ} > 0$  the reaction is not spontaneous in the forward direction but is spontaneous in the reverse direction. As stated previously, under standard conditions

water vapor condenses into liquid water.

## Equilibrium Conditions

At 25.00 °C, liquid water is in equilibrium with water vapor at a pressure of 0.0313 atm; therefore,

$Q = K_p = 0.0313$ . Substituting:

$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^{\circ} + RT \ln (0.0313) \\ &= +8.59 \text{ kJ/mol} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298.15 \text{ K}) \ln (0.0313) \\ &= +8.59 \text{ kJ/mol} + (-8.59 \times 10^3 \text{ J/mol}) \\ &= +8.59 \text{ kJ/mol} - 8.59 \text{ kJ/mol} \\ &= 0\end{aligned}$$

Under equilibrium conditions, the value of  $RT \ln Q$  is always equal in magnitude but opposite in sign to the value of  $\Delta G_{\text{rxn}}^{\circ}$ . Therefore, the value of  $\Delta G_{\text{rxn}}$  is zero. Because  $\Delta G_{\text{rxn}} = 0$ , the reaction is not spontaneous in either direction, as expected for a reaction at equilibrium.

## Other Nonstandard Conditions

To calculate the value of  $\Delta G_{\text{rxn}}$  under any other set of nonstandard conditions, calculate  $Q$  and substitute the calculated value into Equation 18.14. For example, imagine that the partial pressure of water vapor in the air on a dry (nonhumid) day is  $5.00 \times 10^{-3}$  so  $Q = 5.00 \times 10^{-3}$ . Substituting:

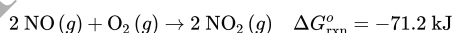
$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^{\circ} + RT \ln (5.00 \times 10^{-3}) \\ &= +8.59 \text{ kJ/mol} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K}) \ln (5.00 \times 10^{-3}) \\ &= +8.59 \text{ kJ/mol} + (-13.1 \times 10^3 \text{ J/mol}) \\ &= +8.59 \text{ kJ/mol} - 13.1 \text{ kJ/mol} \\ &= -4.5 \text{ kJ/mol}\end{aligned}$$

Under these conditions,  $\Delta G_{\text{rxn}} < 0$ , so the reaction is spontaneous in the forward direction, consistent with our experience of water evaporating when spilled on the floor.

A water partial pressure of  $5.00 \times 10^{-3}$  atm corresponds to a relative humidity of 16% at 25 °C.

### Example 18.10 Calculating $\Delta G_{\text{rxn}}$ under Nonstandard Conditions

Consider the reaction at 298 K:



Calculate  $\Delta G_{\text{rxn}}$  under these conditions:

$$P_{\text{NO}} = 0.100 \text{ atm}; \quad P_{\text{O}_2} = 0.100 \text{ atm}; \quad P_{\text{NO}_2} = 2.00 \text{ atm}$$

Is the reaction more or less spontaneous under these conditions than under standard conditions?

**SOLUTION** Use the law of mass action to calculate  $Q$ .

$$Q = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 P_{\text{O}_2}} = \frac{(2.00)^2}{(0.100)^2 (0.100)} = 4.00 \times 10^3$$

Substitute  $Q$ ,  $T$ , and  $\Delta G_{\text{rxn}}^{\circ}$  into Equation 18.13 to calculate  $\Delta G_{\text{rxn}}$ . (Since the units of  $R$  include joules, write  $\Delta G_{\text{rxn}}^{\circ}$  in joules.)

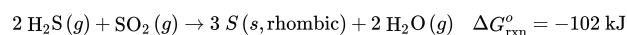
$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^{\circ} + RT \ln Q \\ &= -71.2 \times 10^3 \text{ J} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K}) \ln (4.00 \times 10^3) \\ &= -71.2 \times 10^3 \text{ J} + 20.5 \times 10^3 \text{ J}\end{aligned}$$

$$\begin{aligned}
 &= 1.12 \times 10^3 + 20.0 \times 10^3 \\
 &= -50.7 \times 10^3 \text{ J} \\
 &= -50.7 \text{ kJ}
 \end{aligned}$$

The reaction is spontaneous under these conditions but less spontaneous than it would be under standard conditions (because  $\Delta G_{\text{rxn}}$  is less negative than  $\Delta G_{\text{rxn}}^\circ$ ).

**CHECK** The calculated result is consistent with what you would expect based on Le Châtelier's principle (see [Section 15.9](#)); increasing the concentration of the products and decreasing the concentration of the reactants relative to standard conditions should make the reaction less spontaneous than it was under standard conditions.

**FOR PRACTICE 18.10** Consider the reaction at 298 K:



Calculate  $\Delta G_{\text{rxn}}$  under these conditions:

$$P_{\text{H}_2\text{S}} = 2.00 \text{ atm} \quad P_{\text{SO}_2} = 1.50 \text{ atm}; \quad P_{\text{H}_2\text{O}} = 0.0100 \text{ atm}$$

Is the reaction more or less spontaneous under these conditions than under standard conditions?

**Interactive Worked Example 18.10** Calculating  $\Delta G_{\text{rxn}}$  under Nonstandard Conditions

**Conceptual Connection 18.5** Free Energy Changes and Le Châtelier's Principle

Interactive

Not for Distribution

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