

## 8.7: $\Delta G^\circ$ and K as Functions of Temperature

### Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

As was previously demonstrated, 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:

$$\Delta G = \Delta H - T\Delta S \quad (8.7.1)$$

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:

- 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*.
- 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*.
- $\Delta H$  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*.
- $\Delta H$  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 8.7.1.

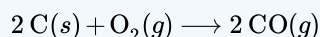
Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (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

Figure 8.7.1: There are four possibilities regarding the signs of enthalpy and entropy changes.

### ✓ Predicting the Temperature Dependence of Spontaneity

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



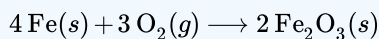
How does the spontaneity of this process depend upon temperature?

#### 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.

### ? Exercise 8.7.3

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:

$$\Delta G = \Delta H - T\Delta S \quad (8.7.2)$$

$$y = b + mx \quad (8.7.3)$$

Such a plot is shown in Figure 8.7.2. 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:

$$\Delta G = 0 = \Delta H - T\Delta S \quad (8.7.4)$$

$$T = \frac{\Delta H}{\Delta S} \quad (8.7.5)$$

And 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, this condition describes a system at equilibrium.

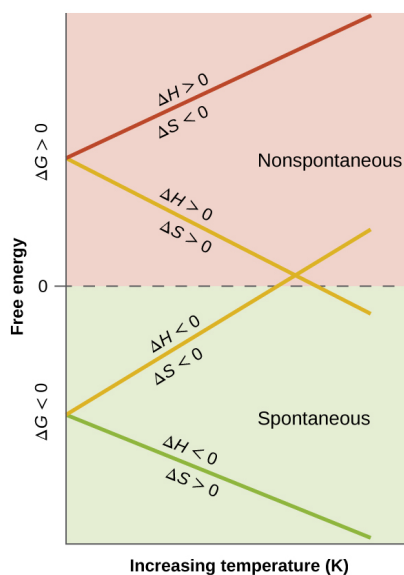


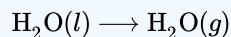
Figure 8.7.2: These plots show the variation in  $\Delta G$  with temperature for the four possible combinations of arithmetic sign for  $\Delta H$  and  $\Delta S$ .

### ✓ 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 solid and liquid 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](#),

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ(\text{H}_2\text{O}(g)) - \Delta H_f^\circ(\text{H}_2\text{O}(l)) \\ &= -241.82 \text{ kJ/mol} - (-285.83 \text{ kJ/mol}) = 44.01 \text{ kJ/mol} \end{aligned} \quad (8.7.6)$$

$$\begin{aligned} \Delta S^\circ &= \Delta S_{298}^\circ(\text{H}_2\text{O}(g)) - \Delta S_{298}^\circ(\text{H}_2\text{O}(l)) \\ &= 188.8 \text{ J/K} \cdot \text{mol} - 70.0 \text{ J/K} \cdot \text{mol} = 118.8 \text{ J/K} \cdot \text{mol} \end{aligned} \quad (8.7.7)$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3 \text{ J/mol}}{118.8 \text{ J/K} \cdot \text{mol}} = 370.5 \text{ K} = 97.3^\circ \text{C}$$

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.

### ? Exercise 8.7.4

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

#### Answer

313 K (accepted value 319 K)

## Temperature Dependence of the Equilibrium Constant

The fact that  $\Delta G^\circ$  and  $K$  are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship can be expressed as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8.7.8)$$

Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are **temperature independent**, for an exothermic reaction ( $\Delta H^\circ < 0$ ), the magnitude of  $K$  decreases with increasing temperature, whereas for an endothermic reaction ( $\Delta H^\circ > 0$ ), the magnitude of  $K$  increases with increasing temperature. The quantitative relationship expressed in Equation 8.7.8 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of  $K$ . Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of  $K$ . Equation 8.7.8 also shows that the magnitude of  $\Delta H^\circ$  dictates how rapidly  $K$  changes as a function of temperature. In contrast, the magnitude and sign of  $\Delta S^\circ$  affect the magnitude of  $K$  but not its temperature dependence.

If we know the value of  $K$  at a given temperature and the value of  $\Delta H^\circ$  for a reaction, we can estimate the value of  $K$  at any other temperature, even in the absence of information on  $\Delta S^\circ$ . Suppose, for example, that  $K_1$  and  $K_2$  are the equilibrium constants for a reaction at temperatures  $T_1$  and  $T_2$ , respectively. Applying Equation 8.7.8 gives the following relationship at each temperature:

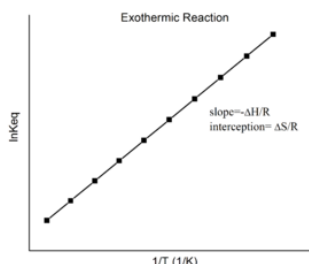
$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \quad (8.7.9)$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \quad (8.7.10)$$

Subtracting  $\ln K_1$  from  $\ln K_2$ ,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (8.7.11)$$

Thus calculating  $\Delta H^\circ$  from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature ( $K_1$ ) allow us to calculate the value of the equilibrium constant at any other temperature ( $K_2$ ), assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature. The linear relation between  $\ln K$  and the standard [enthalpies](#) and [entropies](#) in Equation 8.7.11 is known as the van't Hoff equation. It shows that a plot of  $\ln K$  vs.  $1/T$  should be a line with slope  $-\Delta_r H^\circ/R$  and intercept  $\Delta_r S^\circ/R$ .



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Hence, these thermodynamic enthalpy and entropy changes for a reversible reaction can be determined from plotting  $\ln K$  vs.  $1/T$  data without the aid of [calorimetry](#). Of course, the main assumption here is that  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  are only very weakly dependent on  $T$ , which is usually valid over a narrow temperature range.

#### ✓ Example 8.7.4

The equilibrium constant for the formation of  $\text{NH}_3$  from  $\text{H}_2$  and  $\text{N}_2$  at  $25^\circ\text{C}$  is  $K_p = 5.4 \times 10^5$ . What is  $K_p$  at  $500^\circ\text{C}$ ? (Use the data from Example 10.)

**Given:** balanced chemical equation,  $\Delta H^\circ$ , initial and final  $T$ , and  $K_p$  at  $25^\circ\text{C}$

**Asked for:**  $K_p$  at  $500^\circ\text{C}$

**Strategy:**

Convert the initial and final temperatures to kelvins. Then substitute appropriate values into Equation 8.7.11 to obtain  $K_2$ , the equilibrium constant at the final temperature.

**Solution:**

The value of  $\Delta H^\circ$  for the reaction obtained using Hess's law is  $-91.8 \text{ kJ/mol}$  of  $\text{N}_2$ . If we set  $T_1 = 25^\circ\text{C} = 298 \text{ K}$  and  $T_2 = 500^\circ\text{C} = 773 \text{ K}$ , then from Equation 8.7.11 we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (8.7.12)$$

$$= \frac{(-91.8 \text{ kJ})(1000 \text{ J/kJ})}{8.314 \text{ J/K}} \left( \frac{1}{298 \text{ K}} - \frac{1}{773 \text{ K}} \right) = -22.8 \quad (8.7.13)$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10} \quad (8.7.14)$$

$$K_2 = (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5} \quad (8.7.15)$$

Thus at  $500^\circ\text{C}$ , the equilibrium strongly favors the reactants over the products.

### ? Exercise 8.7.4

In the exercise in Example 8.7.3, you calculated  $K_p = 2.2 \times 10^{12}$  for the reaction of NO with  $O_2$  to give  $NO_2$  at  $25^\circ\text{C}$ . Use the  $\Delta H^\circ_f$  values in the exercise in Example 10 to calculate  $K_p$  for this reaction at  $1000^\circ\text{C}$ .

**Answer:**  $5.6 \times 10^{-4}$



The Van't Hoff Equation: [https://youtu.be/4vk6idAXp\\_A](https://youtu.be/4vk6idAXp_A)

## Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express  $\Delta G$  in terms of the partial pressures of the reactants and products, which gives us a relationship between  $\Delta G$  and  $K_p$ , the equilibrium constant of a reaction involving gases, or  $K$ , the equilibrium constant expressed in terms of concentrations. If  $\Delta G^\circ < 0$ , then  $K$  or  $K_p > 1$ , and products are favored over reactants. If  $\Delta G^\circ > 0$ , then  $K$  or  $K_p < 1$ , and reactants are favored over products. If  $\Delta G^\circ = 0$ , then  $K$  or  $K_p = 1$ , and the system is at equilibrium. We can use the measured equilibrium constant  $K$  at one temperature and  $\Delta H^\circ$  to estimate the equilibrium constant for a reaction at any other temperature.

## Contributors and Attributions

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