

# Chapter 9 : Spontaneity, Entropy, and Free Energy

## Chapter 10 : Spontaneity, Entropy, and Free Energy

10.1 Spontaneous Processes

10.5 Entropy and the Second Law of

Thermodynamics

10.6 The Effect of Temperature on Spontaneity

10.7 Free Energy

10.8 Entropy Changes in Chemical Reactions

10.9 Free Energy and Chemical Reactions

10.10 The Dependence of Free Energy on Pressure

10.11 Free Energy and Equilibrium

A process is said to be *spontaneous* if it *occurs without outside intervention*.

**Spontaneous processes** may be fast or slow.

Thermodynamics can tell us the *direction* in which a process will occur but can say nothing about the *speed (rate)* of the process.

Chemical kinetics (the study of reaction rates) focuses on the pathway between reactants and products; in contrast, thermodynamics considers only the initial and final states.

All spontaneous processes are characterized by an increase in a property called entropy (S).

Positional probability depends on the number of configurations in space (positional microstates).

Positional probability increases in going from solid to liquid to gas. In the solid state the molecules are close together, with relatively few positions available to them; in the gaseous state the molecules are far apart, with many more positions available to them.

### Example 10.1

For each of the following pairs, choose the substance with the higher positional probability (per mole) at a given temperature.

- solid  $\text{CO}_2$  and gaseous  $\text{CO}_2$
- $\text{N}_2$  gas at 1 atm and  $\text{N}_2$  gas at  $1.0 \times 10^{-2}$  atm

### Solution

- Since a mole of gaseous  $\text{CO}_2$  has the greater volume, the molecules have many more available positions than in a mole of solid  $\text{CO}_2$ . Thus gaseous  $\text{CO}_2$  has the higher positional probability.
- A mole of  $\text{N}_2$  gas at  $1 \times 10^{-2}$  atm has a volume 100 times that (at a given temperature) of a mole of  $\text{N}_2$  gas at 1 atm. Thus  $\text{N}_2$  gas at  $1 \times 10^{-2}$  atm has the higher positional probability.

## Example 10.2

---

Predict the sign of the change in positional probability for each of the following processes.

- a. Solid sugar is added to water to form a solution.
- b. Iodine vapor condenses on a cold surface to form crystals.

### Solution

- a. The sugar molecules become randomly dispersed in the water when the solution forms. The sugar molecules have access to a larger volume and therefore have more positions available to them. Thus the positional disorder increases.
- b. Gaseous iodine is forming a solid. This process involves a change from a relatively large volume to a much smaller volume, which results in lower positional probability.

The **second law of thermodynamics** states that *in any spontaneous process there is always an increase in the entropy of the universe.*

The entropy of the universe is increasing.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

where  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  represent the changes in entropy that occur in the system and in the surroundings, respectively.

$\Delta S_{\text{univ}} > 0 \rightarrow$  the process is spontaneous in the direction written.

$\Delta S_{\text{univ}} < 0 \rightarrow$  the process is spontaneous in the *opposite* direction.

$\Delta S_{\text{univ}} = 0 \rightarrow$  the process has no tendency to occur (the system is at equilibrium).

Entropy changes in the surroundings are determined by the flow of energy into or out of the system as heat.

Exothermic processes transfer energy as heat to the surroundings, where it increases the kinetic energy associated with the random motion of atoms. Thus increasing the entropy of the surroundings.  $\Delta S_{\text{surr}} > 0$ .

In endothermic processes, heat flows from the surroundings to the system, causing the random motion of the atoms in the surroundings to decrease. Thus decreasing the entropy of the surroundings.  $\Delta S_{\text{surr}} < 0$ .

The magnitude of  $\Delta S_{\text{surr}}$  depends on the temperature.

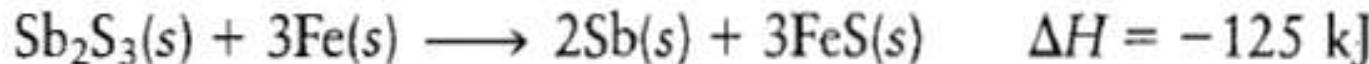
For a reaction that takes place under conditions of constant temperature and pressure:

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

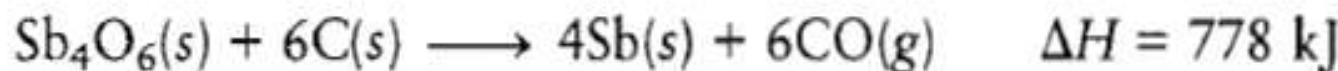
#### Example 10.4

---

In the metallurgy of antimony the pure metal is recovered by different reactions, depending on the composition of the ore. For example, iron is used to reduce antimony in sulfide ores:



Carbon is used as the reducing agent in oxide ores:



Calculate  $\Delta S_{surr}$  for each of these reactions at 25°C and 1 atm.

## Solution

We use

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

where

$$T = 25 + 273 = 298 \text{ K}$$

For the sulfide ore reaction,

$$\Delta S_{\text{surr}} = -\frac{-125 \text{ kJ}}{298 \text{ K}} = 0.419 \text{ kJ/K} = 419 \text{ J/K}$$

Note that  $\Delta S_{\text{surr}}$  is positive, as expected, since this reaction is exothermic; energy flows to the surroundings as heat, increasing the randomness of the surroundings.

For the oxide ore reaction,

$$\Delta S_{\text{surr}} = -\frac{778 \text{ kJ}}{298} = -2.61 \text{ kJ/K} = -2.61 \times 10^3 \text{ J/K}$$

In this case  $\Delta S_{\text{surr}}$  is negative because heat flows from the surroundings to the system.

**Table 10.4**Interplay of  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  in Determining the Sign of  $\Delta S_{\text{univ}}$ 

| Signs of Entropy Changes |                          |                          | Process Spontaneous?   |
|--------------------------|--------------------------|--------------------------|--|
| $\Delta S_{\text{sys}}$  | $\Delta S_{\text{surr}}$ | $\Delta S_{\text{univ}}$ |  |
| +                        | +                        | +                        | Yes  |
| -                        | -                        | -                        | No (process will occur in opposite direction)  |
| +                        | -                        | ?                        | Yes, if $\Delta S_{\text{sys}}$ has a larger magnitude than $\Delta S_{\text{surr}}$ |
| -                        | +                        | ?                        | Yes, if $\Delta S_{\text{surr}}$ has a larger magnitude than $\Delta S_{\text{sys}}$ |

The free energy (G) is defined as

$$G = H - TS$$

where H is the enthalpy, T is the kelvin temperature, and S is the entropy.

For a process that occurs at constant temperature, the change in free energy ( $\Delta G$ ) is

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

All quantities here refer to the system.

*(convention: when no subscript is included, the quantity refers to the system)*

# How is the free energy related to spontaneity?

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

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S$$

but  $-\frac{\Delta H}{T} = \Delta S_{surr}$

$$\Rightarrow -\frac{\Delta G}{T} = \Delta S_{surr} + \Delta S_{sys}$$

remember  $\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$

$$\Rightarrow -\frac{\Delta G}{T} = \Delta S_{univ}$$

A process carried out at constant temperature and pressure will be spontaneous in the direction in which the free energy decreases ( $\Delta G$  is negative).

Consider melting of ice:



for which  $\Delta H^\circ = 6.03 \times 10^3 \text{ J/mol}$  and  $\Delta S^\circ = 22.1 \text{ J K}^{-1} \text{ mol}^{-1}$

**Table 10.5**

Results of the Calculations of  $\Delta S_{\text{univ}}$  and  $\Delta G^\circ$  for the Process  $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$  at  $-10^\circ\text{C}$ ,  $0^\circ\text{C}$ , and  $10^\circ\text{C}^*$

| $T$<br>(°C) | $T$<br>(K) | $\Delta H^\circ$<br>(J/mol) | $\Delta S^\circ$<br>(J K $^{-1}$ mol $^{-1}$ ) | $\Delta S_{\text{surr}} = -\frac{\Delta H^\circ}{T}$<br>(J K $^{-1}$ mol $^{-1}$ ) | $\Delta S_{\text{univ}} = \Delta S^\circ + \Delta S_{\text{surr}}$<br>(J K $^{-1}$ mol $^{-1}$ ) | $T\Delta S^\circ$<br>(J/mol) | $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$<br>(J/mol) |
|-------------|------------|-----------------------------|--|--|--|------------------------------|--|
| -10         | 263        | $6.03 \times 10^3$          | 22.1   | -22.9  | -0.8   | $5.81 \times 10^3$           | $+2.2 \times 10^2$   |
| 0           | 273        | $6.03 \times 10^3$          | 22.1   | -22.1  | 0  | $6.03 \times 10^3$           | 0  |
| 10          | 283        | $6.03 \times 10^3$          | 22.1   | -21.3  | +0.8   | $6.25 \times 10^3$           | $-2.2 \times 10^2$   |

\*Note that at  $10^\circ\text{C}$ ,  $\Delta S^\circ$  ( $\Delta S_{\text{sys}}$ ) controls, and the process occurs even though it is endothermic. At  $-10^\circ\text{C}$ , the magnitude of  $\Delta S_{\text{surr}}$  is larger than that of  $\Delta S^\circ$ , so the process is spontaneous in the opposite (exothermic) direction. In these calculations we are assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature-independent.

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

**Table 10.6**

Various Possible Combinations of  $\Delta H$  and  $\Delta S$  for a Process and the Resulting Dependence of Spontaneity on Temperature

| Case                                     | Result   |
|--|--|
| $\Delta S$ positive, $\Delta H$ negative | Spontaneous at all temperatures  |
| $\Delta S$ positive, $\Delta H$ positive | Spontaneous at high temperatures<br>(where exothermicity is relatively unimportant)                              |
| $\Delta S$ negative, $\Delta H$ negative | Spontaneous at low temperatures<br>(where exothermicity is dominant)   |
| $\Delta S$ negative, $\Delta H$ positive | Process not spontaneous at <i>any</i> temperature<br>(reverse process is spontaneous at <i>all</i> temperatures) |

### Example 10.5

At what temperatures is the following process spontaneous at 1 atm?



where  $\Delta H^\circ = 31.0 \text{ kJ/mol}$  and  $\Delta S^\circ = 93.0 \text{ J K}^{-1} \text{ mol}^{-1}$

What is the normal boiling point of liquid  $\text{Br}_2$ ?

#### Solution

The vaporization process will be spontaneous at all temperatures at which  $\Delta G^\circ$  is negative. Note that  $\Delta S^\circ$  favors the vaporization process because of the increase in positional entropy, and  $\Delta H^\circ$  favors the *opposite* process, which is exothermic. These opposite tendencies will exactly balance at the boiling point of liquid  $\text{Br}_2$ , since at this temperature liquid and gaseous  $\text{Br}_2$  are in equilibrium ( $\Delta G^\circ = 0$ ). We can find this temperature by setting  $\Delta G^\circ = 0$  in the equation

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

Thus we have

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = T\Delta S^\circ$$

and

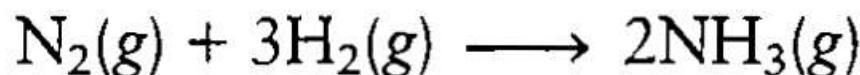
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{3.10 \times 10^4 \text{ J/mol}}{93.0 \text{ J K}^{-1} \text{ mol}^{-1}} = 333 \text{ K}$$

At temperatures above 333 K,  $T\Delta S^\circ$  has a larger magnitude than  $\Delta H^\circ$ , and  $\Delta G^\circ$  (or  $\Delta H^\circ - T\Delta S^\circ$ ) is negative. Above 333 K the vaporization process is spontaneous; the opposite process occurs spontaneously below this temperature. At 333 K liquid and gaseous  $\text{Br}_2$  will coexist in equilibrium. These observations can be summarized as follows (the pressure is 1 atm in each case):

1.  $T > 333$  K. The term  $\Delta S^\circ$  controls. The increase in entropy occurring when liquid  $\text{Br}_2$  is vaporized is dominant.
2.  $T < 333$  K. The process is spontaneous in the direction in which it is exothermic. The term  $\Delta H^\circ$  controls.
3.  $T = 333$  K. The opposing driving forces are just balanced ( $\Delta G^\circ = 0$ ), and the liquid and gaseous phases of  $\text{Br}_2$  coexist. This is the normal boiling point.

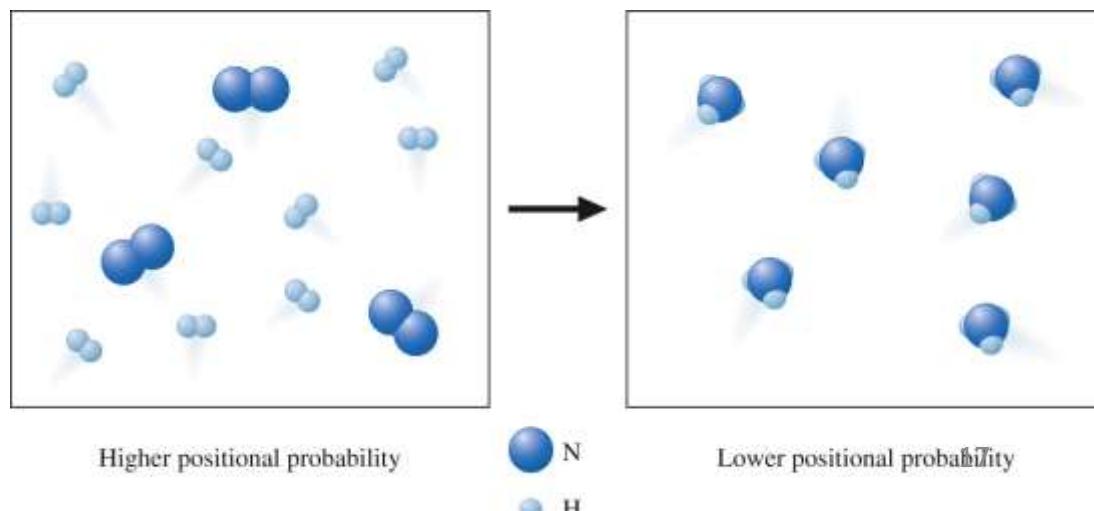
## 10.8 | Entropy Changes in Chemical Reactions

The entropy changes in the system (the reactants and products of the reaction) can be predicted by considering the change in positional probability.



In the ammonia synthesis reaction, four reactant molecules are changed to two product molecules, lowering the number of independent units in the system and thus leading to lower positional disorder.

*Fewer gaseous molecules means fewer possible configurations.*



When a reaction involves gaseous molecules, the change in positional probability is dominated by the relative numbers of molecules of gaseous reactants and products.

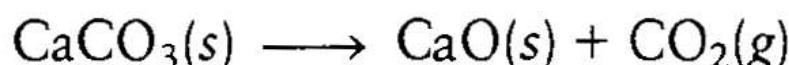
If the number of molecules of the gaseous products is greater than the number of molecules of the gaseous reactants, positional probability typically increases, and  $\Delta S$  is positive for the reaction.

### Example 10.6

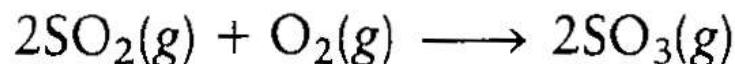
---

Predict the sign of  $\Delta S^\circ$  for each of the following reactions.

- a. the thermal decomposition of solid calcium carbonate:



- b. the oxidation of  $\text{SO}_2$  in air:

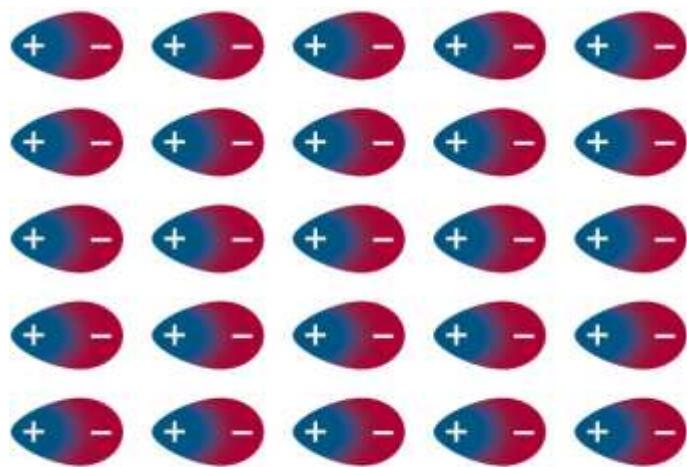


### Solution

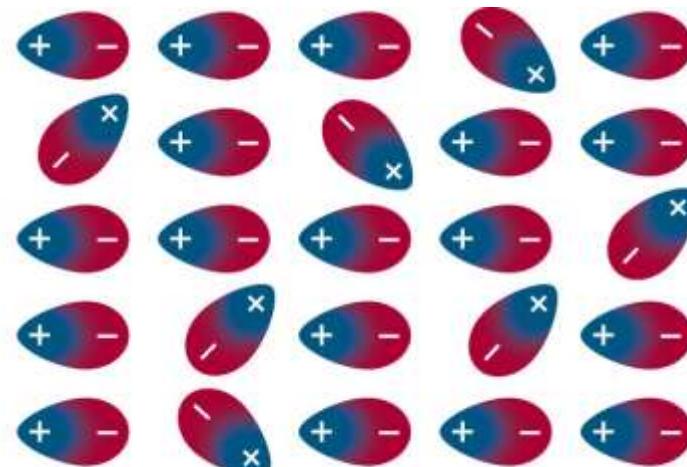
- a. Since in this reaction a gas is produced from a solid reactant, the positional probability increases, and  $\Delta S^\circ$  is positive.
- b. Here three molecules of gaseous reactants become two molecules of gaseous products. Since the number of gas molecules decreases, positional probability decreases, and  $\Delta S^\circ$  is negative.

# Absolute Entropies and the Third Law of Thermodynamics

The **third law of thermodynamics** states that *the entropy of a perfect crystal at 0 K is zero.*



(a)



(b)

- (a) An idealized perfect crystal of hydrogen chloride at 0 K. The entropy is zero ( $S = 0$ ) for this crystal at 0 K.
- (b) As the temperature rises above 0 K, vibrations allow some dipoles to change their orientations, producing some disorder and an increase in entropy ( $S > 0$ ).

Because entropy is a *state function* of the system, the entropy change for a given chemical reaction can be calculated by taking the difference between the standard entropy values of the products and those of the reactants:

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

Note that entropy is an *extensive property* (it depends on the amount of substance present) and the number of moles of a given reactant or product must be taken into account.

### Example 10.7

Calculate  $\Delta S^\circ$  for the reduction of aluminum oxide by hydrogen gas:



using the following standard entropy values.

| Substance                  | $S^\circ \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$ |
|----------------------------|--|
| $\text{Al}_2\text{O}_3(s)$ | 51   |
| $\text{H}_2(g)$            | 131  |
| $\text{Al}(s)$             | 28   |
| $\text{H}_2\text{O}(g)$    | 189  |

*Generally, the more complex the molecule, the higher the standard entropy value.*

#### Solution

$$\begin{aligned}\Delta S^\circ &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\ &= 2S^\circ_{\text{Al}(s)} + 3S^\circ_{\text{H}_2\text{O}(g)} - 3S^\circ_{\text{H}_2(g)} - S^\circ_{\text{Al}_2\text{O}_3(s)} \\ &= 2 \text{ mol} \left( 28 \frac{\text{J}}{\text{K mol}} \right) + 3 \text{ mol} \left( 189 \frac{\text{J}}{\text{K mol}} \right) \\ &\quad - 3 \text{ mol} \left( 131 \frac{\text{J}}{\text{K mol}} \right) - 1 \text{ mol} \left( 51 \frac{\text{J}}{\text{K mol}} \right) \\ &= 56 \text{ J/K} + 567 \text{ J/K} - 393 \text{ J/K} - 51 \text{ J/K} \\ &= 179 \text{ J/K}\end{aligned}$$

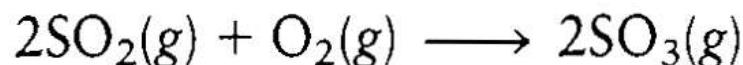
The **standard free energy change** ( $\Delta G^\circ$ ) is the *change in the free energy that occurs if the reactants in their standard states are converted to the products in their standard states*.

One common method to calculate  $\Delta G^\circ$  is to use the equation:

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

### Example 10.8

Consider the reaction



carried out at 25°C and 1 atm. Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  using the following data.

| Substance .         | $\Delta H_f^\circ$ (kJ/mol) | $S^\circ$ (J K $^{-1}$ mol $^{-1}$ ) |
|---------------------|-----------------------------|--------------------------------------|
| SO <sub>2</sub> (g) | −297                        | 248                                  |
| SO <sub>3</sub> (g) | −396                        | 257                                  |
| O <sub>2</sub> (g)  | 0                           | 205                                  |

**Solution**

The value of  $\Delta H^\circ$  can be calculated from the enthalpies of formation using the equation we discussed in Section 9.6:

$$\Delta H^\circ = \Sigma \Delta H_f^\circ \text{ (products)} - \Sigma \Delta H_f^\circ \text{ (reactants)}$$

Then

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ[\text{SO}_3(g)] - 2\Delta H_f^\circ[\text{SO}_2(g)] - \Delta H_f^\circ[\text{O}_2(g)] \\ &= 2 \text{ mol}(-396 \text{ kJ/mol}) - 2 \text{ mol}(-297 \text{ kJ/mol}) - 0 \\ &= -792 \text{ kJ} + 594 \text{ kJ} = -198 \text{ kJ}\end{aligned}$$

The value of  $\Delta S^\circ$  can be calculated by using the standard entropy values and the equation discussed in Section 10.8:

$$\Delta S^\circ = \Sigma S_f^\circ \text{ products} - \Sigma S_f^\circ \text{ reactants}$$

Thus

$$\begin{aligned}\Delta S^\circ &= 2S_f^\circ[\text{SO}_3(g)] - 2S_f^\circ[\text{SO}_2(g)] - S_f^\circ[\text{O}_2(g)] \\ &= 2 \text{ mol}(257 \text{ J K}^{-1} \text{ mol}^{-1}) - 2 \text{ mol}(248 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad - 1 \text{ mol}(205 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 514 \text{ J/K} - 496 \text{ J/K} - 205 \text{ J/K} = -187 \text{ J/K}\end{aligned}$$

We expect  $\Delta S^\circ$  to be negative since three molecules of gaseous reactants give two molecules of gaseous products.

The value of  $\Delta G^\circ$  can now be calculated from the equation

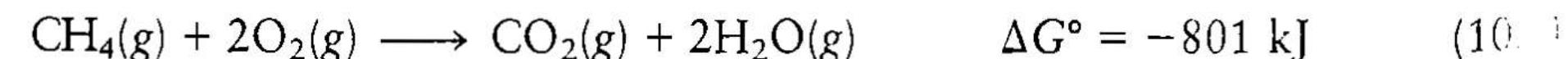
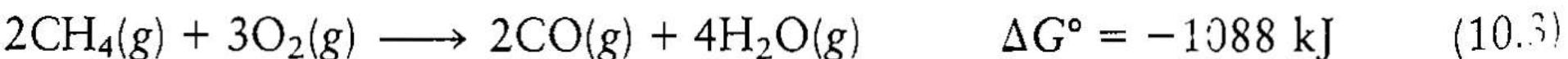
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

So

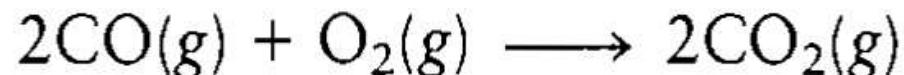
$$\begin{aligned}\Delta G^\circ &= -198 \text{ kJ} - (298 \text{ K})\left(-187 \frac{\text{J}}{\text{K}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -198 \text{ kJ} + 55.7 \text{ kJ} = -142 \text{ kJ}\end{aligned}$$

The free energy is a state function. Thus, we can apply Hess's Law to find  $\Delta G$ .

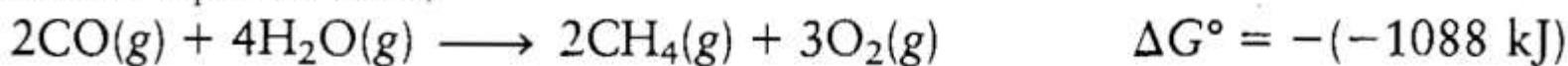
From the following date:



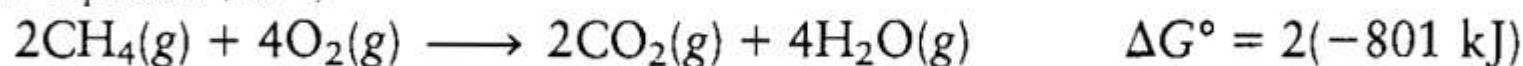
We can obtain  $\Delta G^\circ$  for the reaction:



Reversed Equation (10.3)



2  $\times$  Equation (10.4)



### Example 10.9

Using the following data (at 25°C),

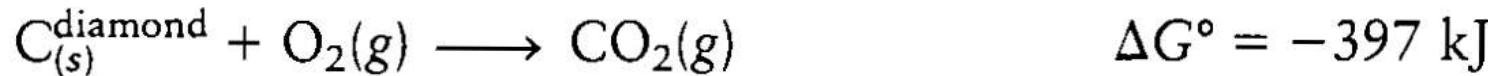


calculate  $\Delta G^\circ$  for the reaction

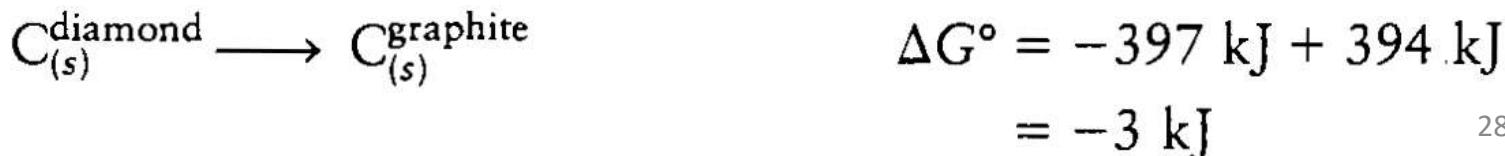
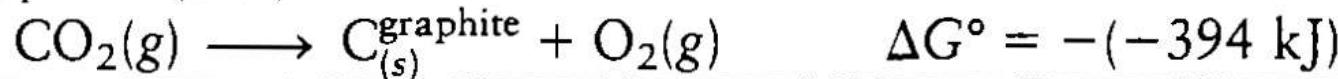


### Solution

We reverse Equation (10.6) to make graphite a product, as required, and then add the new equation to Equation (10.5):

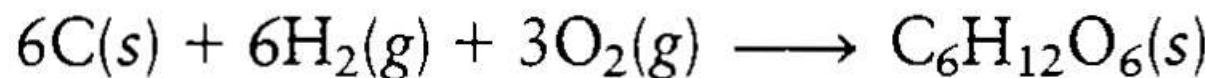


Reversed Equation (10.6)



The **standard free energy of formation** ( $\Delta G_f^0$ ) of a substance is defined as *the change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states.*

Example:



Values of the standard free energy of formation are used to calculate  $\Delta G^0$  using the equation:

$$\Delta G^{\circ} = \sum \Delta G_f^{\circ} \text{ (products)} - \sum \Delta G_f^{\circ} \text{ (reactants)}$$

*The standard free energy of formation of an element in its standard state is zero.*

---

**Example 10.10**

---

Methanol is a high-octane fuel used in high-performance racing engines. Calculate  $\Delta G^\circ$  for the reaction



given the following free energies of formation:

| Substance                 | $\Delta G_f^\circ$ (kJ/mol) |
|---------------------------|-----------------------------|
| $\text{CH}_3\text{OH}(g)$ | -163                        |
| $\text{O}_2(g)$           | 0                           |
| $\text{CO}_2(g)$          | -394                        |
| $\text{H}_2\text{O}(g)$   | -229                        |

**Solution**

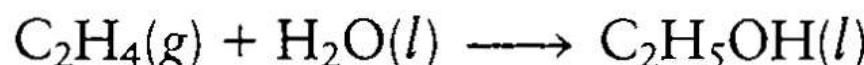
We use

$$\begin{aligned}\Delta G_f^\circ &= \Sigma \Delta G_f^\circ \text{ (products)} - \Sigma \Delta G_f^\circ \text{ (reactants)} \\ &= 2\Delta G_f^\circ [\text{CO}_2(g)] + 4\Delta G_f^\circ [\text{H}_2\text{O}(g)] - 3\Delta G_f^\circ [\text{O}_2(g)] - 2\Delta G_f^\circ [\text{CH}_3\text{OH}(g)] \\ &= 2 \text{ mol}(-394 \text{ kJ/mol}) + 4 \text{ mol}(-229 \text{ kJ/mol}) - 3(0) \\ &\quad - 2 \text{ mol}(-163 \text{ kJ/mol}) \\ &= -1378 \text{ kJ}\end{aligned}$$

The large magnitude and the negative sign of  $\Delta G^\circ$  indicate that this reaction is very favorable thermodynamically. 30

### Example 10.11

A chemical engineer wants to determine the feasibility of making ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) by reacting water with ethylene ( $\text{C}_2\text{H}_4$ ) according to the equation



Is this reaction spontaneous under standard conditions?

#### Solution

To determine the spontaneity of this reaction under standard conditions, we must determine  $\Delta G^\circ$  for the reaction by using the appropriate standard free energies of formation at  $25^\circ\text{C}$  from Appendix 4:

$$\Delta G_f^\circ [\text{C}_2\text{H}_5\text{OH}(l)] = -175 \text{ kJ/mol}$$

$$\Delta G_f^\circ [\text{H}_2\text{O}(l)] = -237 \text{ kJ/mol}$$

$$\Delta G_f^\circ [\text{C}_2\text{H}_4(g)] = 68 \text{ kJ/mol}$$

Thus

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ [\text{C}_2\text{H}_5\text{OH}(l)] - \Delta G_f^\circ [\text{H}_2\text{O}(l)] - \Delta G_f^\circ [\text{C}_2\text{H}_4(g)] \\ &= -175 \text{ kJ} - (-237 \text{ kJ}) - 68 \text{ kJ} = -6 \text{ kJ}\end{aligned}$$

and the process is spontaneous under standard conditions at  $25^\circ\text{C}$ .

## 10.10 | The Dependence of Free Energy on Pressure

For an ideal gas, enthalpy ( $H$ ) is not pressure dependent. However, entropy *does* depend on pressure because of its dependence on volume.

$$S_{\text{large volume}} > S_{\text{small volume}}$$

or since pressure and volume are inversely related,

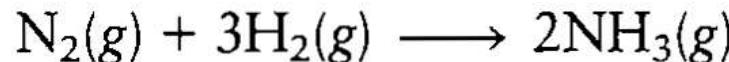
$$S_{\text{low pressure}} > S_{\text{high pressure}}$$

Therefore, the free energy of an ideal gas depend on its pressure.

$$G = G^\circ + RT \ln(P)$$

where  $G^\circ$  is the free energy of the gas at a pressure of 1 atm,  $G$  is the free energy of the gas at a pressure of  $P$  atmospheres,  $R$  is the universal gas constant, and  $T$  is the kelvin temperature.

Consider the ammonia synthesis reaction:



In general,

$$\Delta G = \Sigma G_{\text{products}} - \Sigma G_{\text{reactants}} \quad (10.7)$$

For this reaction

$$\Delta G = 2G_{\text{NH}_3} - G_{\text{N}_2} - 3G_{\text{H}_2}$$

where

$$G_{\text{NH}_3} = G_{\text{NH}_3}^\circ + RT \ln(P_{\text{NH}_3})$$

$$G_{\text{N}_2} = G_{\text{N}_2}^\circ + RT \ln(P_{\text{N}_2})$$

$$G_{\text{H}_2} = G_{\text{H}_2}^\circ + RT \ln(P_{\text{H}_2})$$

Substituting these values into Equation (10.7) gives

$$\begin{aligned}\Delta G &= 2[G_{\text{NH}_3}^\circ + RT \ln(P_{\text{NH}_3})] - [G_{\text{N}_2}^\circ + RT \ln(P_{\text{N}_2})] - 3[G_{\text{H}_2}^\circ + RT \ln(P_{\text{H}_2})] \\ &= 2G_{\text{NH}_3}^\circ - G_{\text{N}_2}^\circ - 3G_{\text{H}_2}^\circ + 2RT \ln(P_{\text{NH}_3}) - RT \ln(P_{\text{N}_2}) - 3RT \ln(P_{\text{H}_2}) \\ &= \underbrace{(2G_{\text{NH}_3}^\circ - G_{\text{N}_2}^\circ - 3G_{\text{H}_2}^\circ)}_{\Delta G_{\text{reaction}}^\circ} + RT [2 \ln(P_{\text{NH}_3}) - \ln(P_{\text{N}_2}) - 3 \ln(P_{\text{H}_2})]\end{aligned}$$

The first term in parentheses is  $\Delta G^\circ$  for the reaction. Thus we have

$$\Delta G = \Delta G_{\text{reaction}}^\circ + RT [2 \ln(P_{\text{NH}_3}) - \ln(P_{\text{N}_2}) - 3 \ln(P_{\text{H}_2})]$$

the equation becomes

$$\Delta G = \Delta G^\circ + RT \ln \left[ \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} \right]$$

But the term

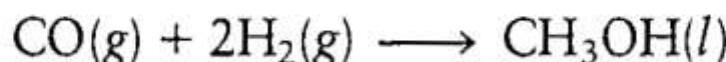
$$\frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)}$$

is the reaction quotient ( $Q$ ) discussed in Section 6.6. Therefore, we have

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

### Example 10.12

One method for synthesizing methanol ( $\text{CH}_3\text{OH}$ ) involves reacting gaseous carbon monoxide and hydrogen:



Calculate  $\Delta G$  at  $25^\circ\text{C}$  for this reaction, in which carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol.

#### Solution

To calculate  $\Delta G$  for this process, we use the equation

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

We must first compute  $\Delta G^\circ$  from standard free energies of formation (see Appendix 4). Since

$$\Delta G_f^\circ [\text{CH}_3\text{OH}(l)] = -166 \text{ kJ}$$

$$\Delta G_f^\circ [\text{H}_2(g)] = 0$$

$$\Delta G_f^\circ [\text{CO}(g)] = -137 \text{ kJ}$$

then

$$\Delta G^\circ = -166 \text{ kJ} - (-137 \text{ kJ}) - 0 = -29 \text{ kJ} = -2.9 \times 10^4 \text{ J}$$

Note that this is the value of  $\Delta G^\circ$  for the reaction of 1 mol CO with 2 mol H<sub>2</sub> to produce 1 mol CH<sub>3</sub>OH. We might call this the value of  $\Delta G^\circ$  for one “unit” of the reaction or for “one mole of the reaction.” Thus the  $\Delta G^\circ$  value might be written more accurately as  $-2.9 \times 10^4$  J/mol of reaction, or  $-2.9 \times 10^4$  J/mol rxn.

We can now calculate  $\Delta G$ , where

$$\Delta G^\circ = -2.9 \times 10^4 \text{ J/mol rxn}$$

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 273 + 25 = 298 \text{ K}$$

$$Q = \frac{1}{(P_{\text{CO}})(P_{\text{H}_2}^2)} = \frac{1}{(5.0)(3.0)^2} = 2.2 \times 10^{-2}$$

Note that the pure liquid methanol is not included in the calculation of  $Q$  because a pure liquid has an activity of 1, as discussed in Chapter 6. Thus

$$\begin{aligned}
 \Delta G &= \Delta G^\circ + RT \ln(Q) \\
 &= (-2.9 \times 10^4 \text{ J/mol rxn}) \\
 &\quad + [8.3145 \text{ J K}^{-1} (\text{mol rxn})^{-1}](298 \text{ K})[\ln(2.2 \times 10^{-2})] \\
 &= (-2.9 \times 10^4 \text{ J/mol rxn}) - (9.4 \times 10^3 \text{ J/mol rxn}) \\
 &= -3.8 \times 10^4 \text{ J/mol rxn} \\
 &= -38 \text{ kJ/mol rxn}
 \end{aligned}$$

Note that  $\Delta G$  is significantly more negative than  $\Delta G^\circ$ , implying that the reaction is more spontaneous at reactant pressures greater than 1 atm. We might expect this result from Le Châtelier's principle.

The equilibrium point occurs at the lowest value of free energy available to the reaction system.

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

and at equilibrium  $\Delta G$  equals 0 and  $Q$  equals  $K$ . So

$$\Delta G = 0 = \Delta G^\circ + RT \ln(K)$$

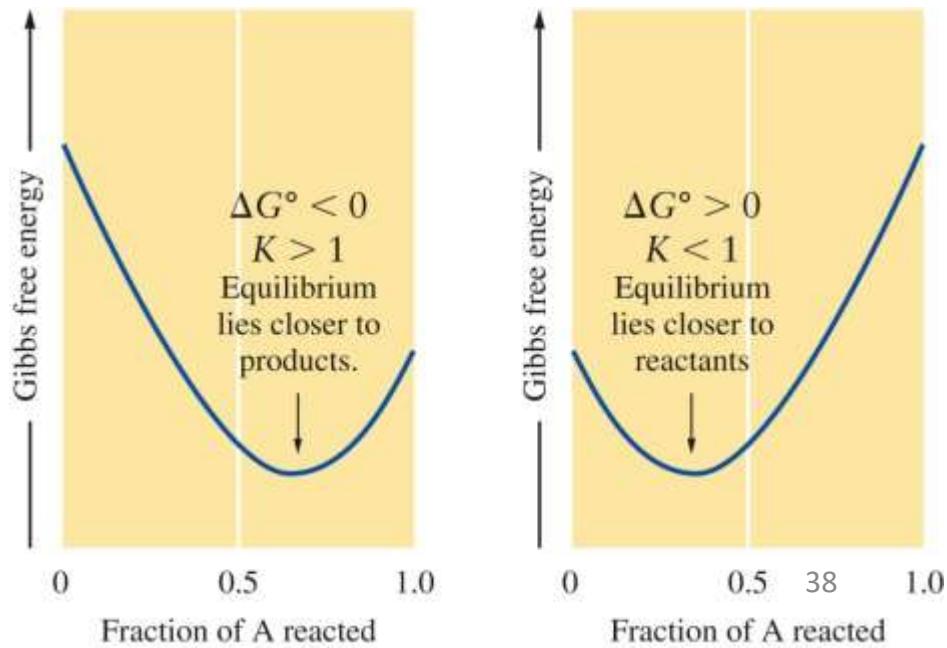
or

$$\Delta G^\circ = -RT \ln(K)$$

Table 10.7

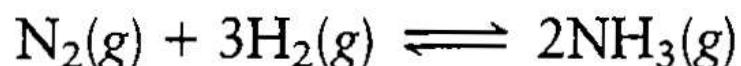
Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction

| $\Delta G^\circ$     | $K$     |
|----------------------|---------|
| $\Delta G^\circ = 0$ | $K = 1$ |
| $\Delta G^\circ < 0$ | $K > 1$ |
| $\Delta G^\circ > 0$ | $K < 1$ |



### Example 10.13

Consider the ammonia synthesis reaction



where  $\Delta G^\circ = -33.3$  kJ per mole of  $\text{N}_2$  consumed at  $25^\circ\text{C}$ . For each of the following mixtures of reactants and products at  $25^\circ\text{C}$ , predict the direction in which the system will shift to reach equilibrium.

- $P_{\text{NH}_3} = 1.00 \text{ atm}$ ,  $P_{\text{N}_2} = 1.47 \text{ atm}$ ,  $P_{\text{H}_2} = 1.00 \times 10^{-2} \text{ atm}$
- $P_{\text{NH}_3} = 1.00 \text{ atm}$ ,  $P_{\text{N}_2} = 1.00 \text{ atm}$ ,  $P_{\text{H}_2} = 1.00 \text{ atm}$

## Solution

- a. We can predict the direction of the shift to equilibrium by calculating the value of  $\Delta G$ , using the equation

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

where  $Q = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} = \frac{(1.00)^2}{(1.47)[(1.00 \times 10^{-2})^3]} = 6.80 \times 10^5$

$$T = 25 + 273 = 298 \text{ K}$$

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$$

and  $\Delta G^\circ = -33.3 \text{ kJ/mol} = -3.33 \times 10^4 \text{ J/mol}$

Thus

$$\begin{aligned}\Delta G &= (-3.33 \times 10^4 \text{ J/mol}) + (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln(6.80 \times 10^5) \\ &= (-3.33 \times 10^4 \text{ J/mol}) + (3.33 \times 10^4 \text{ J/mol}) = 0\end{aligned}$$

Since  $\Delta G = 0$ , the reactants and products have the same free energies at the given partial pressures. The system is already at equilibrium, and no shift occurs.

b. The partial pressures given here are all 1.00 atm, indicating that the system is in the standard state. That is,

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln(Q) = \Delta G^\circ + RT \ln \frac{(1.00)^2}{(1.00)(1.00)^3} \\ &= \Delta G^\circ + RT \ln(1.00) = \Delta G^\circ + 0 = \Delta G^\circ\end{aligned}$$

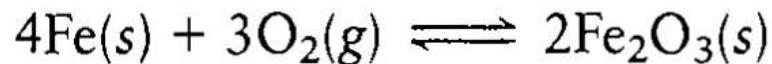
For this reaction at 25°C

$$\Delta G^\circ = -33.3 \text{ kJ/mol}$$

The negative value for  $\Delta G^\circ$  means that in their standard states the products have a lower free energy than the reactants. Thus the system moves to the right to reach equilibrium. That is,  $K$  is greater than 1.

### Example 10.14

The overall reaction for the corrosion (rusting) of iron by oxygen is



Using the following data, calculate the equilibrium constant for this reaction at 25°C.

| Substance                          | $\Delta H_f^\circ$ (kJ/mol) | $S^\circ$ (J K $^{-1}$ mol $^{-1}$ ) |
|------------------------------------|-----------------------------|--------------------------------------|
| Fe <sub>2</sub> O <sub>3</sub> (s) | -826                        | 90                                   |
| Fe(s)                              | 0                           | 27                                   |
| O <sub>2</sub> (g)                 | 0                           | 205                                  |

## Solution

To calculate  $K$  for this reaction, we will use the equation

$$\Delta G^\circ = -RT \ln(K)$$

We must first calculate  $\Delta G^\circ$  from

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

where  $\Delta H^\circ = 2\Delta H_f^\circ [\text{Fe}_2\text{O}_3(s)] - 3\Delta H_f^\circ [\text{O}_2(g)] - 4\Delta H_f^\circ [\text{Fe}(s)]$

$$\begin{aligned} &= 2 \text{ mol}(-826 \text{ kJ/mol}) - 0 - 0 \\ &= -1652 \text{ kJ} = -1.652 \times 10^6 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= 2S_f^\circ [\text{Fe}_2\text{O}_3] - 3S_f^\circ [\text{O}_2] - 4S_f^\circ [\text{Fe}] \\ &= 2 \text{ mol}(90 \text{ J K}^{-1} \text{ mol}^{-1}) - 3 \text{ mol}(205 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &\quad - 4 \text{ mol}(27 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -543 \text{ J/K} \end{aligned}$$

and

$$T = 273 + 25 = 298 \text{ K}$$

Then  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-1.652 \times 10^6 \text{ J}) - (298 \text{ K})(-543 \text{ J/K})$   
 $= -1.490 \times 10^6 \text{ J}$

and

$$\Delta G^\circ = -RT \ln(K) = -1.490 \times 10^6 \text{ J}$$
$$= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln(K)$$

Thus

$$\ln(K) = \frac{1.490 \times 10^6}{2.48 \times 10^3} = 601 \quad \text{and} \quad K = e^{601}$$

In terms of base = 10,  $K = 10^{261}$

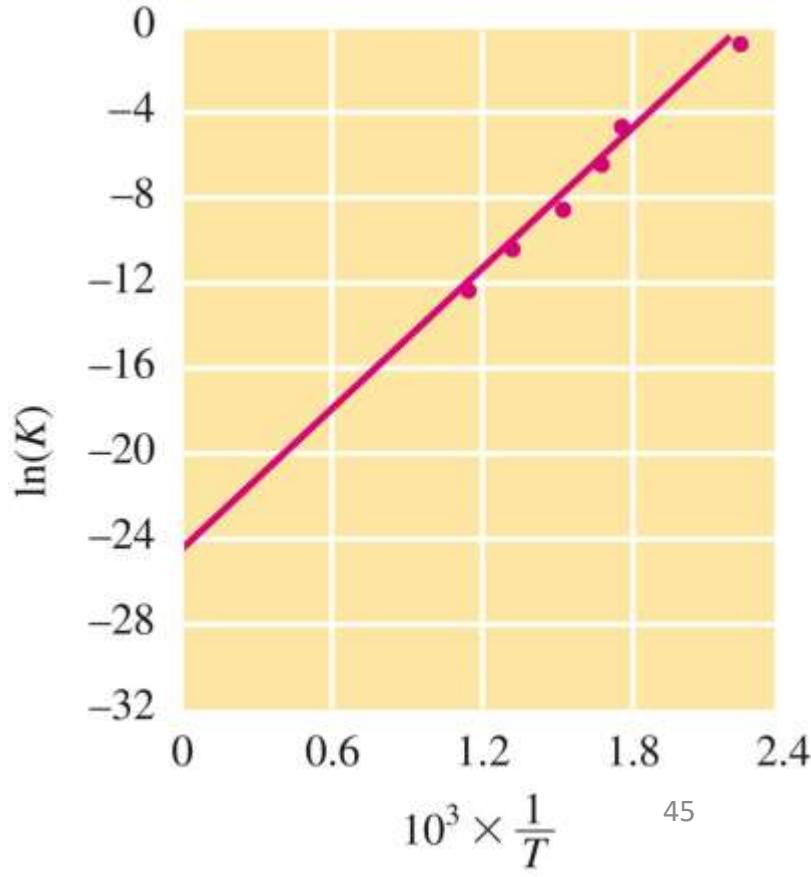
This is a very large equilibrium constant. The rusting of iron is clearly very favorable from a thermodynamic point of view.

# *The Temperature Dependence of K*

$$\Delta G^\circ = -RT \ln(K) = \Delta H^\circ - T\Delta S^\circ$$

We can rearrange this equation to give

$$\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$



*Van't Hoff equation:* once  $\Delta H^\circ$  and  $K$  are known at a given temperature,  $K$  can be calculated at any temperature.

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

and

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

Subtracting the second equation from the first gives the combined equation:

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

### Example 10.15

The value of  $K_p$  is  $3.7 \times 10^{-6}$  at 900. K for the ammonia synthesis reaction. Assuming the value of  $\Delta H^\circ$  for this reaction is  $-92$  kJ, calculate the value of  $K_p$  at 550. K.

#### Solution

We use the van't Hoff equation

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

where  $K_1 = 3.7 \times 10^{-6}$ ,  $T_1 = 900.$  K, and  $T_2 = 550.$  K.

$$\ln\left(\frac{K_2}{3.7 \times 10^{-6}}\right) = -\left(\frac{-92,000 \text{ J/mol}}{8.3145 \frac{\text{J}}{\text{K mol}}}\right)\left(\frac{1}{550.} - \frac{1}{900.}\right)$$

$$\ln(K_2) - \ln(3.7 \times 10^{-6}) = 1.1 \times 10^4 \text{ K} (1.8 \times 10^{-3} - 1.1 \times 10^{-3})$$

Solving this equation gives

$$\ln(K_2) = -4.8$$

$$K_2 = 8.2 \times 10^{-3} = K_p \text{ at 550 K}$$

Notice that the value of  $K_p$  increased as the temperature decreased, as expected for an exothermic reaction.

## Appendix Four Selected Thermodynamic Data\*

| Substance and State                         | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J K $^{-1}$ mol $^{-1}$ ) | Substance and State              | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J K $^{-1}$ mol $^{-1}$ ) |
|---|--------------------------------|--------------------------------|---|----------------------------------|--------------------------------|--------------------------------|---|
| Aluminum                                    |                                |                                |   | Beryllium                        |                                |                                |   |
| Al( <i>s</i> )                              | 0                              | 0                              | 28                                      | Be( <i>s</i> )                   | 0                              | 0                              | 10                                      |
| Al <sub>2</sub> O <sub>3</sub> ( <i>s</i> ) | -1676                          | -1582                          | 51                                      | BeO( <i>s</i> )                  | -599                           | -569                           | 14                                      |
| Al(OH) <sub>3</sub> ( <i>s</i> )            | -1277                          | —                              | —                                       | Be(OH) <sub>2</sub> ( <i>s</i> ) | -904                           | -815                           | 47                                      |
| AlCl <sub>3</sub> ( <i>s</i> )              | -704                           | -629                           | 111                                     | Bromine                          |                                |                                |   |
| Barium                                      |                                |                                |   | Br <sub>2</sub> ( <i>l</i> )     | 0                              | 0                              | 152                                     |
| Ba( <i>s</i> )                              | 0                              | 0                              | 67                                      | Br <sub>2</sub> ( <i>g</i> )     | 31                             | 3                              | 245                                     |
| BaCO <sub>3</sub> ( <i>s</i> )              | -1219                          | -1139                          | 112                                     | Br <sub>2</sub> ( <i>aq</i> )    | -3                             | 4                              | 130                                     |
| BaO( <i>s</i> )                             | -582                           | -552                           | 70                                      | Br <sup>-</sup> ( <i>aq</i> )    | -121                           | -104                           | 82                                      |
| Ba(OH) <sub>2</sub> ( <i>s</i> )            | -946                           | —                              | —                                       | HBr( <i>g</i> )                  | -36                            | -53                            | 199                                     |
| BaSO <sub>4</sub> ( <i>s</i> )              | -1465                          | -1353                          | 132                                     |                                  |                                |                                |   |

(continued)

| Substance and State                                    | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J K <sup>-1</sup> mol <sup>-1</sup> ) | Substance and State                               | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J K <sup>-1</sup> mol <sup>-1</sup> ) |
|--|--------------------------------|--------------------------------|---|---|--------------------------------|--------------------------------|---|
| Cadmium  |                                |                                |   | Copper  |                                |                                |   |
| Cd(s)  | 0                              | 0                              | 52  | Cu(s)   | 0                              | 0                              | 33  |
| CdO(s)   | -258                           | -228                           | 55  | CuCO <sub>3</sub> (s)                             | -595                           | -518                           | 88  |
| Cd(OH) <sub>2</sub> (s)                                | -561                           | -474                           | 96  | Cu <sub>2</sub> O(s)                              | -170                           | -148                           | 93  |
| CdS(s)   | -162                           | -156                           | 65  | CuO(s)  | -156                           | -128                           | 43  |
| CdSO <sub>4</sub> (s)                                  | -935                           | -823                           | 123   | Cu(OH) <sub>2</sub> (s)                           | -450                           | -372                           | 108   |
| Calcium  |                                |                                |   | CuS(s)  | -49                            | -49                            | 67  |
| Ca(s)  | 0                              | 0                              | 41  | Fluorine  |                                |                                |   |
| CaC <sub>2</sub> (s)                                   | -63                            | -68                            | 70  | F <sub>2</sub> (g)                                | 0                              | 0                              | 203   |
| CaCO <sub>3</sub> (s)                                  | -1207                          | -1129                          | 93  | F <sup>-</sup> (aq)                               | -333                           | -279                           | -14   |
| CaO(s)   | -635                           | -604                           | 40  | HF(g)   | -271                           | -273                           | 174   |
| Ca(OH) <sub>2</sub> (s)                                | -987                           | -899                           | 83  | Hydrogen  |                                |                                |   |
| Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (s)    | -4126                          | -3890                          | 241   | H <sub>2</sub> (g)                                | 0                              | 0                              | 131   |
| CaSO <sub>4</sub> (s)                                  | -1433                          | -1320                          | 107   | H(g)  | 217                            | 203                            | 115   |
| CaSiO <sub>3</sub> (s)                                 | -1630                          | -1550                          | 84  | H <sup>+</sup> (aq)                               | 0                              | 0                              | 0   |
| Carbon   |                                |                                |   | OH <sup>-</sup> (aq)                              | -230                           | -157                           | -11   |
| C(s) (graphite)  | 0                              | 0                              | 6   | H <sub>2</sub> O(l)                               | -286                           | -237                           | 70  |
| C(s) (diamond)   | 2                              | 3                              | 2   | H <sub>2</sub> O(g)                               | -242                           | -229                           | 189   |
| CO(g)  | -110.5                         | -137                           | 198   | Iodine  |                                |                                |   |
| CO <sub>2</sub> (g)                                    | -393.5                         | -394                           | 214   | I <sub>2</sub> (s)                                | 0                              | 0                              | 116   |
| CH <sub>4</sub> (g)                                    | -75                            | -51                            | 186   | I <sub>2</sub> (g)                                | 62                             | 19                             | 261   |
| CH <sub>3</sub> OH(l)                                  | -201                           | -163                           | 240   | I <sub>2</sub> (aq)                               | 23                             | 16                             | 137   |
| H <sub>2</sub> CO(g)                                   | -239                           | -166                           | 127   | I <sup>-</sup> (aq)                               | -55                            | -52                            | 106   |
| HCOOH(g)   | -116                           | -110                           | 219   | Iron  |                                |                                |   |
| HCN(g)   | -363                           | -351                           | 249   | Fe(s)   | 0                              | 0                              | 27  |
| C <sub>2</sub> H <sub>2</sub> (g)                      | 135.1                          | 125                            | 202   | Fe <sub>3</sub> C(s)                              | 21                             | 15                             | 108   |
| C <sub>2</sub> H <sub>4</sub> (g)                      | 227                            | 209                            | 201   | Fe <sub>0.95</sub> O(s)<br>(wustite)              | -264                           | -240                           | 59  |
| C <sub>2</sub> H <sub>5</sub> OH(l)                    | 52                             | 68                             | 219   | FeO(s)  | -272                           | -255                           | 61  |
| CH <sub>3</sub> CHO(g)                                 | -166                           | -129                           | 250   | Fe <sub>3</sub> O <sub>4</sub> (s)<br>(magnetite) | -1117                          | -1013                          | 146   |
| C <sub>2</sub> H <sub>5</sub> OH(l)                    | -166                           | -129                           | 250   | Fe <sub>2</sub> O <sub>3</sub> (s)<br>(hematite)  | -826                           | -740                           | 90  |
| C <sub>2</sub> H <sub>6</sub> (g)                      | -278                           | -175                           | 161   | FeS(s)  | -95                            | -97                            | 67  |
| C <sub>3</sub> H <sub>6</sub> (g)                      | -84.7                          | -32.9                          | 229.5   | FeS <sub>2</sub> (s)                              | -178                           | -166                           | 53  |
| C <sub>3</sub> H <sub>8</sub> (g)                      | 20.9                           | 62.7                           | 266.9   | FeSO <sub>4</sub> (s)                             | -929                           | -825                           | 121   |
| C <sub>2</sub> H <sub>4</sub> O(g)<br>(ethylene oxide) | -104                           | -24                            | 270   | Lead  |                                |                                |   |
| CH <sub>2</sub> =CHCN(g)                               | -53                            | -13                            | 242   | Pb(s)   | 0                              | 0                              | 65  |
| CH <sub>2</sub> =CHCN(g)                               | 185.0                          | 195.4                          | 274   | PbO <sub>2</sub> (s)                              | -277                           | -217                           | 69  |
| CH <sub>3</sub> COOH(l)                                | -484                           | -389                           | 160   | PbS(s)  | -100                           | -99                            | 91  |
| C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s)      | -1275                          | -911                           | 212   | PbSO <sub>4</sub> (s)                             | -920                           | -813                           | 149   |
| CCl <sub>4</sub> (l)                                   | -135                           | -65                            | 216   | Magnesium   |                                |                                |   |
| Chlorine   |                                |                                |   | Mg(s)   | 0                              | 0                              | 33  |
| Cl <sub>2</sub> (g)                                    | 0                              | 0                              | 223   | MgCO <sub>3</sub> (s)                             | -1113                          | -1029                          | 66  |
| Cl <sub>2</sub> (aq)                                   | -23                            | 7                              | 121   | MgO(s)  | -602                           | -569                           | 27  |
| Cl <sup>-</sup> (aq)                                   | -167                           | -131                           | 57  | Mg(OH) <sub>2</sub> (s)                           | -925                           | -834                           | 64  |
| HCl(g)   | -92                            | -95                            | 187   |   |                                |                                |   |
| Chromium   |                                |                                |   |   |                                |                                |   |
| Cr(s)  | 0                              | 0                              | 24  |   |                                |                                |   |
| Cr <sub>2</sub> O <sub>3</sub> (s)                     | -1128                          | -1047                          | 81  |   |                                |                                |   |
| CrO <sub>3</sub> (s)                                   | -579                           | -502                           | 72  |   |                                |                                |   |

| Substance and State | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J K $^{-1}$ mol $^{-1}$ ) | Substance and State | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J K $^{-1}$ mol $^{-1}$ ) |
|---------------------|--------------------------------|--------------------------------|---|---------------------|--------------------------------|--------------------------------|---|
| Manganese           |                                |                                |   | $H_3PO_4(l)$        | -1267                          | —                              | —                                       |
| $Mn(s)$             | 0                              | 0                              | 32                                      | $H_3PO_4(aq)$       | -1288                          | -1143                          | 158                                     |
| $MnO(s)$            | -385                           | -363                           | 60                                      | $P_4O_{10}(s)$      | -2984                          | -2698                          | 229                                     |
| $Mn_3O_4(s)$        | -1387                          | -1280                          | 149                                     | Potassium           |                                |                                |   |
| $Mn_2O_3(s)$        | -971                           | -893                           | 110                                     | $K(s)$              | 0                              | 0                              | 64                                      |
| $MnO_2(s)$          | -521                           | -466                           | 53                                      | $KCl(s)$            | -436                           | -408                           | 83                                      |
| $MnO_4^-(aq)$       | -543                           | -449                           | 190                                     | $KClO_3(s)$         | -391                           | -290                           | 143                                     |
| Mercury             |                                |                                |   | $KClO_4(s)$         | -433                           | -304                           | 151                                     |
| $Hg(l)$             | 0                              | 0                              | 76                                      | $K_2O(s)$           | -361                           | -322                           | 98                                      |
| $Hg_2Cl_2(s)$       | -265                           | -211                           | 196                                     | $K_2O_2(s)$         | -496                           | -430                           | 113                                     |
| $HgCl_2(s)$         | -230                           | -184                           | 144                                     | $KO_2(s)$           | -283                           | -238                           | 117                                     |
| $HgO(s)$            | -90                            | -59                            | 70                                      | $KOH(s)$            | -425                           | -379                           | 79                                      |
| $HgS(s)$            | -58                            | -49                            | 78                                      | $KOH(aq)$           | -481                           | -440                           | 9.20                                    |
| Nickel              |                                |                                |   | Silicon             |                                |                                |   |
| $Ni(s)$             | 0                              | 0                              | 30                                      | $SiO_2(s)$ (quartz) | -911                           | -856                           | 42                                      |
| $NiCl_2(s)$         | -316                           | -272                           | 107                                     | $SiCl_4(l)$         | -687                           | -620                           | 240                                     |
| $NiO(s)$            | -241                           | -213                           | 38                                      | Silver              |                                |                                |   |
| $Ni(OH)_2(s)$       | -538                           | -453                           | 79                                      | $Ag(s)$             | 0                              | 0                              | 43                                      |
| $NiS(s)$            | -93                            | -90                            | 53                                      | $Ag^+(aq)$          | 105                            | 77                             | 73                                      |
| Nitrogen            |                                |                                |   | $AgBr(s)$           | -100                           | -97                            | 107                                     |
| $N_2(g)$            | 0                              | 0                              | 192                                     | $AgCN(s)$           | 146                            | 164                            | 84                                      |
| $NH_3(g)$           | -46                            | -17                            | 193                                     | $AgCl(s)$           | -127                           | -110                           | 96                                      |
| $NH_3(aq)$          | -80                            | -27                            | 111                                     | $Ag_2CrO_4(s)$      | -712                           | -622                           | 217                                     |
| $NH_4^+(aq)$        | -132                           | -79                            | 113                                     | $AgI(s)$            | -62                            | -66                            | 115                                     |
| $NO(g)$             | 90                             | 87                             | 211                                     | $Ag_2O(s)$          | -31                            | -11                            | 122                                     |
| $NO_2(g)$           | 34                             | 52                             | 240                                     | $Ag_2S(s)$          | -32                            | -40                            | 146                                     |
| $N_2O(g)$           | 82                             | 104                            | 220                                     | Sodium              |                                |                                |   |
| $N_2O_4(g)$         | 10                             | 98                             | 304                                     | $Na(s)$             | 0                              | 0                              | 51                                      |
| $N_2O_4(l)$         | -20                            | 97                             | 209                                     | $Na^+(aq)$          | -240                           | -262                           | 59                                      |
| $N_2O_5(s)$         | -42                            | 134                            | 178                                     | $NaBr(s)$           | -360                           | -347                           | 84                                      |
| $N_2H_4(l)$         | 51                             | 149                            | 121                                     | $Na_2CO_3(s)$       | -1131                          | -1048                          | 136                                     |
| $N_2H_3CH_3(l)$     | 54                             | 180                            | 166                                     | $NaHCO_3(s)$        | -948                           | -852                           | 102                                     |
| $HNO_3(aq)$         | -207                           | -111                           | 146                                     | $NaCl(s)$           | -411                           | -384                           | 72                                      |
| $HNO_3(l)$          | -174                           | -81                            | 156                                     | $NaH(s)$            | -56                            | -33                            | 40                                      |
| $NH_4ClO_4(s)$      | -295                           | -89                            | 186                                     | $NaI(s)$            | -288                           | -282                           | 91                                      |
| $NH_4Cl(s)$         | -314                           | -203                           | 96                                      | $NaNO_2(s)$         | -359                           | —                              | —                                       |
| Oxygen              |                                |                                |   | $NaNO_3(s)$         | -467                           | -366                           | 116                                     |
| $O_2(g)$            | 0                              | 0                              | 205                                     | $Na_2O(s)$          | -416                           | -377                           | 73                                      |
| $O(g)$              | 249                            | 232                            | 161                                     | $Na_2O_2(s)$        | -515                           | -451                           | 95                                      |
| $O_3(g)$            | 143                            | 163                            | 239                                     | $NaOH(s)$           | -427                           | -381                           | 64                                      |
| Phosphorus          |                                |                                |   | $NaOH(aq)$          | -470                           | -419                           | 50                                      |
| $P(s)$ (white)      | 0                              | 0                              | 41                                      | Sulfur              |                                |                                |   |
| $P(s)$ (red)        | -18                            | -12                            | 23                                      | $S(s)$ (rhombic)    | 0                              | 0                              | 32                                      |
| $P(s)$ (black)      | -39                            | -33                            | 23                                      | $S(s)$ (monoclinic) | 0.3                            | 0.1                            | 33                                      |
| $P_4(g)$            | 59                             | 24                             | 280                                     | $S^{2-}(aq)$        | 33                             | 86                             | -15                                     |
| $PF_5(g)$           | -1578                          | -1509                          | 296                                     | $S_8(g)$            | 102                            | 50                             | 431                                     |
| $PH_3(g)$           | 5                              | 13                             | 210                                     | $SF_6(g)$           | -1209                          | -1105                          | 292                                     |
| $H_3PO_4(s)$        | -1279                          | -1119                          | 110                                     | (continued)         |                                |                                | 50                                      |

| Substance and State         | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J K $^{-1}$ mol $^{-1}$ ) | Substance and State         | $\Delta H_f^\circ$<br>(kJ/mol) | $\Delta G_f^\circ$<br>(kJ/mol) | $S^\circ$<br>(J K $^{-1}$ mol $^{-1}$ ) |
|-----------------------------|--------------------------------|--------------------------------|---|-----------------------------|--------------------------------|--------------------------------|---|
| $\text{H}_2\text{S}(g)$     | -21                            | -34                            | 206                                     | $\text{UO}_2(s)$            | -1084                          | -1029                          | 78                                      |
| $\text{SO}_2(g)$            | -297                           | -300                           | 248                                     | $\text{U}_3\text{O}_8(s)$   | -3575                          | -3393                          | 282                                     |
| $\text{SO}_3(g)$            | -396                           | -371                           | 257                                     | $\text{UO}_3(s)$            | -1230                          | -1150                          | 99                                      |
| $\text{SO}_4^{2-}(aq)$      | -909                           | -745                           | 20                                      | Xenon                       |                                |                                |   |
| $\text{H}_2\text{SO}_4(l)$  | -814                           | -690                           | 157                                     | $\text{Xe}(g)$              | 0                              | 0                              | 170                                     |
| $\text{H}_2\text{SO}_4(aq)$ | -909                           | -745                           | 20                                      | $\text{XeF}_2(g)$           | -108                           | -48                            | 254                                     |
| Tin                         |                                |                                |   | $\text{XeF}_4(s)$           | -251                           | -121                           | 146                                     |
| $\text{Sn}(s)$ (white)      | 0                              | 0                              | 52                                      | $\text{XeF}_6(g)$           | -294                           | —                              | —                                       |
| $\text{Sn}(s)$ (gray)       | -2                             | 0.1                            | 44                                      | $\text{XeO}_3(s)$           | 402                            | —                              | —                                       |
| $\text{SnO}(s)$             | -285                           | -257                           | 56                                      | Zinc                        |                                |                                |   |
| $\text{SnO}_2(s)$           | -581                           | -520                           | 52                                      | $\text{Zn}(s)$              | 0                              | 0                              | 42                                      |
| $\text{Sn}(\text{OH})_2(s)$ | -561                           | -492                           | 155                                     | $\text{ZnO}(s)$             | -348                           | -318                           | 44                                      |
| Titanium                    |                                |                                |   | $\text{Zn}(\text{OH})_2(s)$ | -642                           | —                              | —                                       |
| $\text{TiCl}_4(g)$          | -763                           | -727                           | 355                                     | $\text{ZnS}(s)$             |                                |                                |   |
| $\text{TiO}_2(s)$           | -945                           | -890                           | 50                                      | (wurtzite)                  | -193                           | —                              | —                                       |
| Uranium                     |                                |                                |   | $\text{ZnS}(s)$             |                                |                                |   |
| $\text{U}(s)$               | 0                              | 0                              | 50                                      |                             |                                |                                |   |
| $\text{UF}_6(s)$            | -2137                          | -2008                          | 228                                     |                             |                                |                                |   |
| $\text{UF}_6(g)$            | -2113                          | -2029                          | 380                                     | $(\text{zinc blende})$      | -206                           | -201                           | 58                                      |
|                             |                                |                                |   | $\text{ZnSO}_4(s)$          | -983                           | -874                           | 120                                     |

# HOMEWORK

Chap.10: 14, 39, 41, 42, 49, 53, 59, 60,  
71, 76, 81, 88, 89

# 14

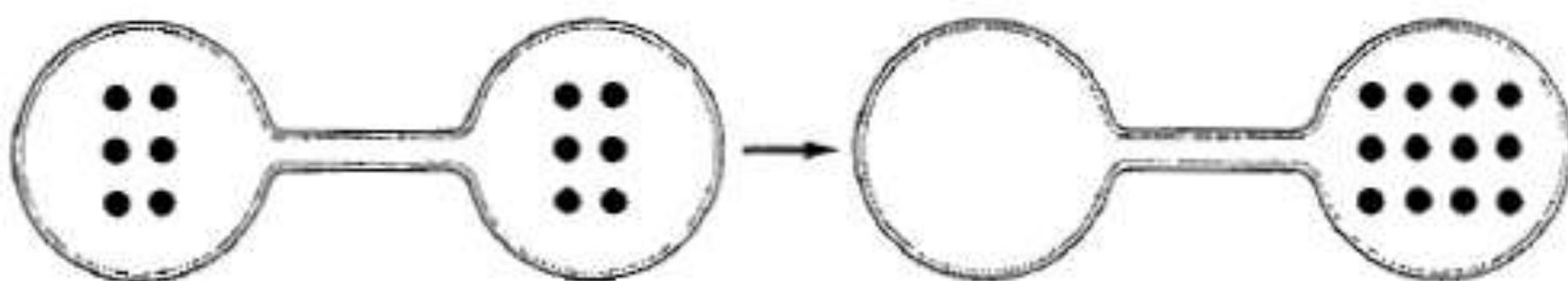
Which of the following involve an increase in the entropy of the system under consideration?

- a. melting of a solid
- b. evaporation of a liquid
- c. sublimation
- d. freezing
- e. mixing
- f. separation
- g. diffusion

## 39

Predict the sign of  $\Delta S^\circ$  for each of the following changes.

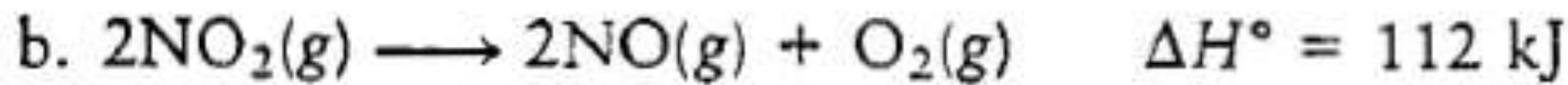
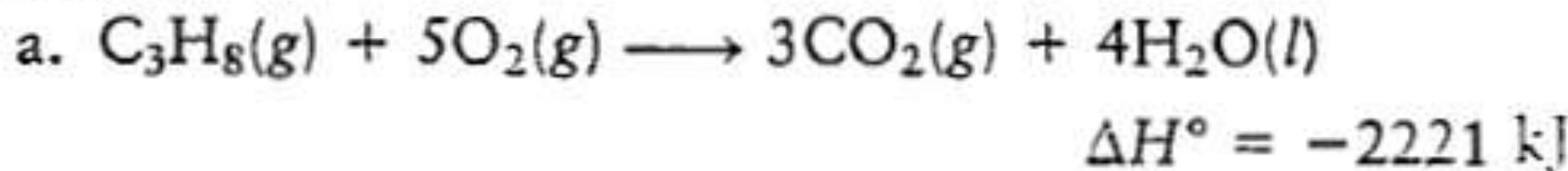
a.



- b.  $\text{AgCl}(s) \rightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$
- c.  $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l)$
- d.  $\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s)$
- e.  $\text{HCl}(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$
- f.  $\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$

# 41

Calculate  $\Delta S_{\text{surr}}$  for the following reactions at 25°C and 1 atm.



# 42

Predict the sign of  $\Delta S^\circ$  and then calculate  $\Delta S^\circ$  for each of the following reactions.

- $2\text{H}_2\text{S}(g) + \text{SO}_2(g) \rightarrow 3\text{S}_{\text{rhombic}}(s) + 2\text{H}_2\text{O}(g)$
- $2\text{SO}_3(g) \rightarrow 2\text{SO}_2(g) + \text{O}_2(g)$
- $\text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) \rightarrow 2\text{Fe}(s) + 3\text{H}_2\text{O}(g)$

# 49

For mercury the enthalpy of vaporization is  $58.51 \text{ kJ/mol}$  and the entropy of vaporization is  $92.92 \text{ J K}^{-1} \text{ mol}^{-1}$ . What is the normal boiling point of mercury?

# 53

The value of  $\Delta G^\circ$  for the reaction



is  $-5490.$  kJ. Use this value and data from Appendix 4 to calculate the standard free energy of formation for  $\text{C}_4\text{H}_{10}(g)$ .

# 59

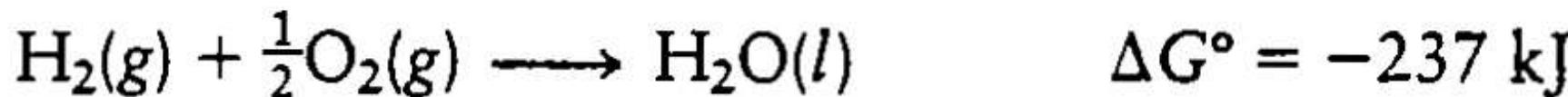
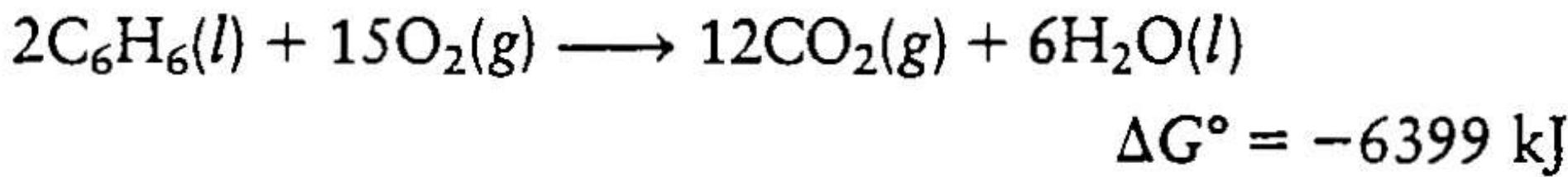
For the reaction at 298 K,



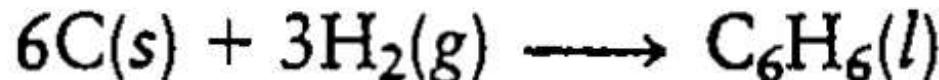
the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are  $-58.03\text{ kJ}$  and  $-176.6\text{ J/K}$ , respectively. What is the value of  $\Delta G^\circ$  at 298 K? Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not depend on temperature, at what temperature is  $\Delta G^\circ = 0$ ? Is  $\Delta G^\circ$  negative above or below this temperature?

60

Given the following data

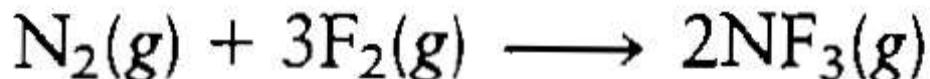


calculate  $\Delta G^\circ$  for the reaction



# 71

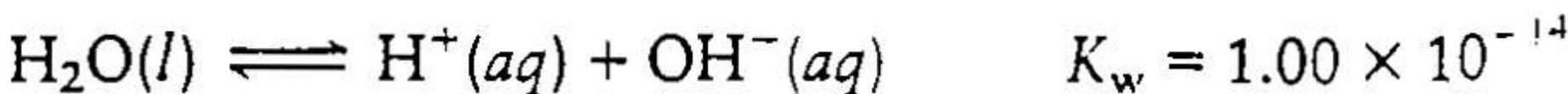
Consider the following reaction at 800. K:



An equilibrium mixture contains the following partial pressures:  $P_{\text{N}_2} = 0.021 \text{ atm}$ ,  $P_{\text{F}_2} = 0.063 \text{ atm}$ ,  $P_{\text{NF}_3} = 0.48 \text{ atm}$ . Calculate  $\Delta G^\circ$  for the reaction at 800. K.

# 76

Consider the autoionization of water at 25°C:



- a. Calculate  $\Delta G^\circ$  for this process at 25°C.
- b. At 40.°C,  $K_w = 2.92 \times 10^{-14}$ . Calculate  $\Delta G^\circ$  at 40.°C.

# 81

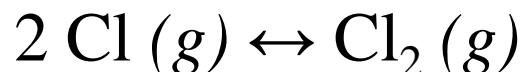
At 25.0°C, for the reaction



the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are  $-58.03 \text{ kJ/mol}$  and  $-176.6 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. Calculate the value of  $K$  at 25.0°C. Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature-independent, estimate the value of  $K$  at 100.0°C.

# 88

The equilibrium constant  $K$  for the reaction



was measured as a function of temperature (in kelvins). A graph of  $\ln(K)$  versus  $1/T$  for this reaction gives a straight line with a slope of  $1.352 \times 10^4 \text{ K}$  and a  $y$  intercept of  $-14.51$ . Determine the values of  $\Delta H^0$  and  $\Delta S^0$  for this reaction.

The equilibrium constant for a certain reaction decreases from 8.84 to  $3.25 \times 10^{-2}$  when the temperature increases from 25°C to 75°C. Estimate the temperature where  $K = 1.00$  for this reaction. Estimate the value of  $\Delta S^\circ$  for this reaction. (*Hint:* Manipulate the equation given in Exercise 72.)