



## Chapter 18: Spontaneity and Chemical Change

### Section 18.1: Review of Thermodynamics

Earlier, we learned that energy can neither be created nor destroyed. Energy can only change from one form into another.

For example: During a chemical reaction, the chemical energy stored in chemical bonds can be transformed into heat and expansion work. This particular example is an application of the First Law of Thermodynamics. Mathematically, the First Law of Thermodynamics is expressed as:

$$\Delta E = q + w$$

where  $\Delta E = E_{\text{final}} - E_{\text{initial}}$  is the change in energy for the system during a process, and,  $w$  and  $q$  are the work and the heat exchanged between the system and its surroundings during the process.

For a chemical reaction with  $q > 0$ , heat flows from the surroundings into the system. This is called an endothermic reaction.

For a chemical reaction with  $q < 0$ , heat flows from the system into the surroundings. This is called an exothermic reaction.

For a chemical reaction,  $w < 0$  indicates that work is done by the system. At constant temperature, this means that more gas molecules are formed than are consumed.

For a chemical reaction,  $w > 0$  indicates that work is done on the system. At constant temperature, this means that more gas molecules are consumed than are formed.

### Section 18.2: Spontaneity and the Second Law of Thermodynamics

Earlier, we studied the change in energy and enthalpy resulting from chemical and physical changes. We also studied the rate at which chemical processes occur. Now, we learn to predict the **natural direction** of chemical processes.

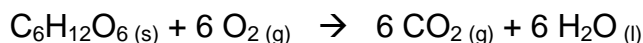
The natural direction of a process is the direction in which the process occurs “spontaneously” or “by itself.”

Hence, a process is called “**spontaneous**” when it occurs without the surroundings doing work on the system. If a process occurs spontaneously from state A to state B, then the reverse process (i.e. from state B to state A) is **non-spontaneous**. Before proceeding further, we must clear up one common misconception. The word “spontaneous” does not imply that the process occurs instantaneously or quickly. It simply means the process does occur!!

Remember: A process is called “spontaneous” when it occurs without the surroundings doing work on the system. If a process occurs spontaneously from state A to state B, then, the reverse process (i.e. from state B to state A) is non-spontaneous.

**Example 1:** Consider a skier on the snow-covered slope of a mountain. The downhill motion of the skier from the mountaintop to the valley is a spontaneous process. The reverse (i.e. uphill) travel is not spontaneous.

**Example 2:** Consider the oxidation of glucose.



This combustion reaction occurs in our bodies. Glucose oxidizes spontaneously, providing the energy necessary to sustain life. The reverse reaction (photosynthesis) occurs in plants only when sufficient energy is provided by the sun. Hence, the reverse reaction is non-spontaneous.

**Example 3:** Consider the reaction:  $2 \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{H}_2\text{O} (\text{l})$ . This reaction is spontaneous, and is the source of energy in some fuel cells. The reverse reaction (i.e. the formation of  $\text{H}_2$  and  $\text{O}_2$  gases from water) can occur if sufficient electric potential is applied to water. The reverse reaction, called electrolysis, is a non-spontaneous process requiring electrical work.

**Example 4:** Consider excited H atoms with their electrons in the  $n = 2$  level. Their electrons spontaneously fall back to the  $n = 1$  level. During this process, the energy of these electrons decreases ( $\Delta E < 0$ ). This energy is not lost; it is emitted into the surroundings as radiation. In contrast, the jump of electrons from  $n = 1$  to  $n = 2$  is non-spontaneous.

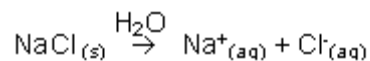
These four examples illustrate the fact that processes usually have a natural or spontaneous direction. Now, the question is: Why does a process have a natural direction and what makes this direction the spontaneous direction?

Considering the skier's descent, the oxidation of glucose or hydrogen and the fall of electrons, one might be tempted to conclude that spontaneous processes are always associated with a decrease in the system's energy ( $\Delta E < 0$ ) or enthalpy ( $\Delta H < 0$ ). However, this is not true.

Knowledge of  $\Delta E$  or  $\Delta H$  is important, but it is not sufficient for determining the natural direction of a process. Many spontaneous processes are not exothermic (i.e. they are associated with  $\Delta H = 0$  or  $\Delta H > 0$ ).

*Remember: Exothermic **DOES NOT** imply spontaneous.*

**Example 1:** Consider the dissolution of water-soluble salt such as NaCl.



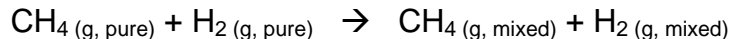
This process is spontaneous and endothermic ( $\Delta H^\circ = +3.9 \text{ kJ}$ ).

**Example 2:** Consider the decomposition of  $\text{PCl}_5$  in the gas phase.



This process is spontaneous and endothermic ( $\Delta H^\circ = +115 \text{ kJ}$ ).

**Example 3:** Consider the mixing of two non-reacting gases at low pressure.



Mixing changes the molecular environment. However, intermolecular interactions are negligible, since gases behave ideally at low pressure. Hence, molecules have the same energy in the pure and mixed states. Mixing of gases is spontaneous and is characterized by  $\Delta E = 0$  and  $\Delta H = 0$ .

These examples show that exothermicity is not required for spontaneity. Upon careful examination of these three examples you may notice that they display a common feature. In all cases, **the spontaneous direction of a process is the direction in which there is an overall increase in the level of disorder.**

**Example 1:** Dissolution of salts leads to the mixing of cations and anions with water, thus to a less orderly arrangement of matter.

**Example 2:** During decomposition, a reactant breaks down into many pieces.

**Example 3:** Mixing of two gases, A and B, also leads to an increase in molecular disorder, since, in the mixed state, molecules of either gas are surrounded by like and unlike molecules.

An increase in the number of chemical species leads to an increase in disorder. A similar conclusion has been reached for ALL spontaneous processes. The thermodynamic property that measures the level of molecular disorder is called the **entropy** and is denoted by the symbol, **S**.

Years of careful observation of the evolution of chemical and physical systems have led scientists to the following conclusion, known as the **Second Law of Thermodynamics**: "A process is spontaneous when it results in an overall increase in the entropy of system plus surroundings."

Mathematically, the Second Law is expressed as:

$$\Delta S + \Delta S_{\text{surr}} > 0$$

where  $\Delta S$  is the change in entropy of the system during the process, and  $\Delta S_{\text{surr}}$  is the corresponding change in the entropy of the surroundings.

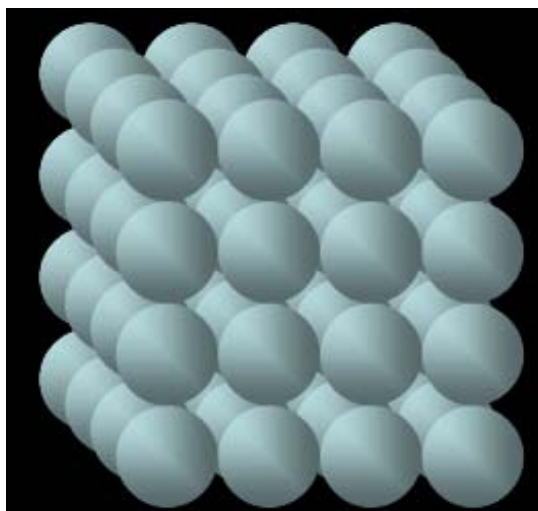
### **Sections 18.3 - 18.4: Entropy and the Boltzmann Formula**

The entropy is a property that measures the disorder in a system. To better understand the concept of entropy, we first discuss the very famous equation proposed in 1877 by Ludwig Boltzmann.

The **Boltzmann equation** states that:  $S = k \times \ln(W)$

where  $S$  is the entropy of the system,  $k$ , the Boltzmann constant, is the ratio of the gas constant,  $R$ , to Avagadro's number,  $N_a$ .  $\ln$  is the natural logarithm, and  $W$  is the number of ways in which the atoms, ions or molecules of a system can be arranged without changing the system's energy.

**For example: Consider a crystal of  $\text{CCl}_4$  at 0 K:**

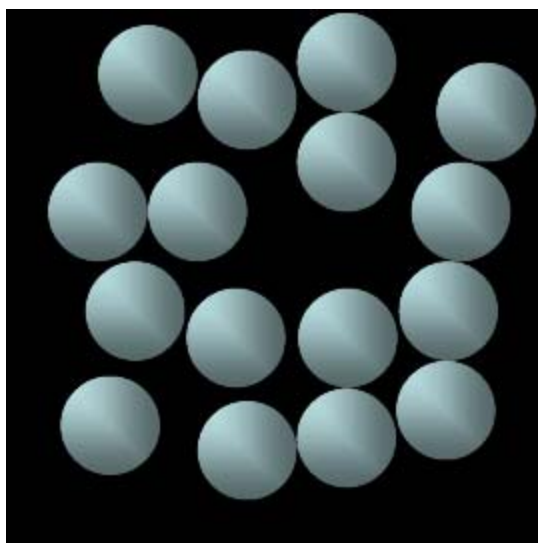


$\text{CCl}_4$  molecules are represented as spheres.

The crystal is represented as a three dimensional periodic array of  $\text{CCl}_4$  molecules. At 0 K, a crystal is so perfectly ordered that there is only one way to arrange its components. When any two  $\text{CCl}_4$  molecules switch positions, the crystal is still the same, because  $\text{CCl}_4$  molecules are indistinguishable.

Hence,  $W = 1$  and  $S = k \times \ln(1) = 0$ . The statement that the entropy of a perfectly ordered crystalline solid is equal to 0 at 0 K is known as the **Third Law of Thermodynamics**.

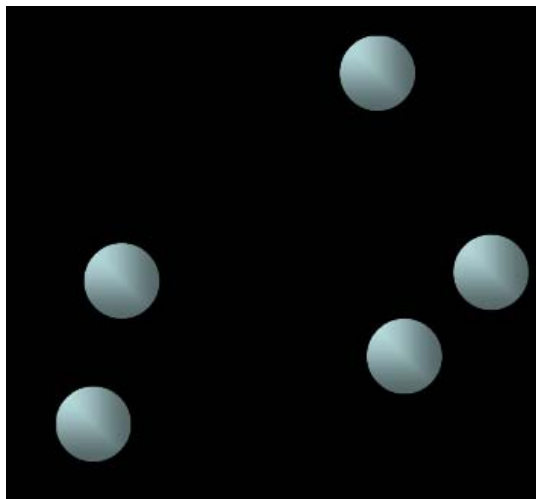
**Now, consider  $\text{CCl}_4$  in the liquid state:**



In the liquid state,  $\text{CCl}_4$  molecules do not pack orderly. The liquid state is usually less dense than the solid state. There is more empty space between molecules. Hence, molecules can occupy different sites. Since there are more ways to

arrange these molecules in the liquid state than in the crystal state,  $W > 1$  and  $S > 0$ .

**Now, consider  $\text{CCl}_4$  in the gas state:**



The gas state is less dense than the liquid state. Hence, there is even more empty space between molecules in the gas state than in the liquid state. Since there are many many more ways to arrange these molecules in the gas state than in the liquid state,  $W_{(\text{gas})} \gg W_{(\text{liquid})}$  and  $S_{(\text{gas})} \gg S_{(\text{liquid})}$ .

**In summary:**

<u>Crystal State</u>		<u>Liquid State</u>		<u>Gas State</u>
Order in crystal	>	Order in liquid	>>	Order in gas
Entropy of a solid	<	Entropy of a liquid	<<	Entropy of a gas

Hence, the entropy depends on the physical state of matter.

**The entropy of matter also varies with:**

### 1. Amount of Matter

The entropy of matter increases proportionally with the amount of matter. Hence, we define the **molar entropy** of a substance as the entropy of one mole of that substance. Molar entropy is expressed by the symbol,  $S_m$ . If a substance contains “n” moles, its entropy,  $S$ , is calculated as:  $S = n \times S_m$ .

### 2. Temperature

As a substance is heated, its particles (atoms, molecules or ions) exhibit a larger range of energies, motions and positions. Hence, the particles of a

substance can be arranged in a more diverse fashion when the temperature is increased (larger  $W$ ). As a result, the entropy of a pure substance always increases with increasing temperature.

### 3. Pressure

As a substance is compressed at constant temperature, its volume decreases (Boyle's Law for gases). Hence, increasing the pressure leads to a decrease in the number of possible sites that the particles of that substance may occupy. Thus, increasing the pressure leads to a decrease in the number of possible arrangements for the particles of that substance (lower  $W$ ). Hence, increasing pressure lowers the entropy at constant temperature.

### 4. Structure of Matter

The entropy of a substance increases with the size of its constituents. For example, consider the following group 2 metals at 25°C and 1 atm.

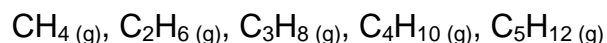


Their molar entropies are, respectively:

$$9.5 < 32.7 < 41.6 < 54.4 < 62.5 \text{ (J.K}^{-1}\text{.mol}^{-1}\text{)}$$

Hence, in a group the molar entropy increases from top to bottom.

Now, consider the following gases at 25° C and 1 atm.



Their molar entropies are, respectively:

$$183.6 < 229.6 < 270.2 < 310.1 < 349.0 \text{ (J.K}^{-1}\text{.mol}^{-1}\text{)}$$

The molar entropy of molecules increases with their size because larger molecules have more chemical bonds and can store energy in more ways than smaller molecules.

Hence, the entropy depends on temperature, pressure, physical state, amount and structure of matter. In examples discussed earlier, we compared the molar entropy of substances in the same physical state (either solids, liquids or gases).

Hence, remember that the entropy of a substance is primarily controlled by the physical state of that substance (solid, liquid or gas) and to a smaller extent by the size or complexity of the substance.

For example, consider benzene ( $C_6H_6$ ) and methane ( $CH_4$ ) at  $25^\circ C$ . The standard molar entropies of  $C_6H_6$  and  $CH_4$  are  $173.3$  and  $186.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively. While benzene is a larger molecule than methane, at  $25^\circ C$  benzene is a liquid, hence, it has a lower molar entropy than methane, which is a gas at the same temperature.

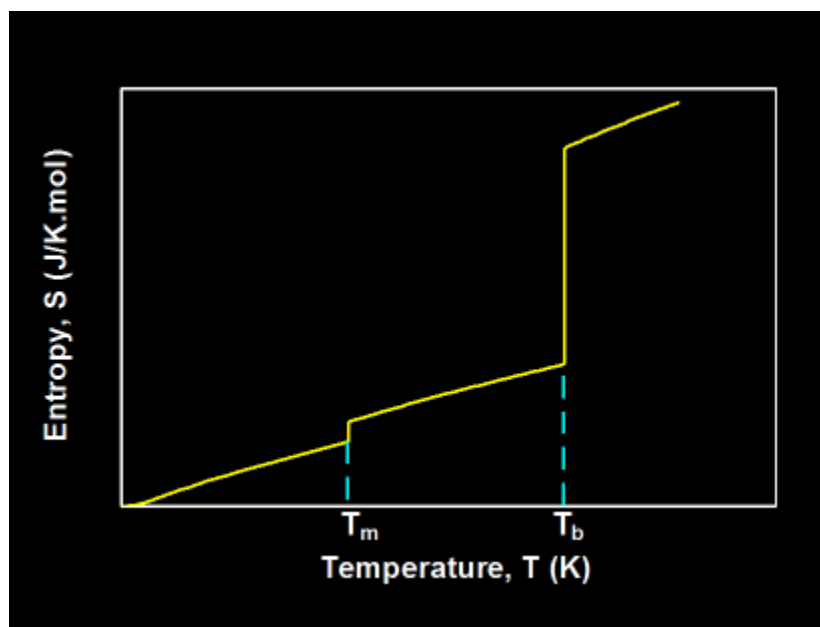
When comparing entropies of substances or calculating the change in entropy for a reaction, we always use **standard molar entropies**. Standard molar entropies are expressed with the symbol  $S^\circ_m$ .

Recall the definition of **standard states**:

- For gases: pure gas at 1 atmosphere,
- For solutions: solute at 1 M concentration,
- For liquids: pure liquid,
- For solids: pure solid in its most stable form.

The S.I. unit for entropy is joule per kelvin or  $J/K$ . The S.I. unit for molar entropy and standard molar entropy is joule per kelvin per mol,  $J/(K\cdot\text{mol})$  or  $J\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

In the figure below, we show the change in the standard molar entropy of a typical substance, as it is heated from low temperatures, where the substance is a solid, to high temperatures, where the substance is a gas.





Note the steady increase in the standard molar entropy with increasing temperature for:

1. the solid crystal phase between 0 K and the melting point,  $T_m$ .
2. the liquid phase between the melting point,  $T_m$ , and the boiling point,  $T_b$ .
3. the gas phase above the boiling point,  $T_b$ .

Note the large increase in the standard molar entropy at the melting point,  $T_m$ , where the crystalline solid transforms into a liquid. The change in entropy at  $T_m$  between the solid and the liquid is called the **entropy of melting** or **entropy of fusion**. The entropy of melting is denoted by  $\Delta S^\circ_{\text{melting}}$  and is defined by:

$$\Delta S^\circ_{\text{melting}} = S^\circ_m (\text{liquid}) - S^\circ_m (\text{crystal})$$

Note the dramatic increase in the standard molar entropy at the boiling point,  $T_b$ , where the substance transforms from a liquid into gas. The large change in entropy at  $T_b$  between one mole of liquid and one mole of gas is called the **entropy of vaporization**. The standard entropy of vaporization is denoted by  $\Delta S^\circ_{\text{vap}}$  and defined by:

$$\Delta S^\circ_{\text{vap}} = S^\circ_m (\text{gas}) - S^\circ_m (\text{liquid})$$

In Section 18.4, practice the Interactive Problems.

## Sections 18.5 - 18.6: Standard Entropy Change for Chemical Reactions

To predict the direction in which a chemical reaction occurs spontaneously, we use the Second Law of Thermodynamics. Recall: The Second Law of Thermodynamics states that a process is spontaneous if:  $\Delta S + \Delta S_{\text{surr}} > 0$

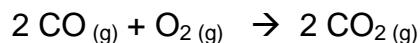
Hence, to determine whether a chemical reaction proceeds spontaneously, we must determine  $\Delta S$ , the entropy change for the reaction system, and  $\Delta S_{\text{surr}}$ , the entropy change for the surroundings. The entropy change for a reaction system is generally denoted  $\Delta S^\circ_{\text{rxn}}$ , since it is calculated for reactants and products in their standard state. In this section, we learn to calculate  $\Delta S^\circ_{\text{rxn}}$  using thermodynamic tables of standard molar entropies ( $S^\circ_m$  values).

Note: The  $S_m^\circ$  values in the Thermo Table on the DVD are given for ONE mole of each substance

The **standard entropy change for a chemical reaction**,  $\Delta S_{\text{rxn}}^\circ$ , is calculated using the following equation:

$$\Delta S_{\text{rxn}}^\circ = \Sigma S_m^\circ (\text{products}) - \Sigma S_m^\circ (\text{reactants})$$

**Example: Consider the gaseous reaction of carbon monoxide with oxygen to form carbon dioxide.** This reaction is written as:



Consider the equation defining the standard reaction entropy:

$$\Delta S_{\text{rxn}}^\circ = \Sigma S_m^\circ (\text{products}) - \Sigma S_m^\circ (\text{reactants})$$

First, we calculate the contribution arising from the products:

$$\Sigma S_m^\circ (\text{products}) = 2 \text{ mol}(\text{CO}_{2(g)}) \times S_m^\circ(\text{CO}_{2(g)})$$

$$\Sigma S_m^\circ (\text{products}) = 2 \text{ mol}(\text{CO}_{2(g)}) \times 213.7 \text{ J.K}^{-1}.\text{mol}^{-1}(\text{CO}_{2(g)})$$

$$\Sigma S_m^\circ (\text{products}) = 427.4 \text{ J.K}^{-1}$$

Next, we calculate the contribution arising from the reactants:

$$\Sigma S_m^\circ (\text{reactants}) = 2 \text{ mol}(\text{CO}_{(g)}) \times S_m^\circ(\text{CO}_{(g)}) + 1 \text{ mol}(\text{O}_{2(g)}) \times S_m^\circ(\text{O}_{2(g)})$$

$$\Sigma S_m^\circ (\text{reactants}) = 2 \text{ mol} \times 197.5 \text{ J.K}^{-1}.\text{mol}^{-1} + 1 \text{ mol} \times 205.0 \text{ J.K}^{-1}.\text{mol}^{-1}$$

$$\Sigma S_m^\circ (\text{reactants}) = 600.0 \text{ J.K}^{-1}$$

Now, we calculate the standard reaction entropy:

$$\Delta S_{\text{rxn}}^\circ = \Sigma S_m^\circ (\text{products}) - \Sigma S_m^\circ (\text{reactants})$$

$$\Delta S_{\text{rxn}}^\circ = 427.4 \text{ J.K}^{-1} - 600.0 \text{ J.K}^{-1}$$

$$\Delta S_{\text{rxn}}^\circ = -172.6 \text{ J.K}^{-1}$$

Note: In this reaction, we have 2 moles of gaseous product and 3 moles of gaseous reactant. Hence, the change in entropy for the reaction must be negative.

In Section 18.6, practice the Interactive Problems.

## Sections 18.7 - 18.8: Entropy Change for the Surroundings in Chemical Reactions

The Second Law of Thermodynamics states that a chemical reaction occurs spontaneously if:

$$\Delta S_{\text{rxn}} + \Delta S_{\text{surr}} > 0$$

Hence, to determine whether a chemical reaction proceeds spontaneously, we must determine  $\Delta S_{\text{rxn}}$ , the entropy change for the reaction system, and  $\Delta S_{\text{surr}}$ , **the entropy change for the surroundings**.

In this section, we learn to calculate  $\Delta S_{\text{surr}}$ . The change in entropy for the surroundings,  $\Delta S_{\text{surr}}$ , is expressed mathematically as:

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} \quad \text{Remember this!!!}$$

where  $q_{\text{surr}}$  is the heat received ( $q_{\text{surr}} > 0$ ) or lost ( $q_{\text{surr}} < 0$ ) by the surroundings at the temperature  $T$  (expressed in kelvin).

Now, we show that the expression for  $\Delta S_{\text{surr}}$  is consistent with the fact that the entropy is a measure of the disorder.  $\Delta S_{\text{surr}}$  is proportional to  $q_{\text{surr}}$  at constant  $T$ .

Hence, the larger the transfer of heat from the system to the surroundings ( $q_{\text{surr}} > 0$ ), the larger the increase in the entropy of the surroundings. Indeed, the larger the heat transferred into the surroundings, the more chaotic the motion of atoms, ions or molecules in the surroundings.

$\Delta S_{\text{surr}}$  is inversely proportional to the temperature,  $T$ . Consider an exothermic reaction at low and high temperatures. If a reaction is exothermic ( $q < 0$ ), heat is transferred from the system into the surroundings ( $q_{\text{surr}} > 0$ ). Hence, there is an increase in disorder for the surroundings.

Is the increase in disorder more noticeable at low temperatures or at high temperatures?

Recall: The entropy increases with increasing temperature ( $T$ ). Thus, the surroundings are more ordered at low temperature than at high temperature. Hence, the transfer of a given amount of heat from the system into the surroundings creates more disorder in the surroundings when it takes place at lower temperature ( $T$ ). This is why the change in entropy is inversely proportional to the temperature ( $T$ ).

*To remember this concept, consider the analogy of the “sneeze.” A sneeze creates more disturbance when it occurs in the peace and quiet of a library than when it is one of the minor sounds in the roaring crowd of a football stadium.*

The change in entropy for the surroundings,  $\Delta S_{\text{surr}}$ , is expressed as:

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T}$$

During an exothermic process, heat flows out of the system ( $q < 0$ ) and into the surroundings ( $q_{\text{surr}} > 0$ ). Conversely, during an endothermic process, heat flows into the system ( $q > 0$ ) from the surroundings ( $q_{\text{surr}} < 0$ ). Hence, we can always relate  $q_{\text{surr}}$  to  $q$  by the expression:

$$q_{\text{surr}} = -q$$

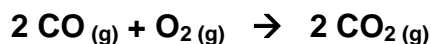
Recall: for a reaction occurring under a constant pressure of 1 atmosphere, the heat,  $q$ , is equal to the standard enthalpy of reaction,  $\Delta H_{\text{rxn}}^{\circ}$ .

$$q = \Delta H_{\text{rxn}}^{\circ}$$

By combining the above equations, the entropy change for the surroundings can be expressed as:

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{rxn}}^{\circ}}{T}$$

**Example:** Consider the gaseous reaction of carbon monoxide with oxygen to form carbon dioxide:



**Calculate the entropy change for the surroundings at 25°C.**

First, the standard reaction enthalpy is calculated from the standard enthalpies of formation of substances using the equation:

$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_{\text{f}}^{\circ} (\text{products}) - \sum \Delta H_{\text{f}}^{\circ} (\text{reactants})$$

The contribution from the products is given by:

$$\Sigma\Delta H_f^\circ(\text{products}) = 2 \text{ mol}(\text{CO}_2(\text{g})) \times \Delta H_f^\circ(\text{CO}_2(\text{g}))$$

$$\Sigma\Delta H_f^\circ(\text{products}) = 2 \text{ mol}(\text{CO}_2(\text{g})) \times (-393.5 \text{ kJ}\cdot\text{mol}^{-1}(\text{CO}_2(\text{g})))$$

$$\Sigma\Delta H_f^\circ(\text{products}) = -787.0 \text{ kJ}$$

The contribution from the reactants is given by:

$$\Sigma\Delta H_f^\circ(\text{reactants}) = 2 \text{ mol}(\text{CO}(\text{g})) \times \Delta H_f^\circ(\text{CO}(\text{g})) + 1 \text{ mol}(\text{O}_2(\text{g})) \times \Delta H_f^\circ(\text{O}_2(\text{g}))$$

$$\Sigma\Delta H_f^\circ(\text{reactants}) = 2 \text{ mol} \times (-110.5 \text{ kJ}\cdot\text{mol}^{-1}) + 1 \text{ mol} \times 0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Sigma\Delta H_f^\circ(\text{reactants}) = -221.0 \text{ kJ}$$

$$\text{Hence, } \Delta H_{\text{rxn}}^\circ = -787.0 \text{ kJ} - (-221.0 \text{ kJ})$$

$$\Delta H_{\text{rxn}}^\circ = -566.0 \text{ kJ}$$

T is the temperature, in kelvin, at which the reaction takes place.

$$\text{Thus, } T = (273.15 + 25) \text{ K} = 298 \text{ K}$$

$$\text{Hence, } \Delta S_{\text{surr}} = \frac{-(-566.0 \text{ kJ})}{298 \text{ K}} = \frac{566,000 \text{ J}}{298 \text{ K}} = 1900 \text{ J}\cdot\text{K}^{-1}$$

In Section 18.8 practice the Interactive Problems.

## **Sections 18.9 - 18.10: Total Entropy Change in Chemical Reactions and the Second Law**

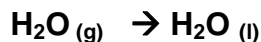
Recall: The Second Law of Thermodynamics states that a process occurs spontaneously if:

$$\Delta S + \Delta S_{\text{surr}} > 0 \quad \text{Remember this!}$$

To determine whether a process is spontaneous requires three steps.

1. Calculate  $\Delta S$  for the system.
2. Calculate  $\Delta S_{\text{surr}}$  for the surroundings.
3. Add  $\Delta S$  and  $\Delta S_{\text{surr}}$  to obtain the total change in entropy for the process and determine the sign of this quantity.

**Example:** Consider the condensation of 1 mol H<sub>2</sub>O (g):



**Show that this process is spontaneous at 25°C and 1 atm.**

1. Calculate  $\Delta S$  for the system.

The system is 1 mole of H<sub>2</sub>O. The process is the condensation of water under standard conditions. Since the condensation process is written as a chemical reaction, the expression for the change in entropy of the system is:

$$\Delta S_{\text{cond}}^{\circ} = 69.91 \text{ J.K}^{-1}.\text{mol}^{-1} - 188.83 \text{ J.K}^{-1}.\text{mol}^{-1}$$

$$\Delta S_{\text{cond}}^{\circ} = -118.92 \text{ J.K}^{-1}.\text{mol}^{-1}$$

2. Calculate  $\Delta S_{\text{surr}}$  for the surroundings.

$$\text{Recall : } \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} \text{ and } q_{\text{surr}} = -q$$

For a process taking place at constant pressure (standard pressure),

$$q = \Delta H^{\circ}$$

Here,  $\Delta H^{\circ}$  is the standard enthalpy change for the condensation of 1 mol H<sub>2</sub>O (g). Hence, it is written as  $\Delta H_{\text{cond}}^{\circ}$ .

$$\text{Hence, } \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{cond}}^{\circ}}{T}$$

The standard enthalpy change for the condensation of 1 mol H<sub>2</sub>O is then obtained using the expression:

$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_{\text{f}}^{\circ} (\text{products}) - \sum \Delta H_{\text{f}}^{\circ} (\text{reactants})$$

Here, the reaction is the condensation, the product is H<sub>2</sub>O (l), and, the reactant is H<sub>2</sub>O (g).

$$\text{Hence, } \Delta H_{\text{cond}}^{\circ} = \Delta H_{\text{f}}^{\circ} (\text{H}_2\text{O (l)}) - \Delta H_{\text{f}}^{\circ} (\text{H}_2\text{O (g)})$$

Using the thermodynamic table to determine the standard formation enthalpies of water in the liquid and gas phases, we obtain:

$$\Delta H^{\circ}_{\text{cond}} = (-285.83 \text{ kJ/mol}) - (-241.82 \text{ kJ/mol})$$

$$\Delta H^{\circ}_{\text{cond}} = -44.01 \text{ kJ/mol}$$

The temperature,  $T$ , in kelvin is:  $T = (273.15 + 25) \text{ K} = 298 \text{ K}$

$$\text{Hence, } \Delta S_{\text{surr}} = \frac{-(-44.01 \text{ kJ/mol})}{298 \text{ K}} = 0.1477 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 147.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

3. Add  $\Delta S$  and  $\Delta S_{\text{surr}}$  to obtain the total change in entropy for the process and determine the sign of this quantity.

$$\Delta S + \Delta S_{\text{surr}} = -118.92 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 147.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = +28.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

We note that the entropy of the system (1 mol of water) decreases. This was expected because water transforms from the gas state (greater disorder) to the liquid state (lesser disorder). Condensation at 298 K is spontaneous because the overall entropy change for the Universe (i.e. system + surroundings) is positive. Here, the increase in the order of the system is outweighed by the increase in the disorder of the surroundings.

In Section 18.10 practice the Interactive Problems.

## Section 18.11: Equilibrium and the Second Law of Thermodynamics

In this section, we explore the concept of “Equilibrium” in the context of the Second Law of Thermodynamics.

**Consider a thermally insulated calorimeter filled with 1 mol H<sub>2</sub>O at 25°C. An aluminum block initially at 80°C is dropped in the water. What happens?**

We know from experience that heat flows spontaneously from the hot object (Al) to the cold one (H<sub>2</sub>O) until they reach the same temperature. As long as their temperatures differ, the water will spontaneously warm up and the aluminum block will spontaneously cool down. The process is spontaneous because the increase in disorder due to the warming up of

water is larger than the increase in order associated with the cooling of the aluminum block. (i.e.  $\Delta S_{\text{universe}} = \Delta S + \Delta S_{\text{surr}} > 0$ )

Hence, as long as the aluminum block is cooling down and the water is warming up, the entropy of the universe is increasing (i.e.  $\Delta S_{\text{universe}} > 0$ ).

When the aluminum block and the water reach the same temperature, their temperature no longer changes. We say that "they have reached equilibrium."

When a system reaches equilibrium, the entropy of the universe no longer changes (i.e.  $\Delta S_{\text{universe}} = 0$  or  $\Delta S = -\Delta S_{\text{surr}}$ ).

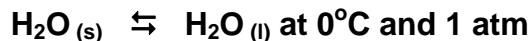
Hence, for any process occurring under equilibrium conditions, the Second Law of Thermodynamics states:

$$\Delta S_{\text{universe}} = \Delta S + \Delta S_{\text{surr}} = 0$$

This version of the Second Law is particularly useful for the calculation of the entropy change during a phase transformation.

**Consider the melting of ice:  $\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$  at  $0^\circ\text{C}$  and  $1 \text{ atm}$ .**

Under these conditions of temperature and pressure, the liquid and the solid are in equilibrium with each other. Hence, the single arrow is replaced by a double arrow to indicate that the process can occur in either direction (i.e. it is reversible).



From the second law for equilibrium processes, we write:  $\Delta S = -\Delta S_{\text{surr}}$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} \text{ with } q_{\text{surr}} = -q = -\Delta H_{\text{fus}}^\circ$$

*Note: Melting occurs at constant pressure ( $P^\circ = 1 \text{ atm}$ ), hence,  $q = \Delta H_{\text{fus}}^\circ$*

Combining these three equations, we obtain:

$$\Delta S = \frac{\Delta H_{\text{fus}}^\circ}{T}$$

For the above process (melting of ice),  $\Delta S$ , the change in entropy is the standard entropy of fusion, which is defined as:



$$\Delta S_{\text{fusion}}^{\circ} = S_{\text{m}}^{\circ}(\text{H}_2\text{O}_{(\text{l})}) - S_{\text{m}}^{\circ}(\text{H}_2\text{O}_{(\text{s})}) = \frac{\Delta H_{\text{fusion}}^{\circ}}{T}$$

Using the standard formation enthalpies of water in the liquid and solid phases, we determine the standard enthalpy of fusion,  $\Delta H_{\text{fusion}}^{\circ}$ .

$$\Delta H_{\text{fusion}}^{\circ} = \Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}_{(\text{l})}) - \Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}_{(\text{s})})$$

$$\Delta H_{\text{fus}}^{\circ} = (-286 \text{ kJ/mol}) - (-292 \text{ kJ/mol}) = +6 \text{ kJ/mol}$$

Hence, the standard entropy of fusion is expressed as:

$$\Delta S_{\text{fusion}}^{\circ} = \frac{6000 \text{ J/mol}}{273 \text{ K}} = 22 \text{ J.K}^{-1}.\text{mol}^{-1}$$

## Section 18.12: Gibbs Free Energy, Spontaneity and Equilibrium

Many chemical, physical and biological processes occur under conditions of constant temperature and pressure. In such situations, it is useful and actually more practical to discuss spontaneity using another thermodynamic quantity, **the Free Energy**. The symbol, G, for the Free Energy is used in honor of Josiah W. Gibbs, an American scientist who laid many of the foundations in chemical thermodynamics at the end of the 19<sup>th</sup> century.

The Gibbs Free Energy of a system, G, is defined by:

$$G = H - TS$$

H is the enthalpy of the system

S is the entropy of the system

T is the absolute temperature

For a process occurring at constant temperature, the change in free energy, G, can be expressed in terms of enthalpy and entropy changes as:

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

This equation can be rearranged as:

$$\Delta G = -T \times \left( \frac{-\Delta H}{T} + \Delta S \right)$$

We learned earlier that for a process occurring at constant pressure:

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

Hence, we conclude that:

$$\Delta G = -T \times (\Delta S_{\text{surr}} + \Delta S) = -T \times \Delta S_{\text{universe}}$$

The Second Law of Thermodynamics states that:

- a process occurs spontaneously if  $\Delta S_{\text{universe}} > 0$
- a process has reached equilibrium if  $\Delta S_{\text{universe}} = 0$
- a process does not occur spontaneously if  $\Delta S_{\text{universe}} < 0$

Now, we can restate the Second Law of Thermodynamics in a new form on the basis of the free energy change,  $\Delta G = \Delta H - T\Delta S$ .

“A process occurring at constant temperature and pressure:

- is spontaneous if  $\Delta G < 0$  (i.e.  $\Delta S_{\text{universe}} > 0$ );
- has reached equilibrium if  $\Delta G = 0$  (i.e.  $\Delta S_{\text{universe}} = 0$ );
- is non-spontaneous if  $\Delta G > 0$  (i.e.  $\Delta S_{\text{universe}} < 0$ ).”

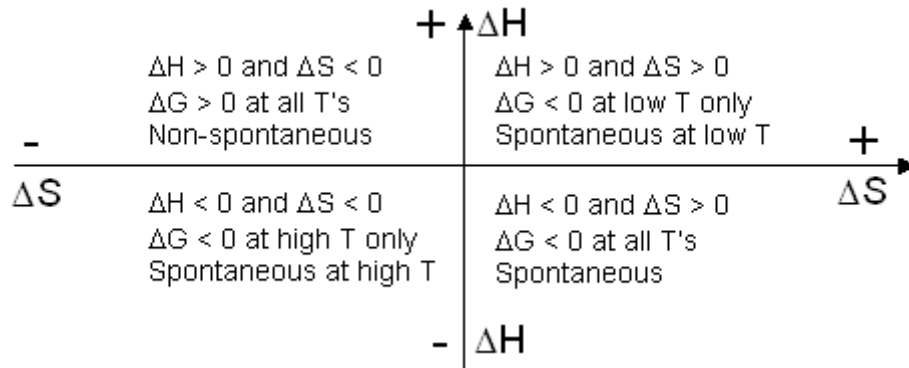
Memorize this, as this is the Second Law!!!

An equivalent statement of the Second Law is: During a spontaneous process occurring at constant T and P, the free energy of the system is steadily decreasing. When a system achieves equilibrium, its free energy is minimum.

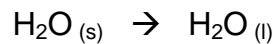
Many processes are found to be spontaneous at low temperatures and non-spontaneous at high temperatures or vice-versa. How can we understand that and predict the conditions under which a process will be spontaneous? The answer to these questions lies in the expression for  $\Delta G$ :

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

It is often found that  $\Delta H$  and  $\Delta S$  do not vary significantly with temperature. Hence,  $\Delta G$  will mainly take different values at different temperatures because of the term “T” in front of the entropy change. It is therefore often possible to predict the sign of  $\Delta G$  from the respective signs of  $\Delta H$  and  $\Delta S$ .



Consider the melting process for ice at  $P^\circ = 1 \text{ atm}$ .



For this process,  $\Delta H^\circ_{\text{fus}} = 6000 \text{ J/mol}$  and  $\Delta S^\circ_{\text{fus}} = 22 \text{ J/(mol.K)}$ .

The solid and liquid phases are in equilibrium when  $\Delta G^\circ_{\text{fus}} = 0$ .

$$\Delta G^\circ_{\text{fus}} \text{ is expressed as: } \Delta G^\circ_{\text{fus}} = \Delta H^\circ_{\text{fus}} - T\Delta S^\circ_{\text{fus}}$$

$$\text{Hence, at equilibrium (} T = T_{\text{fus}} \text{): } 0 = \Delta H^\circ_{\text{fus}} - T_{\text{fus}}\Delta S^\circ_{\text{fus}}$$

$$\text{Thus, } T_{\text{fus}} = \frac{\Delta H^\circ_{\text{fus}}}{\Delta S^\circ_{\text{fus}}} = \frac{6000 \text{ J/mol}}{22 \text{ J/(K.mol)}} = 273 \text{ K or } 0^\circ \text{C!}$$

If  $T > 273 \text{ K}$ , then, multiplying the inequality by  $\Delta S^\circ_{\text{fus}}$ , we get:

$$T \times \Delta S^\circ_{\text{fus}} > 273 \times \Delta S^\circ_{\text{fus}}$$

Switching the sign leads to reversing the inequality:

$$-T \times \Delta S^\circ_{\text{fus}} < -273 \times \Delta S^\circ_{\text{fus}}$$

Adding  $\Delta H^\circ_{\text{fus}}$  to both sides leads to:

$$\Delta H^\circ_{\text{fus}} - T \times \Delta S^\circ_{\text{fus}} < \Delta H^\circ_{\text{fus}} - 273 \times \Delta S^\circ_{\text{fus}}$$

This term is equal to the free energy of fusion at T.  
 $(\Delta G^\circ_{\text{fus}} \text{ at } T)$

This term is equal to the free energy of fusion at  $T_{\text{fus}}$   
 Hence, it is equal to 0.

Hence, we conclude:  $\Delta G^\circ_{\text{fus}} < 0$  for  $T < T_{\text{fus}}$

The fusion or melting of ice to water is spontaneous when the temperature,  $T$ , is greater than 273 K. Conversely, fusion of ice to water is non-spontaneous when the temperature,  $T$ , is lower than 273 K (i.e. ice is stable below 273 K). In the latter case, freezing of water (the reverse process) is spontaneous.

### Sections 18.13 - 18.14: Standard Reaction Free Energy

To determine whether a reaction is spontaneous or not at temperature  $T$ , we need to calculate the standard reaction free energy change,  $\Delta_R G^\circ$  at that temperature.

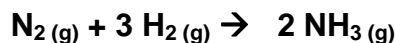
Two methods are available:

**In the first method**,  $\Delta_R G^\circ$  is calculated using the expression:

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

Then calculate  $\Delta_R H^\circ$  and  $\Delta_R S^\circ$  at temperature ( $T$ ) using the appropriate enthalpies of formation ( $\Delta_f H^\circ(\text{substance})$ ) and the molar entropies  $S_m^\circ(\text{substance})$  for the products and the reactants. Values for the standard molar entropies and the standard enthalpies of formation are found in the "Thermo Table" on the DVD.

**For example: Let us calculate  $\Delta_R G^\circ$  for the following reaction:**



The standard reaction enthalpy at 298 K and 1 atm is:

$$\Delta_R H^\circ = 2 \text{ mol}(\text{NH}_3(\text{g})) \times \Delta_f H^\circ(\text{NH}_3(\text{g}))$$

Recall that  $\Delta_f H^\circ(\text{N}_2(\text{g})) = \Delta_f H^\circ(\text{H}_2(\text{g})) = 0$  since  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  are the standard reference states for the elements N and H.

Using the "Thermo Table," we obtain:

$$\Delta_R H^\circ = 2 \times (-46.11) = -92.22 \text{ kJ}$$

The standard reaction entropy  $\Delta_R S^\circ$  is expressed as:

$$\Delta_R S^\circ = 2 \times S_m^\circ(\text{NH}_3(\text{g})) - S_m^\circ(\text{N}_2(\text{g})) - 3 \times S_m^\circ(\text{H}_2(\text{g}))$$

Using the "Thermo Table," we obtain:

$$\Delta_{\text{R}}S^{\circ} = 2 \times (192.45) - (191.61) - 3 \times (130.68) \text{ J.K}^{-1} = -198.75 \text{ J.K}^{-1}$$

$$\Delta_{\text{R}}S^{\circ} = -0.19875 \text{ kJ.K}^{-1}$$

$$\text{At } 298 \text{ K, } \Delta_{\text{R}}G^{\circ} = \Delta_{\text{R}}H^{\circ} - 298 \text{ K} \times \Delta_{\text{R}}S^{\circ}$$

$$\Delta_{\text{R}}G^{\circ} = -92.22 \text{ kJ} - 298 \text{ K} \times (-0.19875 \text{ kJ.K}^{-1}) = - 32.98 \text{ kJ}$$

**In the second method**,  $\Delta_{\text{R}}G^{\circ}$  is calculated using the expression:

$$\Delta_{\text{R}}G^{\circ} = \Sigma\Delta_{\text{f}}G^{\circ}(\text{products}) - \Sigma\Delta_{\text{f}}G^{\circ}(\text{reactants})$$

where  $\Delta_{\text{f}}G^{\circ}$ (substance) (products or reactants) is the standard free energy of formation of one mole of the pure substance from its elements, all species in their standard reference state.  $\Delta_{\text{f}}G^{\circ}$  values are listed in the "Thermo Table" on the DVD for most substances at 298 K.

Note:  $\Delta_{\text{f}}G^{\circ}$ , like  $\Delta_{\text{f}}H^{\circ}$ , are equal to zero for all elements in their standard reference state. Review 6.15 and 6.16 (reference state of elements.)

**For example: Consider the following reaction:  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$**

The contribution from the products is given by:

$$\Sigma\Delta_{\text{f}}G^{\circ}(\text{products}) = 2 \times \Delta_{\text{f}}G^{\circ}(\text{NH}_3(\text{g}))$$

$$\Sigma\Delta_{\text{f}}G^{\circ}(\text{products}) = 2 \times \Delta_{\text{f}}G^{\circ}(-16.49 \text{ kJ.mol}^{-1})$$

$$\Sigma\Delta_{\text{f}}G^{\circ}(\text{products}) = - 32.98 \text{ kJ}$$

The contribution from the reactants is given by:

$$\Sigma\Delta_{\text{f}}G^{\circ}(\text{reactants}) = \Delta_{\text{f}}G^{\circ}(\text{N}_2(\text{g})) + 3 \times \Delta_{\text{f}}G^{\circ}(\text{H}_2(\text{g})) = 0$$

Thus,  $\Delta_{\text{R}}G^{\circ} = - 32.98 \text{ kJ}$

Remember that  $\Delta_{\text{f}}G^{\circ}$  values are given at 298 K. Hence,  $\Delta_{\text{R}}G^{\circ}$  can only be calculated at 298 K with this method.

In Section 18.14, practice the Interactive Problems.

## Sections 18.15 - 18.17: Reaction Free Energy, Reaction Quotient and the Equilibrium Constant

In the preceding sections, we learned to calculate the standard free energy change for a reaction,  $\Delta_R G^\circ$ . The sign of  $\Delta_R G^\circ$  tells us whether the reaction is spontaneous or not, when carried out under standard conditions. Unfortunately, reactions are rarely carried out under standard conditions. Recall that standard conditions imply that reactants and products must be pure and at a pressure of 1 atm. In the laboratory, as well as in chemical plants, reactants and products are generally mixed with each other, and their pressure differs from the standard pressure.

Hence, we must distinguish  $\Delta G$ , the reaction free energy change, where reactants and products are present in some specified, but non-standard concentration or partial pressure from  $\Delta G^\circ$ , the STANDARD reaction free energy change, where reactants and products are in their standard state (pure, 1 atm, etc.).

Hence, to predict the reaction spontaneity, we need to use  $\Delta_R G$  rather than  $\Delta_R G^\circ$ .  $\Delta_R G$  and  $\Delta_R G^\circ$  are related to each other by:

$$\Delta_R G = \Delta_R G^\circ + RT \ln Q_p$$

where: R is the gas constant ( $8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$ )  
T is the absolute temperature (K)

$Q_p$  is the reaction quotient expressed in terms of partial pressure of reactants and products present at that time, in the reaction mixture.

Recall our discussion of  $Q_p$  in [Chapter 14](#) (section 14.12).  $Q_p$  is expressed as the ratio of the partial pressures of products to those of the reactants, each raised to a power equal to the corresponding stoichiometric coefficient.

As a reaction proceeds from left to right (forward direction), reactants are consumed and products are formed. Hence,  $Q_p$  increases when the reaction proceeds in the forward direction. Conversely,  $Q_p$  decreases when a reaction proceeds in the reverse direction (from right to left). A reaction is said to have reached equilibrium when  $Q_p$  is equal to  $K_p$ , the equilibrium constant.

The second law of thermodynamics states that a reaction has reached equilibrium when  $\Delta_R G = 0$ . Hence at chemical equilibrium,

$$0 = \Delta_R G^\circ + RT \ln K_p$$

$$\text{or } \ln K_p = -\frac{\Delta_R G^\circ}{RT}$$

You must remember these two very important equations:

$$\Delta_R G = \Delta_R G^\circ + RT \ln Q_p$$

$$\ln K_p = -\frac{\Delta_R G^\circ}{RT}$$

The first equation allows you to determine whether a reaction is proceeding spontaneously in the forward or the reverse direction. The second equation allows you to determine the equilibrium constant for a reaction from the standard reaction free energy (i.e. from the Thermo Table) and from temperature. These two equations can be combined to yield.

$$\Delta_R G = \Delta_R G^\circ + RT \ln Q_p$$

$$\text{Recall that: } \Delta_R G^\circ = -RT \ln K_p$$

$$\text{Hence, } \Delta_R G = -RT \ln K_p + RT \ln Q_p$$

$$\Delta_R G = RT \ln(Q_p/K_p)$$

If  $(Q_p/K_p) < 1$  (i.e.  $(Q_p < K_p)$ , then  $\ln(Q_p/K_p) < 0$  and  $\Delta_R G < 0$ , which implies that the reaction is spontaneous in the forward direction.

If  $(Q_p/K_p) > 1$  (i.e.  $(Q_p > K_p)$ , then  $\ln(Q_p/K_p) > 0$  and  $\Delta_R G > 0$ , which implies that the reaction is non-spontaneous in the forward direction or the reaction is spontaneous in the reverse direction.

If  $(Q_p/K_p) = 1$  (i.e.  $(Q_p = K_p)$ , then  $\ln(Q_p/K_p) = 0$  and  $\Delta_R G = 0$ , which implies that the reaction has reached equilibrium (products and reactants are present at their equilibrium concentrations).

In Sections 18.16 and 18.17, practice the Interactive Problems.

### **Sections 18.18 - 18.19: Effect of Temperature on Standard Reaction Free Energy and Equilibrium Constant**

Thermodynamic tables provide values of  $\Delta_f H^\circ$ ,  $\Delta_f G^\circ$  and  $S_m^\circ$  for many common substances at the temperature of 298 K. With these Thermo Tables, one can

calculate quantities such as  $\Delta_R H^\circ$ ,  $\Delta_R S^\circ$ , and  $\Delta_R G^\circ$  for chemical reactions at 298 K.

However, chemical reactions are often carried out at different temperatures, either because their kinetics become more favorable or because the reactions are non-spontaneous at 298 K.

How can we estimate  $\Delta_R G^\circ$  and K at different temperatures? To answer this question, we recall the expression for  $\Delta_R G^\circ$  given earlier for processes at constant temperature.

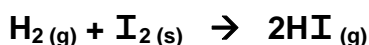
$$\Delta_R G^\circ = \Delta_R H^\circ - T \Delta_R S^\circ$$

Rigorously,  $\Delta_R G^\circ$ ,  $\Delta_R H^\circ$ , and  $\Delta_R S^\circ$  should refer to the same temperature T which appears in the above equation. However, it is often possible to assume that  $\Delta_R H^\circ$  and  $\Delta_R S^\circ$  depend very little on temperature.

Hence, to calculate  $\Delta_R G^\circ$  at a temperature (T) other than 298 K, it is often possible to use the  $\Delta_R H^\circ$  and  $\Delta_R S^\circ$  values determined at 298 K using the Thermo Table.

Hence, we conclude that:  $\Delta_R G^\circ = \Delta_R H^\circ - T \times \Delta_R S^\circ$

**For example: Consider the following reaction at 350 K.**



**Calculate  $\Delta_R G^\circ$  and K at 350 K.**

Assuming that  $\Delta_R H^\circ$  and  $\Delta_R S^\circ$  values at 350 K do not differ from these at 298 K, we write:

$$\Delta_R G^\circ = \Delta_R H^\circ - 350 \text{ K} \times \Delta_R S^\circ$$

Next, we calculate  $\Delta_R H^\circ$  and  $\Delta_R S^\circ$  at 298 K.

$$\Delta_R H^\circ = 2 \text{ mol} \times \Delta_f H^\circ(\text{HI}(\text{g})) - [1 \text{ mol} \times \Delta_f H^\circ(\text{H}_2(\text{g})) + 1 \text{ mol} \times \Delta_f H^\circ(\text{I}_2(\text{s}))]$$



$$\Delta_{\text{R}}H^{\circ} = 2 \text{ mol} \times 26.48 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{R}}H^{\circ} = 52.96 \text{ kJ}$$

$$\Delta_{\text{R}}S^{\circ} = 2 \text{ mol} \times S^{\circ}_{\text{m}}(\text{HI}_{(\text{g})}) - [1 \text{ mol} \times S^{\circ}_{\text{m}}(\text{H}_{2(\text{g})}) + 1 \text{ mol} \times S^{\circ}_{\text{m}}(\text{I}_{2(\text{s})})]$$

$$\Delta_{\text{R}}S^{\circ} = 2 \text{ mol} \times 206.59 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - [1 \text{ mol} \times 130.68 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 1 \text{ mol} \times 116.14 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}]$$

$$\Delta_{\text{R}}S^{\circ} = 166.36 \text{ J}\cdot\text{K}^{-1}$$

Hence, at 350 K,  $\Delta_{\text{R}}G^{\circ} = 52960 \text{ J} - 350 \text{ K} \times 166.36 \text{ J}\cdot\text{K}^{-1} = -5266 \text{ J}$

Don't forget to express  $\Delta_{\text{R}}H^{\circ}$  and  $T \times \Delta_{\text{R}}S^{\circ}$  in the same unit (here, we used J).

Now we can calculate K using the expression:

$$\ln K = \frac{-\Delta_{\text{R}}G^{\circ}}{RT}$$

$$\text{Hence, at 350 K, } \ln K = \frac{-(-5266 \text{ J})}{8.314 \text{ J}/(\text{K}\cdot\text{mol}) \times 350 \text{ K}} = +1.81$$

$$\text{Hence, } K = e^{(1.81)} = 6.1$$

In Section 18.19, practice the Interactive Problems.

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