CHEMICAL THERMODYNAMICS

The content in this topic is the basis for mastering Learning Objectives 5.12–5.15 and 6.25 as found in the Curriculum Framework.
When you finish reviewing this topic, be sure you are able to:

- Distinguish between exothermic and endothermic changes and understand the direction of energy flow for each

- Explain using the kinetic-molecular theory the concept of entropy in a chemical system

- Explain the direction and relative magnitudes of changes in entropy when solids change to liquids or gases

- Use models and representations to explain how molecular complexity affects entropy

- Calculate entropy changes from thermodynamic data

- Use $\Delta G° = \Delta H° - T\Delta S°$ to predict the thermodynamic favorability of a chemical or physical change

- Calculate $\Delta G°$ to determine the thermodynamic favorability of a chemical change

- Use the relationship between $\Delta G°$ and K ($\Delta G° = -RT \ln K$) to estimate the magnitude of K and the thermodynamic favorability of a process

Chemical thermodynamics answers a fundamental question. Why does change occur?

The driving influences for any chemical and physical change are:

1. **Change in enthalpy,** ΔH (heat transferred between the system and the surroundings).

2. **Change in entropy,** ΔS (randomness or disorder of the system).

Generally, chemical and physical systems tend to change in a direction that moves toward lower enthalpy (they release heat to the environment) and higher entropy (they become more random or disordered).

Sometimes, these two influences are in direct conflict with each other and the reaction seeks a balance between moving toward lower enthalpy and higher entropy. Systems reach this balance at **equilibrium**.

Section 19.1

Spontaneous Processes

A **spontaneous process** is one that is thermodynamically favored. It continues on its own without outside assistance. A thermodynamically favored change occurs in a definite direction. Processes that are thermodynamically favored in one direction are not favored in the opposite direction. For example, a rock falls to the ground spontaneously. The opposite process, a rock rising from the ground, is not thermodynamically favored. Similarly, a burning campfire is thermodynamically favored. The "un-burning" of a campfire is not thermodynamically favored.

Review Section 5.3

Enthalpy

Recall from Topic 5 that **enthalpy** is the heat transferred between a chemical or physical system and its surroundings during a constant-pressure process.

The **change in enthalpy, ΔH,** is the **heat absorbed** by a system at constant pressure.

An **endothermic process** is one that absorbs heat from the environment. ΔH is positive.

An **exothermic process** is one that releases heat to the environment. ΔH is negative.

The **first law of thermodynamics**, also called the law of conservation of energy, states that, in all cases, energy is conserved. Energy can be neither created nor destroyed. This means that the amount of energy gained by a system must equal the amount of energy lost by the environment and vice versa.

A major driving influence for any chemical or physical change is the tendency for systems to move toward lower enthalpy by releasing energy to the environment. Thus, exothermic processes, those that release energy to the environment, usually but not always, are thermodynamically favored. They occur on their own without any outside assistance.

Recall from Section 5.7 of *Chemistry: The Central Science* that the enthalpy change for a given reaction can be calculated from the enthalpies of formation for products minus the enthalpies of formation for reactants:

$$\Delta H^\circ_{rxn} = \Sigma\, H^\circ_{products} - \Sigma\, H^\circ_{reactants}$$

Entropy and the Second Law of Thermodynamics

Section 19.2

Entropy for qualitative purposes can be considered to be the extent of randomness or disorder in a chemical or physical system. Entropy increases when matter or energy is dispersed. For example, gases are more random than are liquids because the molecules are more dispersed. A gas at a higher temperature is more dispersed than a gas at a lower temperature because the distribution of kinetic energy among the gas particles increases at higher temperatures.

Kinetic-molecular theory states that gases consist of a large number of atoms and/or molecules having a high kinetic energy, so they are in continuous, random motion. The attractive forces between gas particles are negligible compared to their kinetic energy (see Section 10.1). In contrast, liquids have low kinetic energy and the attractive forces between the particles are sufficiently significant to hold the molecules together but still allow them to freely move past one another. Solids have relatively low kinetic energy and the attractive forces work to lock the molecules into place, often in a very ordered crystal lattice (see Section 11.1). Gases, because of their relative disorder, have higher entropy than do liquids. Solids generally have lower entropy than either liquids or gases.

The **change in entropy,** ΔS, for any process is a measure of the change in randomness or disorder of the system. Generally, as the phase of a given system changes from solid to liquid to gas, the entropy of the system increases and ΔS is positive for such changes. Phase changes from gas to liquid, gas to solid, or liquid to solid all happen with a decrease in entropy and ΔS is negative. Table 19.1 illustrates examples of entropy changes for various physical and chemical processes.

Table 19.1 Changes that increase entropy: ΔS is positive.

Generally, Entropy Increases When	Example
solids change to liquids or gases	$CO_2(s) \rightarrow CO_2(g)$
liquids change to gases	$H_2O(l) \rightarrow H_2O(g)$
solids dissolve in liquid solutions	$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
the number of gas molecules increase	$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
temperature increases	Water increases in temperature
volume increases	A gas expands
the number of particles increase	A rock is crushed
two or more pure substances are mixed	Sugar dissolves in water

Your Turn 19.1

a. When helium is released from a toy balloon, does the entropy of the system increase or decrease? Explain your answer.

b. Draw a distribution plot of the number of gas molecules versus their kinetic energies in a sealed rigid container at two different temperatures and explain how entropy changes. Write your answers in the space provided.

Section 19.3   **Molecular Interpretation of Entropy**

Entropy also increases for substances with increasing molecular complexity. For example, under the same conditions, O_3 has a higher entropy than O_2 because it is more complex. Figure 19.1 shows three hydrocarbons and the entropy associated with each.

Methane, CH_4
$S° = 186.3$ J/mol-K

Ethane, C_2H_6
$S° = 229.6$ J/mol-K

Propane, C_3H_8
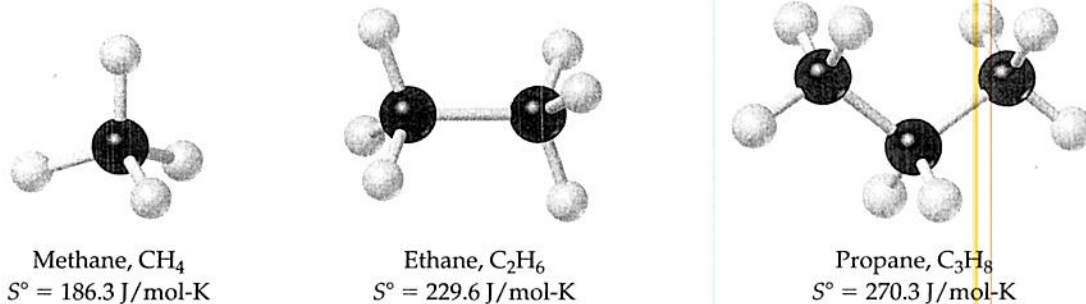$S° = 270.3$ J/mol-K

Figure 19.1   Entropy increases with increasing molecular complexity.

Your Turn 19.2

Under the same conditions of pressure and temperature, which has greater entropy, gaseous propane or gaseous butane? Explain. Which has greater entropy, steam or ice? Explain. Write your answers in the space provided.

The **second law of thermodynamics** states that any thermodynamically favored change is always accompanied by an overall increase in entropy in the universe.

The **third law of thermodynamics** states that the entropy of a pure crystalline substance at absolute zero is zero. Upon heating, the entropy of a pure crystalline substance gradually increases. Continued heating brings upon a sharp increase in entropy upon melting and another marked increase upon boiling as illustrated in Figure 19.2.
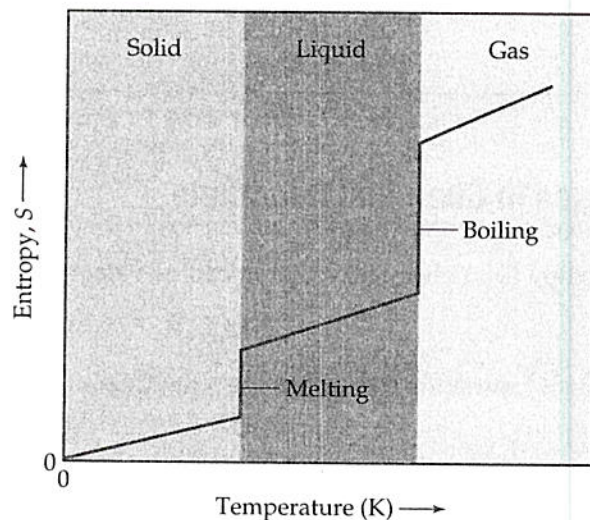

Figure 19.2 As the temperature of a substance increases, its entropy increases. Large changes in entropy are associated with phase changes.

Standard molar entropies, $S°$, are values for pure substances at 1 atm pressure and 298 K. The unit most often used for $S°$ is J/mol K. Table 19.2 lists some examples. Notice that $S°$ is comparatively larger for gases than for liquids or solids. Also, substances having the same phase but having higher molar mass and/or higher molecular complexity have higher entropy values. A more detailed list of standard entropy values is given in Appendix C of *Chemistry: The Central Science*.

Table 19.2 Standard molar entropies of selected substances at 298 K.

Substance	$S°$, J/mol k	Substance	$S°$, J/mol k
$I_2(s)$	116.73	$NO(g)$	210.62
$I_2(l)$	180.66	$NO_2(g)$	240.45
$I_2(g)$	260.57	$N_2O_4(g)$	304.30
$O(g)$	161.0	$H_2O(l)$	69.91
$O_2(g)$	205.0	$H_2O(g)$	188.83
$O_3(g)$	237.6		

Your Turn 19.3 ←

Rationalize the difference in the standard molar entropy values of solid, liquid, and gaseous iodine as listed in Table 19.2. Write your answer in the space provided.

Section 19.4   Entropy Changes in Chemical Reactions

The change in entropy for a chemical reaction can be calculated by the following equation:

$$\Delta S^\circ_{rxn} = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$$

Example:

What is the entropy change for the reaction,
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)?$$

Solution:

Substitute the entropy values listed in Table 19.2 into the equation. Do not forget to use the coefficients that balance the equation!

$$\Delta S^\circ_{rxn} = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$$
$$\Delta S^\circ_{rxn} = 2(240.45 \; J/mol \; K) - 205.0 \; J/mol \; K - 2(210.62 \; J/mol \; K)$$
$$\Delta S^\circ_{rxn} = -145.34 \; J/mol \; K$$

The answer is negative and makes sense because the system moves from three moles of gas to two moles of gas with a decrease in entropy.

Section 19.5   Gibbs Free Energy

Free energy (or **change in free energy, ΔG**) represents the amount of useful work that can be obtained from a process at constant temperature and pressure. Free energy, enthalpy, and entropy are related by the equation:

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

ΔG is change in free energy measured in kJ/mol.

ΔH is change in enthalpy measured in kJ/mol.

ΔS is change in entropy measured in J/mol K.

T is absolute temperature in K.

The sign of ΔG tells if any given process is thermodynamically favored as illustrated by Table 19.3.

Table 19.3 The sign of ΔG and its thermodynamic meaning.

If ΔG Is	The Process Is
negative $(-)$	thermodynamically favored (spontaneous)
positive $(+)$	not thermodynamically favored (nonspontaneous) (the reverse reaction is spontaneous)
zero (0)	at equilibrium

The change in free energy of a reaction can be calculated by the following equation:

$$\Delta G°_{rxn} = \Sigma\, \Delta G°_{f\,products} - \Sigma\, \Delta G°_{f\,reactants}$$

The standard free energies of formation, $\Delta G°_f$, of various substances are listed in Appendix C of *Chemistry: The Central Science*.

> **Exampie:**
>
> *What is the standard free energy change for the reaction,*
> $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$?
>
> **Solution:**
>
> *Obtain the values of standard free energy of formation for each of the reactants and products from Appendix C of* Chemistry: The Central Science *and substitute them into the equation. Do not forget to take into account the number of moles of each substance as defined by the coefficients of the balanced equation.*
>
> $\Delta G°_{rxn} = \Sigma\, G°_{products} - \Sigma\, G°_{reactants}$
> $\Delta G°_{rxn} = 2(+51.58\ kJ/mol) - 0 - 2(+86.71\ kJ/mol)$
> $\qquad = -70.26\ kJ/mol$
>
> *The sign of $\Delta G°$ for the reaction is negative, indicating that this is a thermodynamically favored process at 298 K.*

Free Energy and Temperature

Section 19.6

What causes a process to be thermodynamically favored? What influences chemical and physical change? Every process involves the two thermodynamic properties, enthalpy and entropy. Often a balance exists between enthalpy and entropy, and temperature determines in which direction a reversible reaction will continue spontaneously.

Phase change provides a good example of the role that temperature plays in determining thermodynamic favorability. Consider the melting of ice and freezing of

liquid water. Ice melts spontaneously at temperatures above $0\,^\circ C$ and liquid water freezes spontaneously at temperatures below $0\,^\circ C$. Whether ice melts spontaneously or liquid water freezes spontaneously depends on the temperature.

Ice melts spontaneously at temperatures higher than $0\,^\circ C$ because liquid water is more random than is solid water. The increase in entropy (the positive ΔS), as ice melts, is the driving influence for the change from solid to liquid.

Liquid water freezes spontaneously at temperatures lower than $0\,^\circ C$ because freezing is exothermic (ΔH is negative) and the move to lower enthalpy as liquid changes to solid influences the change.

$$H_2O(l) \rightarrow H_2O(s) + \text{heat}$$

At exactly $0\,^\circ C$, an equilibrium is established. At $0\,^\circ C$, ice changes to liquid water at the same rate that liquid water changes to ice. At equilibrium, the drive toward lower enthalpy exactly balances the drive toward higher entropy.

The equation, $\Delta G = \Delta H - T\Delta S$, and the signs of ΔH and ΔS are useful to predict qualitatively the spontaneity of any given reaction. It provides a model to guide our thinking in determining whether a reaction will be thermodynamically favored or not (see Table 19.4).

Table 19.4   The effect of temperature on the spontaneity of reactions.

ΔH	ΔS	$-T\Delta S$	ΔG	**The Reaction Is Thermodynamically**
$-$	$+$	$-$	$-$	favored at all temperatures
$+$	$-$	$+$	$+$	not favored at all temperatures
$-$	$-$	$+$	$+/-$	favored only at low temperatures
$+$	$+$	$-$	$+/-$	favored only at high temperatures

If ΔH is negative and ΔS is positive, ΔG is always negative and the reaction is thermodynamically favored at all temperatures because the reaction goes toward lower enthalpy and higher entropy.

If ΔH is positive and ΔS is negative, ΔG is always positive and the reaction is not thermodynamically favored at any temperature. (However, the reverse reaction is favored at all temperatures.)

Table 19.5 illustrates that often the change in free energy represents a balance between systems tending toward decreasing enthalpy and increasing entropy. If ΔH and ΔS both are positive, ΔG is negative only when the temperature is high enough for the entropy term to outweigh the enthalpy term. On the other hand, if ΔH and ΔS both are negative, ΔG is negative only when the temperature is low enough for the enthalpy term to outweigh the entropy term.

Table 19.5 A summary of important thermodynamic quantities.

Quantity	Change in Enthalpy	Change in Entropy	Change in Free Energy
Symbol	ΔH	ΔS	ΔG
Unit	kJ/mol	J/mol K	kJ/mol
Definition	Heat gained by a system	Change in randomness of a system	Available useful work
Comments	+ for endothermic − for exothermic	+ for increasing randomness − for decreasing randomness	+ for non-favored reactions − for thermodynamically favored reactions $\Delta G = 0$ at equilibrium

→

Is ΔG for a burning campfire positive or negative? Explain citing the positive or negative signs of ΔH and ΔS for the process. Is there a temperature at which ΔG for a burning campfire will change signs? Explain. Write your answers in the space provided.

Free Energy and the Equilibrium Constant

Section 19.7

The free energy change for any reaction under nonstandard conditions, ΔG, can be calculated from the standard free energy change, $\Delta G°$, by the following equation:

$$\Delta G = \Delta G° + RT \ln Q$$

ΔG = the free energy change under nonstandard conditions

$\Delta G°$ = the free energy change under standard conditions: 25°C and 1 atm partial pressure of all gases and 1 M concentration for all solutes

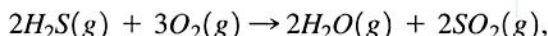$R = 8.314$ J/mol K, the ideal-gas constant

T = the absolute temperature in K

Q = the reaction quotient

Example:

Using standard free energies of formation for the reaction,

$$2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g),$$

calculate $\Delta G°$ and ΔG for a mixture at 25°C with the composition below.

$$P_{H_2S} = 1.00 \text{ atm} \quad P_{H_2O} = 0.500 \text{ atm} \quad P_{O_2} = 2.00 \text{ atm}$$
$$P_{SO_2} = 0.750 \text{ atm}$$

Solution:

Using the standard free energies of formation from Appendix C of Chemistry: The Central Science, *calculate $\Delta G°$ for the reaction.*

$$\Delta G°_{rxn} = \Sigma \Delta G°_{products} - \Sigma \Delta G°_{reactants}$$
$$\Delta G°_{rxn} = 2(-300.4) + 2(-228.57) - 2(-33.01) - 0$$
$$\Delta G°_{rxn} = -991.9 \text{ kJ}$$

Evaluate Q and use the equation, $\Delta G = \Delta G° + RT \ln Q$, to calculate ΔG.
$$Q = P^2_{SO_2} P^2_{H_2O} / P^2_{H_2S} P^3_{O_2} = (0.750)^2(0.500)^2/(1.00)^2(2.0)^3$$
$$= 0.0176$$

$$\Delta G = \Delta G° + RT \ln Q$$
$$= -991.9 \text{ kJ} + (8.314 \text{ J/mol K})(298 \text{ K})(1 \text{ kJ }/1000 \text{ J}) \ln (0.0176)$$
$$= -1002 \text{ kJ}$$

**Common misconception:** When using the equation $\Delta G = \Delta G° + RT \ln Q$, keep in mind that $\Delta G°$ is usually given in kJ/mol, whereas R is in units of J/mol K. Be sure to convert J to kJ using 1 kJ = 1000 J.

The standard free energy for any reaction is related to the equilibrium constant. At equilibrium, $\Delta G = 0$ and $Q = K$, the equilibrium constant. At equilibrium,

$$\Delta G° = -RT \ln K$$

Example:

The standard free energy change for the following reaction at 25°C is −118.4 kJ/mol:
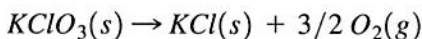
$$KClO_3(s) \rightarrow KCl(s) + 3/2 \, O_2(g)$$
Calculate K_p for the reaction at 25°C and the equilibrium pressure of O_2 gas.

Solution:

$\Delta G° = -RT \ln K$

$-118.4 \, kJ/mol = -(8.314 \, J/mol \, K)(298 \, K)(1 \, kJ/1000 \, J) \ln K_p$

$\ln K_p = 47.8$

$K_p = e^{47.8} = 5.68 \times 10^{20}$

$K_p = P_{O_2}^{3/2}$

$P_{O_2} = K_p^{2/3} = (5.68 \times 10^{20})^{2/3} = 6.9 \times 10^{13} \, atm$