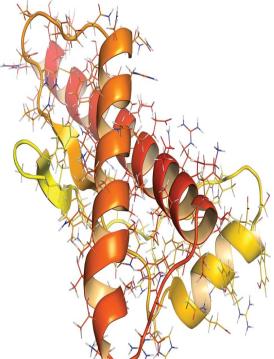


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*Chapter 17*

## Entropy, Free Energy, and Equilibrium

Pieter Van de Vijver/molekul/123RF

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### Spontaneous Physical and Chemical Processes

- A waterfall runs downhill.
- A lump of sugar dissolves in a cup of coffee.
- At 1 atm, water freezes below 0°C and ice melts above 0°C.
- Heat flows from a hotter object to a colder object.
- A gas expands in an evacuated bulb.
- Iron exposed to oxygen and water forms rust.

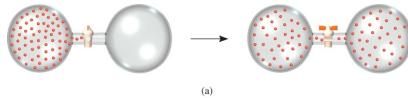
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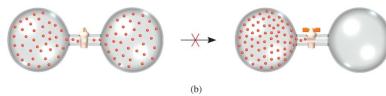
## Spontaneous Physical and Chemical Processes 2

spontaneous



(a)

nonspontaneous



(b)

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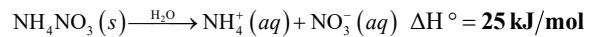
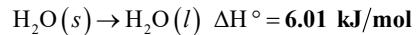
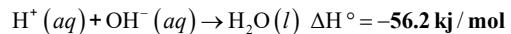
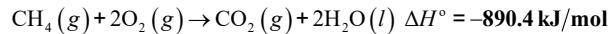
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## Spontaneity and Enthalpy

Does a decrease in enthalpy mean a reaction proceeds spontaneously?

### Spontaneous reactions



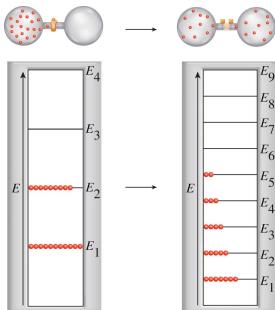
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## Entropy 1

**Entropy ( $S$ )** is a measure of how spread out or dispersed the energy of a system is among the different possible ways that system can contain energy.



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## Entropy 2

**Entropy ( $S$ )** is a measure of how spread out or dispersed the energy of a system is among the different possible ways that system can contain energy.

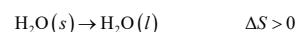
$$\Delta S = S_f - S_i$$

If the change from initial to final results in an increase in energy dispersal

$$S_f > S_i \quad \Delta S > 0$$

For any substance, the solid state is more ordered than the liquid state and the liquid state is more ordered than gas state.

$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$



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## Entropy 3

$W = \text{number of microstates}$

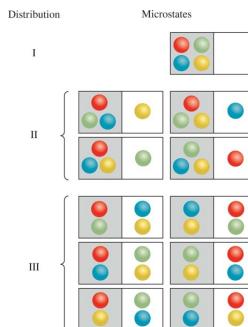
$$S = k \ln W$$

$$\Delta S = S_f - S_i$$

$$\Delta S = k \ln \frac{W_f}{W_i}$$

$W_f > W_i$  then  $\Delta S > 0$

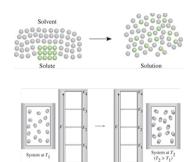
$W_f < W_i$  then  $\Delta S < 0$



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## Processes that lead to an increase in entropy ( $\Delta S > 0$ )



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## Examples of Spontaneous Reactions

Example:  $\text{Br}_2(l) \rightarrow \text{Br}_2(g)$



$$\Delta S > 0$$

Example:  $\text{I}_2(s) \rightarrow \text{I}_2(g)$



$$\Delta S > 0$$

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## Entropy is a State Function

**State functions** are properties that are determined by the state of the system, regardless of how that condition was achieved.

Examples:

energy, enthalpy, pressure, volume, temperature, **entropy**

Review



Potential energy of **hiker 1** and **hiker 2** is the same even though they took different paths.

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## Standard Entropy Values

**Table 17.1** Standard Entropy Values ( $S^\circ$ ) for Some Substances at 25°C

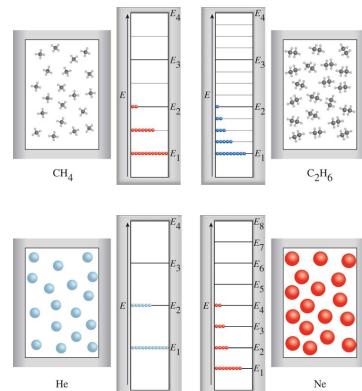
Substance	$S^\circ$ (J/K mol)
H <sub>2</sub> O( <i>l</i> )	69.9
H <sub>2</sub> O( <i>g</i> )	188.7
Br <sub>2</sub> ( <i>l</i> )	152.3
Br <sub>2</sub> ( <i>g</i> )	245.3
I <sub>2</sub> ( <i>s</i> )	116.7
I <sub>2</sub> ( <i>g</i> )	260.3
C(diamond)	2.4
C(graphite)	5.69
CH <sub>4</sub> (methane)	186.2
C <sub>2</sub> H <sub>6</sub> (ethane)	229.5
He( <i>g</i> )	126.1
Ne( <i>g</i> )	146.2

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## Standard Entropy

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### Example 17.1<sub>1</sub>

Predict whether the entropy change is greater or less than zero for each of the following processes:

- a) freezing ethanol
- b) evaporating a beaker of liquid bromine at room temperature
- c) dissolving glucose in water
- d) cooling nitrogen gas from 80°C to 20°C

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### Example 17.1<sub>2</sub>

#### *Strategy*

To determine the entropy change in each case, we examine whether the number of microstates of the system increases or decreases. The sign of  $\Delta S$  will be positive if there is an increase in the number of microstates and negative if the number of microstates decreases.

#### *Solution*

- (a) Upon freezing, the ethanol molecules are held rigid in position. This phase transition reduces the number of microstates and therefore the entropy decreases; that is,  $\Delta S < 0$ .

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### Example 17.1 <sub>3</sub>

- (b) Evaporating bromine increases the number of microstates because the Br<sub>2</sub> molecules can occupy many more positions in nearly empty space. Therefore,  $\Delta S > 0$
- (c) Glucose is a nonelectrolyte. The solution process leads to a greater dispersal of matter due to the mixing of glucose and water molecules so we expect  $\Delta S > 0$
- (d) The cooling process decreases various molecular motions. This leads to a decrease in microstates and so  $\Delta S < 0$

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## First and Second Laws of Thermodynamics

### *First Law of Thermodynamics*

Energy can be converted from one form to another but energy cannot be created or destroyed.

### *Second Law of Thermodynamics*

The entropy of the **universe** increases in a spontaneous process and remains unchanged in an equilibrium process.

$$\text{Spontaneous process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\text{Equilibrium process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

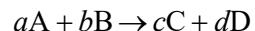
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## Entropy Changes in the System ( $\Delta S_{\text{sys}}$ )

The **standard entropy of reaction** ( $\Delta S^{\circ}_{\text{rxn}}$ ) is the entropy change for a reaction carried out at 1 atm and 25°C.



$$\Delta S^{\circ}_{\text{rxn}} = [cS^{\circ}(C) + dS^{\circ}(D)] - [aS^{\circ}(A) + bS^{\circ}(B)]$$

$$\Delta S^{\circ}_{\text{rxn}} = \sum nS^{\circ}(\text{products}) - \sum mS^{\circ}(\text{reactants})$$

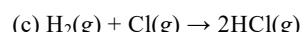
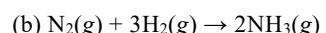
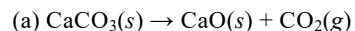
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## Example 17.2

From the standard entropy values in Appendix 3, calculate the standard entropy changes for the following reactions at 25°C.



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## Example 17.2<sub>2</sub>

### *Strategy*

To calculate the standard entropy of a reaction, we look up the standard entropies of reactants and products in Appendix 3 and apply Equation (17.7). As in the calculation of enthalpy of reaction [see Equation (6.18)], the stoichiometric coefficients have no units, so  $\Delta S^\circ_{\text{rxn}}$  is expressed in units of J/K · mol.

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## Example 17.2<sub>3</sub>

### *Solution*

$$\begin{aligned}
 \text{(a)} \quad \Delta S^\circ_{\text{rxn}} &= [S^\circ(\text{CaO}) + S^\circ(\text{CO}_2)] - [S^\circ(\text{CaCO}_3)] \\
 &= [(39.8 \text{ J/K} \cdot \text{mol}) + (213.6 \text{ J/K} \cdot \text{mol})] \\
 &\quad - (92.9 \text{ J/K} \cdot \text{mol}) \\
 &= \mathbf{160.5 \text{ J/K} \cdot \text{mol}}
 \end{aligned}$$

Thus, when 1 mole of CaCO<sub>3</sub> decomposes to form 1 mole of CaO and 1 mole of gaseous, CO<sub>2</sub> there is an increase in entropy equal to 160.5 J/K · mol.

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### Example 17.2<sub>4</sub>

$$\begin{aligned}
 \text{(b)} \quad \Delta S^\circ_{\text{rxn}} &= [2S^\circ(\text{NH}_3)] - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\
 &= (2)(193 \text{ J/K} \cdot \text{mol}) - [(192 \text{ J/K} \cdot \text{mol}) + (3)(131 \text{ J/K} \cdot \text{mol})] \\
 &= \mathbf{-199 \text{ J/K} \cdot \text{mol}}
 \end{aligned}$$

This result shows that when 1 mole of gaseous nitrogen reacts with 3 moles of gaseous hydrogen to form 2 moles of gaseous ammonia, there is a decrease in entropy equal to  $-199 \text{ J/K} \cdot \text{mol}$ .

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### Example 17.2<sub>5</sub>

$$\begin{aligned}
 \text{(c)} \quad \Delta S^\circ_{\text{rxn}} &= [2S^\circ(\text{HCl})] - [S^\circ(\text{H}_2) + S^\circ(\text{Cl}_2)] \\
 &= (2)(187 \text{ J/K} \cdot \text{mol}) - [(131 \text{ J/K} \cdot \text{mol}) + (223 \text{ J/K} \cdot \text{mol})] \\
 &= \mathbf{20 \text{ J/K} \cdot \text{mol}}
 \end{aligned}$$

Thus, the formation of 2 moles of gaseous HCl from 1 mole of gaseous and 1 mole of gaseous Cl<sub>2</sub> results in a small increase in entropy equal to  $20 \text{ J/K} \cdot \text{mol}$ .

***Comment***

The  $\Delta S^\circ_{\text{rxn}}$  values all apply to the system.

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## Entropy Changes in the System ( $\Delta S_{\text{sys}}$ ) 2

### When gases are produced (or consumed)

If a reaction produces more gas molecules than it consumes,  
 $\Delta S^\circ > 0$ .

If the total number of gas molecules diminishes,  $\Delta S^\circ < 0$ .

If there is no net change in the total number of gas molecules, then  $\Delta S^\circ$  may be positive or negative BUT  $\Delta S^\circ$  will be a small number.

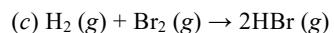
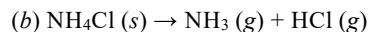
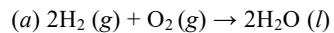
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## Example 17.3 1

Predict whether the entropy change of the system in each of the following reactions is positive or negative.



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## Example 17.3<sub>2</sub>

### *Strategy*

We are asked to predict, not calculate, the sign of entropy change in the reactions. The factors that lead to an increase in entropy are: (1) a transition from a condensed phase to the vapor phase and (2) a reaction that produces more product molecules than reactant molecules in the same phase. It is also important to compare the relative complexity of the product and reactant molecules. In general, the more complex the molecular structure, the greater the entropy of the compound.

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## Example 17.3<sub>3</sub>

### *Solution*

(a) Two reactant molecules combine to form one product molecule. Even though H<sub>2</sub>O is a more complex molecule than either H<sub>2</sub> and O<sub>2</sub>, the fact that there is a net decrease of one molecule and gases are converted to liquid ensures that the number of microstates will be diminished and hence  $\Delta S^\circ$  is negative.

(b) A solid is converted to two gaseous products. Therefore,  $\Delta S^\circ$  is positive.

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### Example 17.3 <sub>4</sub>

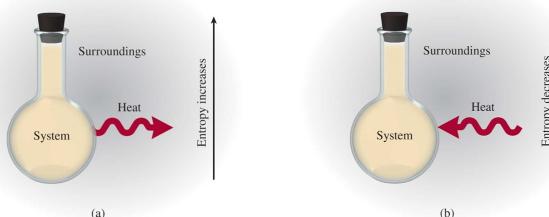
(c) The same number of molecules is involved in the reactants as in the product. Furthermore, all molecules are diatomic and therefore of similar complexity. As a result, we cannot predict the sign of  $\Delta S^\circ$ , but we know that the change must be quite small in magnitude.

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### Entropy Changes in the Surroundings ( $\Delta S_{\text{surr}}$ )



Exothermic process:

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

Endothermic process:

$$\Delta S_{\text{surr}} < 0$$

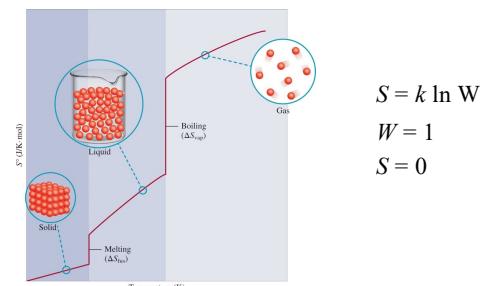
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## Third Law of Thermodynamics

The entropy of a perfect crystalline substance is zero at the absolute zero of temperature.

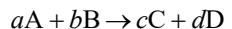


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## Standard Free Energy

The **standard free-energy of reaction** ( $\Delta G_{rxn}^\circ$ ) is the free-energy change for a reaction when it occurs under standard-state conditions.



$$\begin{aligned}\Delta G_{rxn}^\circ &= [c \Delta G_f^\circ(C) + d \Delta G_f^\circ(D)] - [a \Delta G_f^\circ(A) + b \Delta G_f^\circ(B)] \\ \Delta G_{rxn}^\circ &= \sum n \Delta G_f^\circ(\text{products}) - \sum m \Delta G_f^\circ(\text{reactants})\end{aligned}$$

The **standard free energy of formation** ( $\Delta G_f^\circ$ ) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

$\Delta G_f^\circ$  of any element in its stable form is zero

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## Gibbs Free Energy

Spontaneous process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Equilibrium process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

For a constant temperature and  
constant pressure process:

$$\begin{array}{ll} \textit{Gibbs free} & \Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}} \\ \textit{energy (G)} & \end{array}$$

$\Delta G < 0$  The reaction is spontaneous in the forward direction

$\Delta G > 0$  The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.

$\Delta G = 0$  The reaction is at equilibrium.

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## Conventions for Standard States

**Table 17.2** Conventions for Standard States

State of Matter	Standard State
Gas	1 atm pressure
Liquid	Pure liquid
Solid	Pure Solid
Elements*	$\Delta G_f^\circ = 0$
Solution	1 molar Concentration

\*The most stable allotropic form at 25° C And 1 atm

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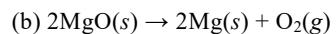
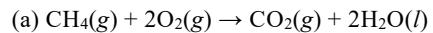
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### Example 17.4<sub>1</sub>

Calculate the standard free-energy changes for the following reactions at 25°C



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### Example 17.4<sub>2</sub>

#### *Strategy*

To calculate the standard free-energy change of a reaction, we look up the standard free energies of formation of reactants and products in Appendix 3 and apply Equation (17.12). Note that all the stoichiometric coefficients have no units so  $\Delta G^\circ_{\text{rxn}}$  is expressed in units of kJ/mol, and  $\Delta G^\circ_f$  for O<sub>2</sub> is zero because it is the stable allotropic element at 1 atm and 25°C.

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### Example 17.4 <sub>3</sub>

*Solution*

- a) According to Equation (17.12), we write

$$\Delta G_{rxn}^{\circ} = [\Delta G_f^{\circ}(CO_2) + 2\Delta G_f^{\circ}(H_2O)] - [\Delta G_f^{\circ}(CH_4) + 2\Delta G_f^{\circ}(O_2)]$$

We insert the appropriate values from Appendix 3:

$$\begin{aligned}\Delta G_{rxn}^{\circ} &= [(-394.4 \text{ kJ/mol}) + (2)(-237.2 \text{ kJ/mol})] \\ &\quad - [(-50.8 \text{ kJ/mol}) + (2)(0 \text{ kJ/mol})] \\ &= \mathbf{-818.0 \text{ kJ / mol}}\end{aligned}$$

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### Example 17.4 <sub>4</sub>

- b) The equation is

$$\Delta G_{rxn}^{\circ} = [2\Delta G_f^{\circ}(Mg) + \Delta G_f^{\circ}(O_2)] - [2\Delta G_f^{\circ}(MgO)]$$

From data in Appendix 3 we write

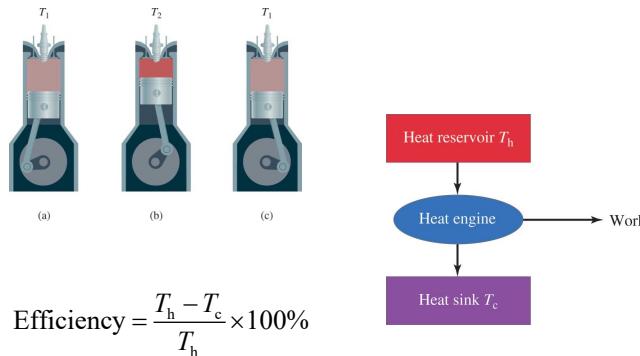
$$\begin{aligned}\Delta G_{rxn}^{\circ} &= [(2)(0 \text{ kJ/mol}) + (0 \text{ kJ/mol})] - [(2)(-569.6 \text{ kJ/mol})] \\ &= \mathbf{1139 \text{ kJ/mol}}\end{aligned}$$

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## Chemistry In Action: The Efficiency of Heat Engines



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## Relationship of $\Delta G$ , $\Delta H$ and $\Delta S$

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

**Table 17.3** Factors affecting the sign of  $\Delta G$  in the relationship  $\Delta G = \Delta H - T\Delta S$

$\Delta_H$	$\Delta_S$	$\Delta_G$	Example
+	+		Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.
+	-		$2\text{HgO}(s) \rightarrow 2\text{Hg}(l) + \text{O}_2(g)$ Reaction is spontaneous in the reverse direction at all temperatures.
-	+		$3\text{O}_2(g) \rightarrow 2\text{O}_3(g)$ Reaction proceeds spontaneously at all temperatures.
-	-		$2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$ Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.
-	+		$\text{NH}_3(g) \rightarrow \text{HCl}(g) + \text{NH}_4\text{Cl}(g)$

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## Temperature and Spontaneity of Chemical Reactions



### Equilibrium Pressure of CO<sub>2</sub>

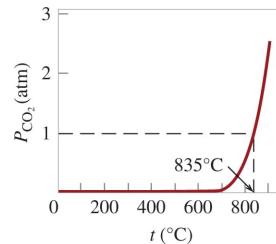
$$\Delta H^\circ = 177.8 \text{ kJ/mol}$$

$$\Delta S^\circ = 160.5 \text{ J / K} \cdot \text{mol}$$

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

$$\text{At } 25^\circ\text{C}, \Delta G^\circ = 130.0 \text{ kJ/mol}$$

$$\Delta G^\circ = 0 \text{ at } 835.6^\circ\text{C}$$



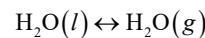
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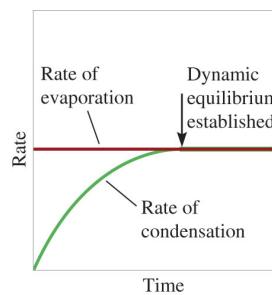
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## Gibbs Free Energy and Phase Transitions

$$\Delta G = 0 = \Delta H - T\Delta S$$



$$\begin{aligned}\Delta S &= \frac{\Delta H}{T} = \frac{40.79 \text{ kJ/mol}}{373 \text{ K}} \\ &= 1.09 \times 10^{-1} \text{ kJ/K} \cdot \text{mol} \\ &= 109 \text{ J / K} \cdot \text{mol}\end{aligned}$$

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## Example 17.5<sub>1</sub>

The molar heats of fusion and vaporization of benzene are 10.9 kJ/mol and 31.0 kJ/mol, respectively. Calculate the entropy changes for the solid → liquid and liquid → vapor transitions for benzene. At 1 atm pressure, benzene melts at 5.5°C and boils at 80.1°C.

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## Example 17.5<sub>2</sub>

### *Strategy*

At the melting point, liquid and solid benzene are at equilibrium, so  $\Delta G = 0$ . From Equation (17.10) we have  $\Delta G = 0 = \Delta H - T\Delta S$  or  $\Delta S = \Delta H/T$ . To calculate the entropy change for the solid benzene → liquid benzene transition, we write  $\Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_f$ . Here  $\Delta H_{\text{fus}}$  is positive for an endothermic process, so  $\Delta S_{\text{fus}}$  is also positive, as expected for a solid to liquid transition. The same procedure applies to the liquid benzene → vapor benzene transition. What temperature unit should be used?

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### Example 17.5 <sub>3</sub>

*Solution*

The entropy change for melting 1 mole of benzene at 5.5°C is

$$\begin{aligned}\Delta S_{\text{fus}} &= \frac{\Delta H_{\text{fus}}}{T_f} \\ &= \frac{(10.9 \text{ kJ/mol})(1000 \text{ J/1 kJ})}{(5.5 + 273) \text{ K}} \\ &= 39.1 \text{ J / K} \cdot \text{mol}\end{aligned}$$

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### Example 17.5 <sub>4</sub>

Similarly, the entropy change for boiling 1 mole of benzene at 80.1°C is

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_b} \\ &= \frac{(31.0 \text{ kJ/mol})(1000 \text{ J/kJ})}{(80.1 + 273) \text{ K}} \\ &= 87.8 \text{ J / K} \cdot \text{mol}\end{aligned}$$

**Check** Because vaporization creates more microstates than the melting process,  $\Delta S_{\text{vap}} > \Delta S_{\text{fus}}$ .

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## Gibbs Free Energy and Chemical Equilibrium

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

$R$  is the gas constant (8.314 J/K·mol)

$T$  is the absolute temperature (K)

$Q$  is the reaction quotient

At Equilibrium

$$\Delta G = 0, \quad Q = K$$

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

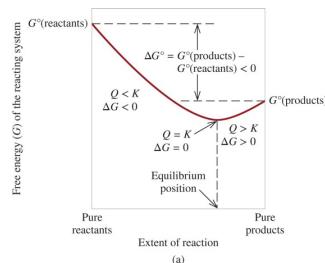
$$\Delta G^\circ = -RT \ln K$$

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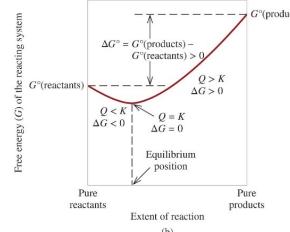
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## Free Energy Versus Extent of Reaction



$$\Delta G^\circ < 0$$



$$\Delta G^\circ > 0$$

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## Relationship of $\Delta G$ and $K$

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

**Table 17.4** Relation Between  $\Delta G^\circ$  and  $K$  as Predicted by the equation

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

$K$	$\ln K$	$\Delta G^\circ$	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
= 1	0	0	Products and reactants are equally favored at Equilibrium
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

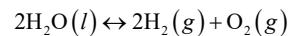
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## Example 17.6

Using data listed in Appendix 3, calculate the equilibrium constant ( $K_p$ ) for the following reaction at 25°C:



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## Example 17.6<sub>2</sub>

### *Strategy*

According to Equation (17.14), the equilibrium constant for the reaction is related to the standard free-energy change; that is,  $\Delta G^\circ = -RT \ln K$ . Therefore, we first need to calculate  $\Delta G^\circ$  by following the procedure in Example 17.4. Then we can calculate  $K_p$ . What temperature unit should be used?

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## Example 17.6<sub>3</sub>

### *Solution*

According to Equation (17.12),

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [2\Delta G_f^\circ(\text{H}_2) + \Delta G_f^\circ(\text{O}_2)] - [2\Delta G_f^\circ(\text{H}_2\text{O})] \\ &= [(2)(0 \text{ kJ/mol}) + (0 \text{ kJ/mol})] - [(2)(-237.2 \text{ kJ})] \\ &= \mathbf{474.4 \text{ kJ/mol}}\end{aligned}$$

Using Equation (17.14)

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= -RT \ln K_p \\ 474.4 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} &= -(8.314 \text{ J / K} \cdot \text{mol})(298 \text{ K}) \ln K_p \\ \ln K_p &= -191.5 \\ K_p &= e^{-191.5} = 7 \times 10^{-84}\end{aligned}$$

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### Example 17.6 4

#### *Comment*

This extremely small equilibrium constant is consistent with the fact that water does not spontaneously decompose into hydrogen and oxygen gases at 25°C. Thus, a large positive  $\Delta G^\circ$  favors reactants over products at equilibrium.

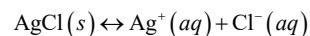
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### Example 17.7 1

In Chapter 16 we discussed the solubility product of slightly soluble substances. Using the solubility product of silver chloride at 25°C ( $1.6 \times 10^{-10}$ ), calculate  $\Delta G^\circ$  for the process



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## Example 17.7<sub>2</sub>

### *Strategy*

According to Equation (17.14), the equilibrium constant for the reaction is related to standard free-energy change; that is,  $\Delta G^\circ = -RT \ln K$ . Because this is a heterogeneous equilibrium, the solubility product ( $K_{sp}$ ) is the equilibrium constant. We calculate the standard free-energy change from the  $K_{sp}$  value of AgCl. What temperature unit should be used?

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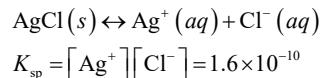
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## Example 17.7<sub>3</sub>

### *Solution*

The solubility equilibrium for AgCl is



Using Equation (17.14) we obtain

$$\begin{aligned}\Delta G^\circ &= -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln(1.6 \times 10^{-10}) \\ &= 5.6 \times 10^4 \text{ J/mol} \\ &= \mathbf{56 \text{ kJ/mol}}\end{aligned}$$

### *Check*

The large, positive  $\Delta G^\circ$  indicates that AgCl is slightly soluble and that the equilibrium lies mostly to the left.

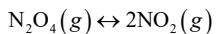
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### Example 17.8 <sub>1</sub>

The equilibrium constant ( $K_p$ ) for the reaction



is 0.113 at 298 K, which corresponds to a standard free-energy change of 5.40 kJ/mol. In a certain experiment, the initial pressures are

$$P_{\text{NO}_2} = 0.122 \text{ atm} \text{ and } P_{\text{N}_2\text{O}_4} = 0.453 \text{ atm.}$$

Calculate  $\Delta G$  for the reaction at these pressures and predict the direction of the net reaction toward equilibrium.

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### Example 17.8 <sub>2</sub>

#### *Strategy*

From the information given we see that neither the reactant nor the product is at its standard state of 1 atm. To determine the direction of the net reaction, we need to calculate the free-energy change under nonstandard-state conditions ( $\Delta G$ ) using Equation (17.13) and the given  $\Delta G^\circ$  value. Note that the partial pressures are expressed as dimensionless quantities in the reaction quotient  $Q_p$  because they are divided by the standard-state value of 1 atm (see Table 17.2).

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### Example 17.8<sub>3</sub>

**Solution**

Equation (17.13) can be written as

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q_p \\ &= \Delta G^\circ + RT \ln \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \\ &= 5.40 \times 10^3 \text{ J/mol} + (8.314 \text{ J / K} \cdot \text{mol})(298 \text{ K}) \times \ln \frac{(0.122)^2}{0.453} \\ &= 5.40 \times 10^3 \text{ J/mol} - 8.46 \times 10^3 \text{ J/mol} \\ &= -3.04 \times 10^3 \text{ J/mol} = \mathbf{-3.06 \text{ kJ/mol}}\end{aligned}$$

Because  $\Delta G < 0$ , the net reaction proceeds from left to right to reach equilibrium.

### Example 17.8<sub>4</sub>

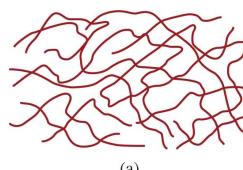
**Check**

Note that although  $\Delta G^\circ < 0$ , the reaction can be made to favor product formation initially by having a small concentration (pressure) of the product compared to that of the reactant. Confirm the prediction by showing that  $Q_p < K_p$ .

## Chemistry In Action: The Thermodynamics of a Rubber Band

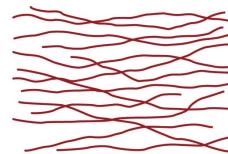
$$T\Delta S = \Delta H - \Delta G$$

High Entropy



(a)

Low Entropy



(b)

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## Mechanical Analog of Coupled Reactions



Make the smaller weight move upward (a nonspontaneous process) by coupling it with the falling of a larger weight.

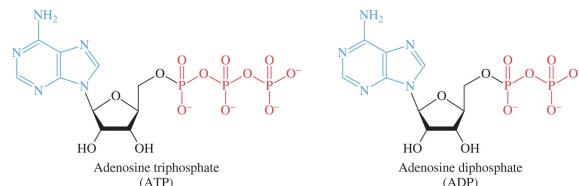
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## The Structure of ATP and ADP in Ionized Forms

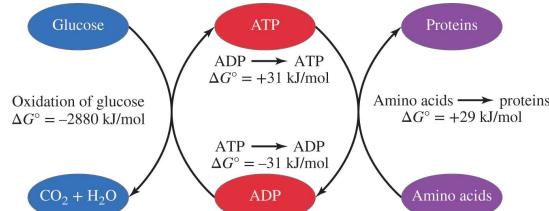


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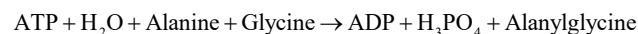
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## Coupled Reactions



Example: Alanine + Glycine → Alanylglucose

$$\Delta G^\circ = +29 \text{ kJ} \quad K < 1$$



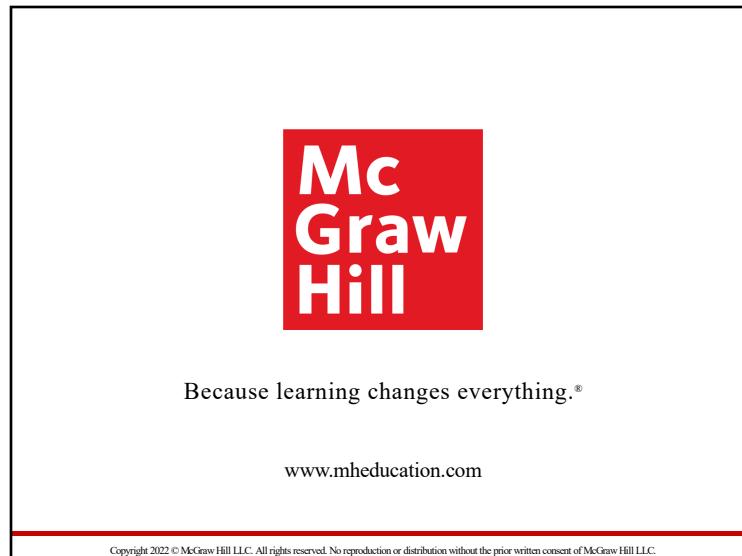
$$\Delta G^\circ = -2 \text{ kJ} \quad K > 1$$

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