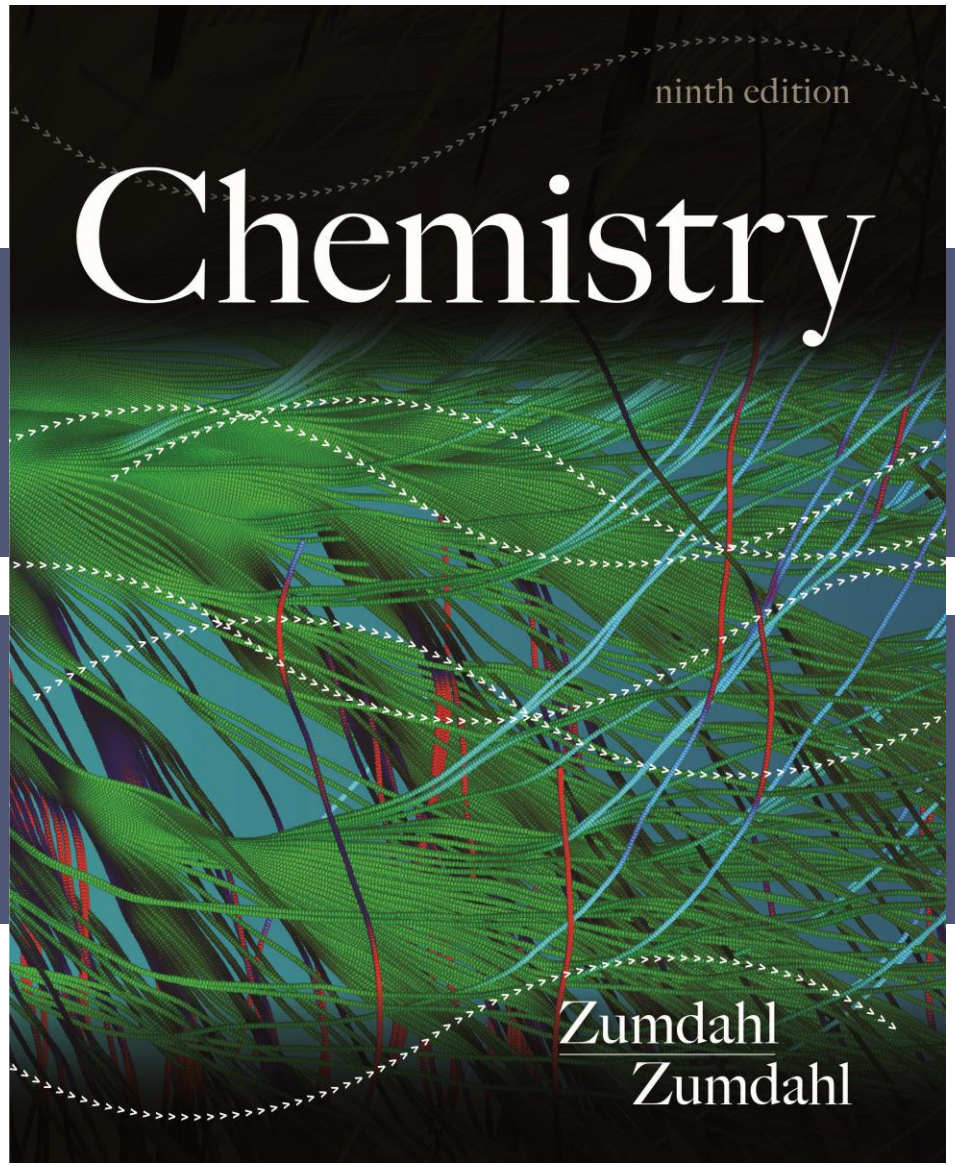
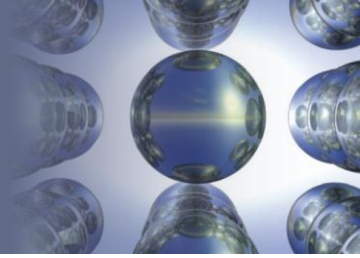


Chapter 17

Spontaneity, Entropy, and Free Energy

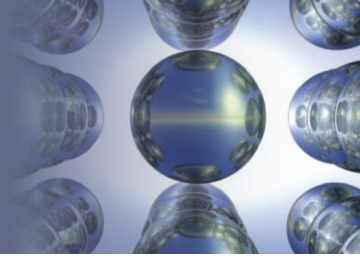
Copyright ©2017 Cengage Learning. All Rights Reserved.

Chapter 17
Table of Contents



- (17.1) Spontaneous processes and entropy
- (17.2) Entropy and the second law of thermodynamics
- (17.3) The effect of temperature on spontaneity
- (17.4) Free energy
- (17.5) Entropy changes in chemical reactions
- (17.6) Free energy and chemical reactions
- (17.7) The dependence of free energy on pressure
- (17.8) Free energy and equilibrium
- (17.9) Free energy and work

Copyright ©2017 Cengage Learning. All Rights Reserved.



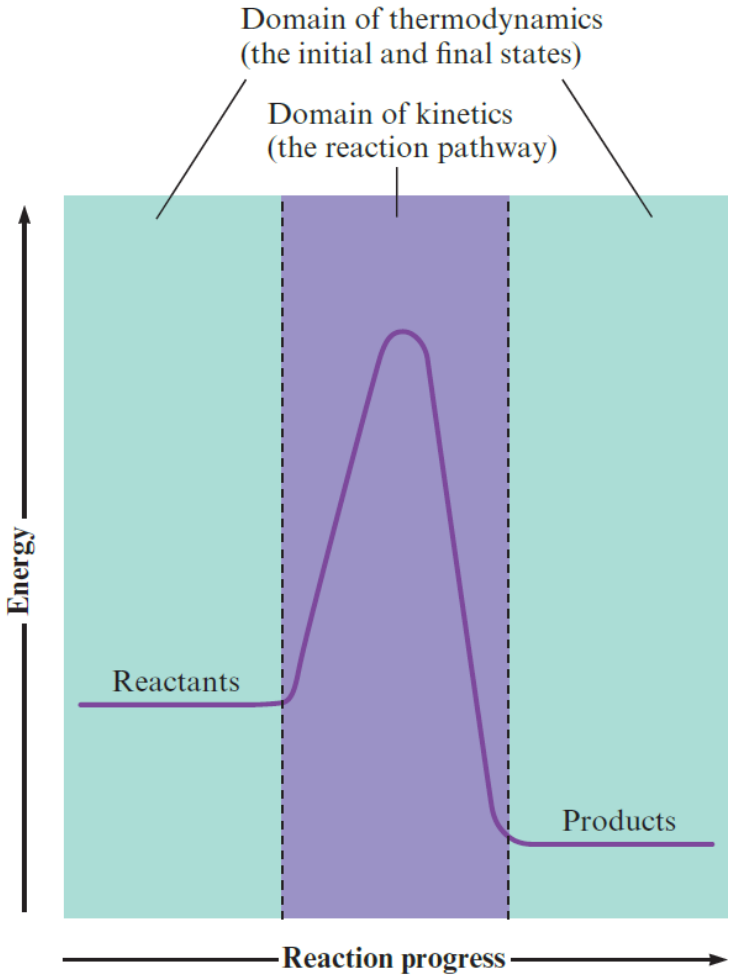
Thermodynamics - An Introduction

- First law of thermodynamics states that the energy of the universe is constant
  - Statement of law of conservation of energy
- **Spontaneous process**: Occurs without external intervention
  - Can be fast or slow

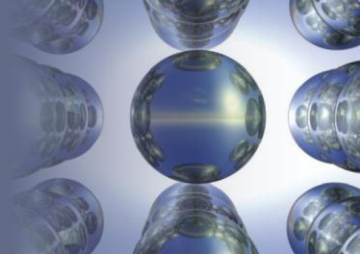
Copyright ©2017 Cengage Learning. All Rights Reserved.

Thermodynamics versus Kinetics

- Domain of kinetics
  - Rate of a reaction depends on the pathway from reactants to products
- Thermodynamics
  - Provides information on whether a reaction is spontaneous based only on the properties of the reactants and products



Copyright ©2017 Cengage Learning. All Rights Reserved.



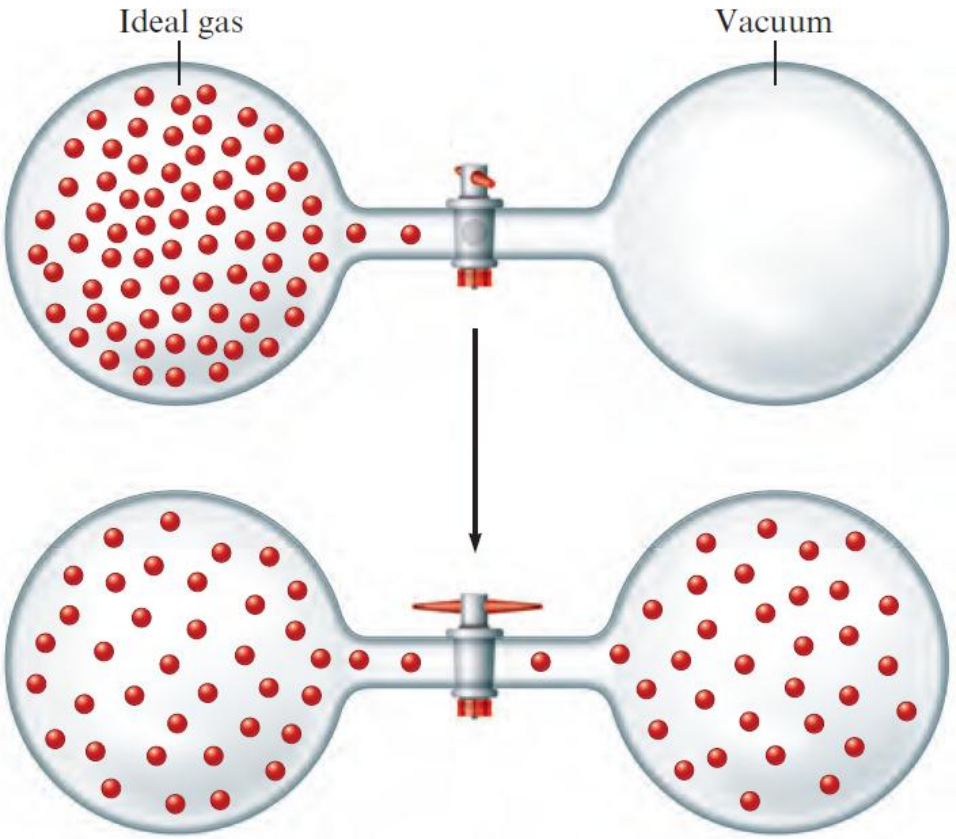
Entropy (*S*)

- Thermodynamic function that describes the number of arrangements that are available to a system existing in a given state
- Measure of molecular randomness or disorder

Copyright ©2017 Cengage Learning. All Rights Reserved.

The Expansion of an Ideal Gas into an Evacuated Bulb

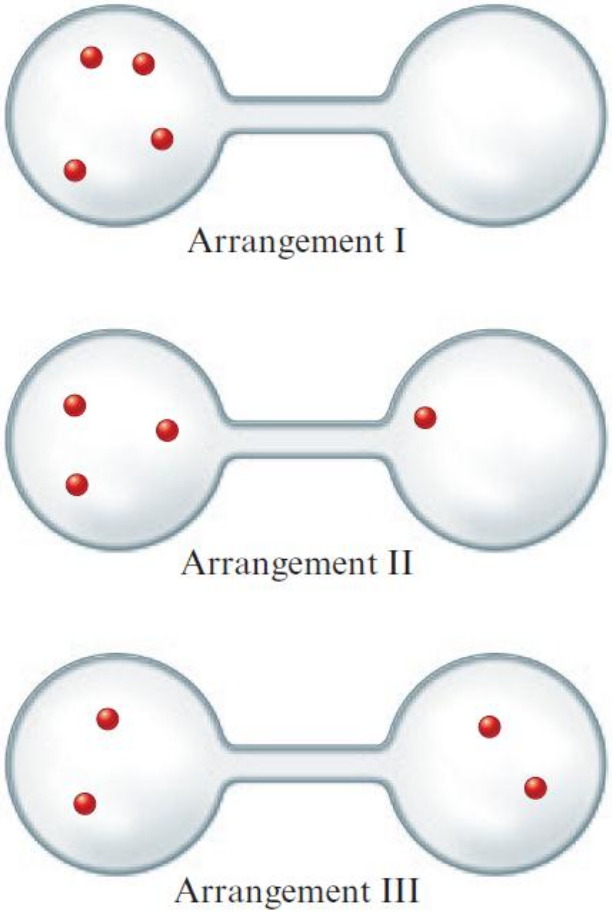
- Nature spontaneously proceeds toward the states that have the highest probabilities of existing



Copyright ©2017 Cengage Learning. All Rights Reserved.

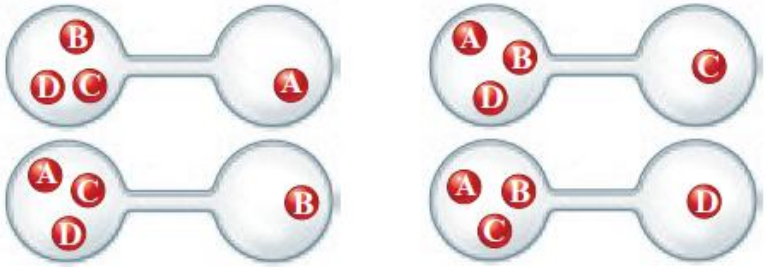
Microstate

- Each configuration that gives a particular arrangement
- Probability of occurrence of a state depends on the number of microstates in which the arrangement can be achieved



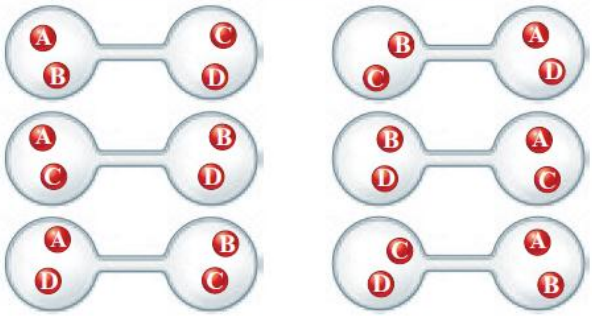
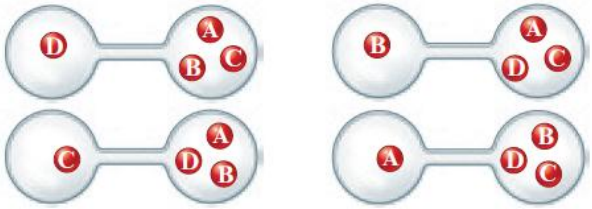
Copyright ©2017 Cengage Learning. All Rights Reserved.

Table 17.1 - The Microstates That Give a Particular Arrangement (State)

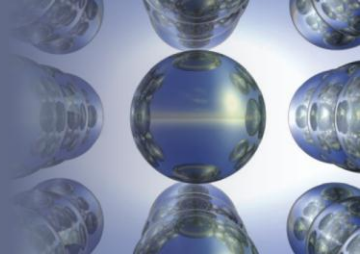
Arrangement	Microstates	Number of Microstates
I		1
II		4

Copyright ©2017 Cengage Learning. All Rights Reserved.

Table 17.1 - The Microstates That Give a Particular Arrangement (State) (Continued)

Arrangement	Microstates	Number of Microstates
III		6
IV		4
V		1

Copyright ©2017 Cengage Learning. All Rights Reserved.



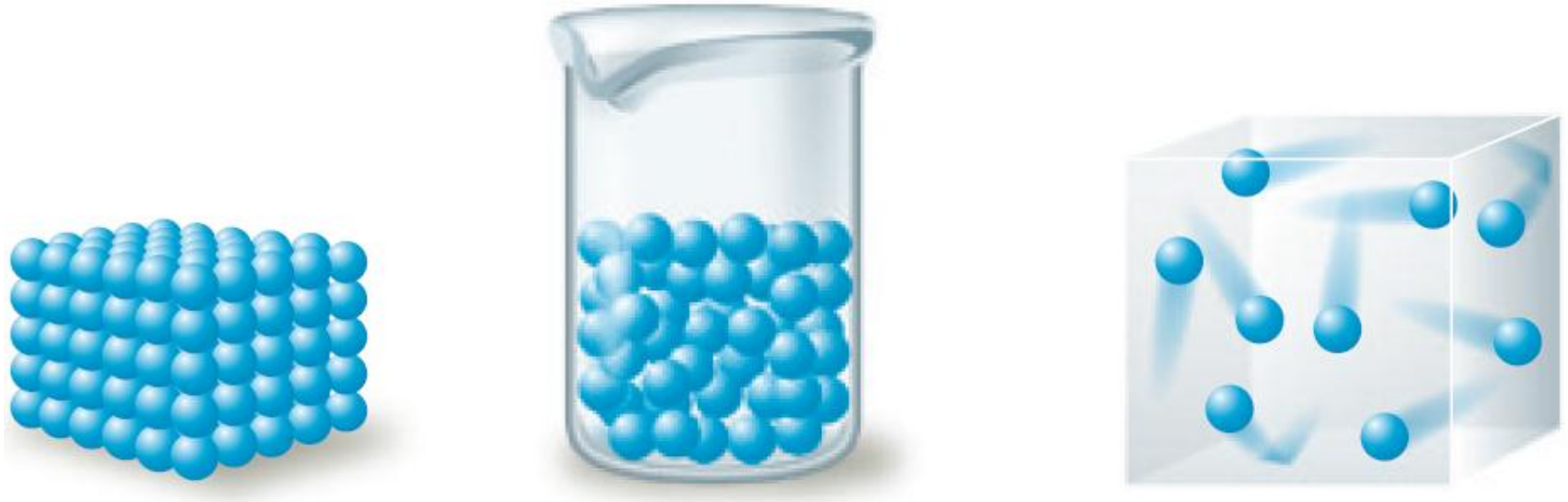
Positional Probability

- Depends on the number of configurations in space that yield a particular state
- Gas expands into a vacuum to give a uniform distribution
  - Expanded state has the highest positional probability of the states available to the system

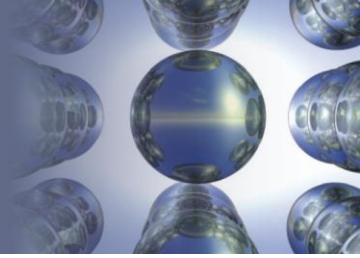
Copyright ©2017 Cengage Learning. All Rights Reserved.

Positional Probability and Changes of State

- Positional entropy increases when going from solid to gaseous state



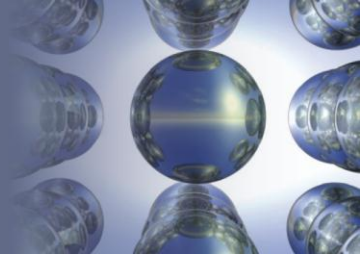
Copyright ©2017 Cengage Learning. All Rights Reserved.



Positional Entropy and Solutions

- Entropy change when mixing two pure substances is expected to be positive
  - Result of the presence of more microstates for the mixed condition
  - Caused due to the increased volume available to a given particle after mixing occurs
- Formation of solutions is favored by an increase in positional entropy that is associated with mixing

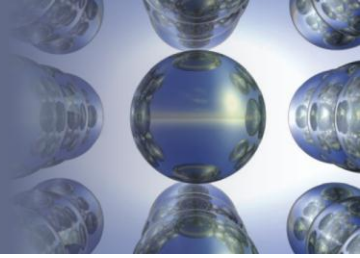
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.1 - Positional Entropy

- For each of the following pairs, choose the substance with the higher positional entropy (per mole) at a given temperature
  a. Solid CO_2 and gaseous CO_2
  b. N_2 gas at 1 atm and N_2 gas at 1.0×10^{-2} atm

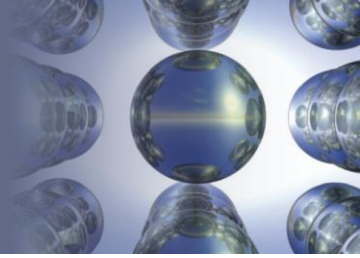
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.1 - Solution (a)

- Since a mole of gaseous CO_2 has the greater volume by far, the molecules have many more available positions than in a mole of solid CO_2
  - Thus, gaseous CO_2 has the higher positional entropy

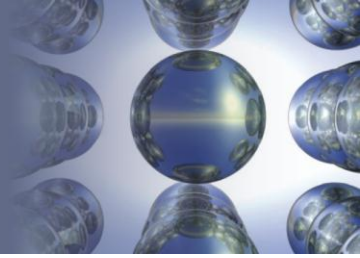
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.1 - Solution (b)

- A mole of N_2 gas at 1.0×10^{-2} atm has a volume 100 times that (at a given temperature) of a mole of N_2 gas at 1 atm
  - Thus, N_2 gas at 1.0×10^{-2} atm has the higher positional entropy

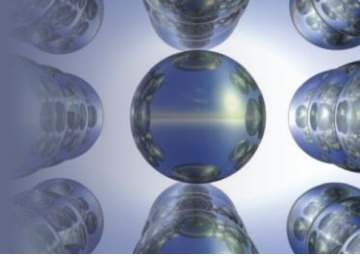
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.2 - Predicting Entropy Changes

- Predict the sign of the entropy change for each of the following processes
  a. Solid sugar is added to water to form a solution
  b. Iodine vapor condenses on a cold surface to form crystals

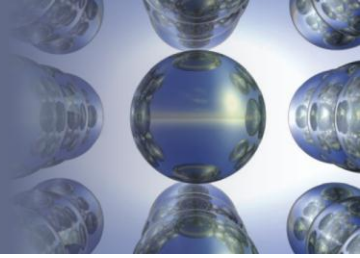
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.2 - Solution (a)

- Sugar molecules become randomly dispersed in the water when the solution forms and thus have access to a larger volume and a larger number of possible positions
  - Positional disorder is increased, and there will be an increase in entropy
  - ΔS is positive, since the final state has a larger entropy than the initial state, and $\Delta S = S_{\text{final}} - S_{\text{initial}}$

Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.2 - Solution (b)

- Gaseous iodine is forming a solid
  - This process involves a change from a relatively large volume to a much smaller volume, which results in lower positional disorder
  - For this process ΔS is negative, implying that the entropy decreases

Copyright ©2017 Cengage Learning. All Rights Reserved.

Second Law of Thermodynamics

- In any spontaneous process, there is always an increase in the entropy of the universe
- First law of thermodynamics
  - Energy of the universe is constant
  - Energy is conserved, entropy is not

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Changes in Entropy of the Universe

- ΔS_{univ} is positive
  - Entropy of the universe increases
  - Process is spontaneous in the direction written
- ΔS_{univ} is negative
  - Process is spontaneous in the opposite direction
- ΔS_{univ} is zero
  - Process has no tendency to occur
  - System is at equilibrium

Copyright ©2017 Cengage Learning. All Rights Reserved.

Critical Thinking

- What if ΔS_{univ} was a state function?
  - How would the world be different?

Copyright ©2017 Cengage Learning. All Rights Reserved.

Example 17.3 - The Second Law

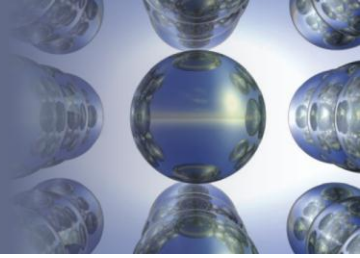
- In a living cell, large molecules are assembled from simple ones
  - Is this process consistent with the second law of thermodynamics?

Copyright ©2017 Cengage Learning. All Rights Reserved.

Example 17.3 - Solution

- To reconcile the operation of an order-producing cell with the second law of thermodynamics, we must remember that ΔS_{univ}, not ΔS_{sys}, must be positive for a process to be spontaneous
- A process for which ΔS_{sys} is negative can be spontaneous if the associated ΔS_{surr} is both larger and positive
  - The operation of a cell is such a process

Copyright ©2017 Cengage Learning. All Rights Reserved.



Entropy Changes in the Surroundings (ΔS_{surr})

- ΔS_{surr} is determined by flow of energy as heat
- Exothermic process increases ΔS_{surr}
  - Important driving force for spontaneity
- Endothermic process decreases ΔS_{surr}
- Impact of transfer of energy as heat to or from the surroundings is greater at lower temperatures

Copyright ©2017 Cengage Learning. All Rights Reserved.

Entropy Changes in the Surroundings (ΔS_{surr}) (Continued)

- Sign of ΔS_{surr} depends on the direction of the heat flow
  - At constant temperature:
    - ΔS_{surr} for exothermic processes is positive
    - ΔS_{surr} for endothermic processes is negative
- Magnitude of ΔS_{surr} depends on the temperature

$$\begin{matrix}\text{Driving force}\\ \text{provided by}\\ \text{the energy flow}\\ \text{(heat)}\end{matrix} = \begin{matrix}\text{magnitude of the}\\ \text{entropy change of}\\ \text{the surroundings}\end{matrix} = \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Characteristics of the Entropy Changes That Occur in the Surroundings - Summary

Exothermic process: $\Delta S_{\text{surr}} = + \dfrac{\text{quantity of heat (J)}}{\text{temperature (K)}}$

Endothermic process: $\Delta S_{\text{surr}} = - \dfrac{\text{quantity of heat (J)}}{\text{temperature (K)}}$

Copyright ©2017 Cengage Learning. All Rights Reserved.

ΔS_{surr} and ΔH

- ΔS_{surr} can be expressed in terms of ΔH for a process occurring at constant pressure
  - Heat flow = change in enthalpy = ΔH
- Components of ΔH
  - Sign - Indicates the direction of flow
    - Determined in accordance with the reaction system
  - Number - Indicates the quantity of energy

Copyright ©2017 Cengage Learning. All Rights Reserved.

ΔS_{surr} and ΔH (Continued)

- Reaction takes place under conditions of constant temperature (in Kelvins) and pressure

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

- If the reaction is exothermic:
  - ΔH has a negative sign
  - ΔS_{surr} is positive since heat flows into the surroundings

Copyright ©2017 Cengage Learning. All Rights Reserved.

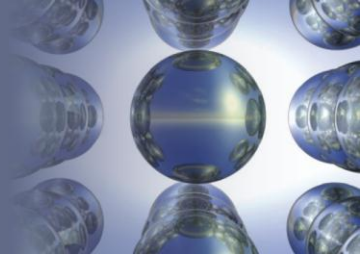


Table 17.3 - Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	Process Spontaneous?
+	+	+	Yes
−	−	−	No (reaction will occur in opposite direction)
+	−	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
−	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.4 - Determining ΔS_{surr}

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

$$Sb_2S_3(s) + 3Fe(s) \rightarrow 2Sb(s) + 3FeS(s) \qquad \Delta H = -125\text{kJ}$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.4 - Determining ΔS_{surr} (Continued)

- Carbon is used as the reducing agent for oxide ores:

$$Sb_4O_6(s) + 6C(s) \rightarrow 4Sb(s) + 6CO(g) \qquad \Delta H = 778 \text{ kJ}$$

- Calculate ΔS_{surr} for each of these reactions at 25° C and 1 atm

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.4 - Solution

$$\Delta S_{surr} = -\frac{\Delta H}{T}, \text{ where } T = 25 + 273 = 298 \text{ K}$$

- For the sulfide ore reaction,

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

  - ΔS_{surr} is positive since this reaction is exothermic, and heat flow occurs to the surroundings, increasing the randomness of the surroundings

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.4 - Solution (Continued)

- For the oxide ore reaction,

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

  - In this case ΔS_{surr} is negative because heat flow occurs from the surroundings to the system

Copyright ©2017 Cengage Learning. All Rights Reserved.

Free Energy (*G*)

$$G = H - TS$$

- *H* - Enthalpy
- *T* - Temperature in K
- *S* - Entropy

- At constant temperature,

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

- All quantities refer to the system

Copyright ©2017 Cengage Learning. All Rights Reserved.

Relationship between Free Energy (*G*) and Spontaneity

- Divide both sides of the equation $\Delta G = \Delta H - T\Delta S$ by $-T$

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

- At constant temperature (T) and pressure (P),

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

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S = \Delta S_{\text{surr}} + \Delta S = \Delta S_{\text{univ}}$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Relationship between Free Energy (*G*) and Spontaneity (Continued)

$$\Delta S_{\text{univ}} = -\frac{\Delta G}{T} \text{ at constant } T \text{ and } P$$

- Processes that occur at constant *T* and *P* are spontaneous in the direction in which the free energy decreases
  - Negative ΔG means positive ΔS_{univ}

Copyright ©2017 Cengage Learning. All Rights Reserved.

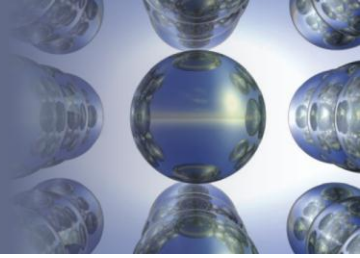
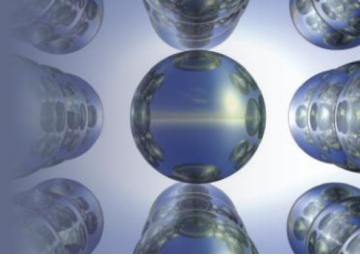


Table 17.5 - Various Possible Combinations of ΔH and ΔS

Case	Result
ΔS positive, ΔH negative	Spontaneous at all temperatures
ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
ΔS negative, ΔH negative	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	Process not spontaneous at *any* temperature (reverse process is spontaneous at *all* temperatures)

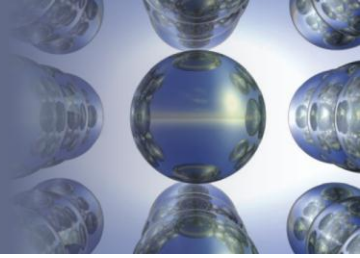
Copyright ©2017 Cengage Learning. All Rights Reserved.



Critical Thinking

- Consider an ideal gas in a container fitted with a frictionless, massless piston
  - What if weight is added to the top of the piston?
  - We would expect the gas to be compressed at constant temperature
  - For this to be true, ΔS would be negative (since the gas is compressed) and ΔH would be zero (since the process is at constant temperature)

Copyright ©2017 Cengage Learning. All Rights Reserved.



Critical Thinking (Continued)

- This would make ΔG positive
- Does this mean the isothermal compression of the gas is not spontaneous?
- Defend your answer

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.5 - Free Energy and Spontaneity

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

$$\mathrm{Br_2}(l) \rightarrow \mathrm{Br_2}(g)$$

$$\Delta H^\circ = 31.0\ \mathrm{kJ/mol} \text{ and } \Delta S^\circ = 93.0\ \mathrm{J/K \cdot mol}$$

- What is the normal boiling point of liquid Br_2?

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.5 - Solution

- The vaporization process will be spontaneous at all temperatures where ΔG° is negative
  - Note that ΔS° favors the vaporization process because of the increase in positional entropy, and ΔH° favors the opposite process, which is exothermic
  - These opposite tendencies will exactly balance at the boiling point of liquid Br_2, since at this temperature liquid and gaseous Br_2 are in equilibrium ($\Delta G^\circ = 0$)

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.5 - Solution (Continued 1)

- We can find this temperature by setting $\Delta G^\circ = 0$ in the following equation:

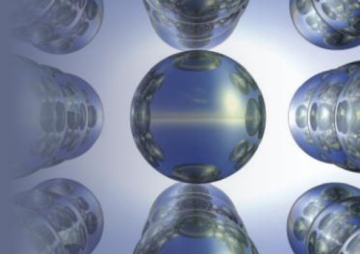
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

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

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

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

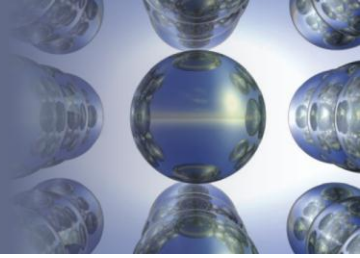
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.5 - Solution (Continued 2)

- At temperatures above 333 K, $T\Delta S^\circ$ has a larger magnitude than ΔH°, and ΔG° is negative
  - Above 333 K, the vaporization process is spontaneous
  - The opposite process occurs spontaneously below this temperature
- At 333 K, liquid and gaseous Br_2 coexist in equilibrium

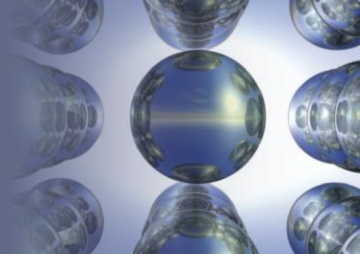
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.5 - Solution (Continued 3)

- Summary of observations (the pressure is 1 atm in each case)
  - $T > 333$ K
    - The term ΔS° controls, and the increase in entropy when liquid Br_2 is vaporized is dominant
  - $T < 333$ K
    - The process is spontaneous in the direction in which it is exothermic, and the term ΔH° controls

Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.5 - Solution (Continued 4)

- T = 333 K
  - The opposing driving forces are just balanced ($\Delta H^\circ = 0$), and the liquid and gaseous phases of bromine coexist
  - This is the normal boiling point

Copyright ©2017 Cengage Learning. All Rights Reserved.

Exercise

- Ethanethiol (C_2H_5SH; also called ethyl mercaptan) is commonly added to natural gas to provide the "rotten egg" smell of a gas leak
  - The boiling point of ethanethiol is 35° C and its heat of vaporization is 27.5 kJ/mol
  - What is the entropy of vaporization for this substance?

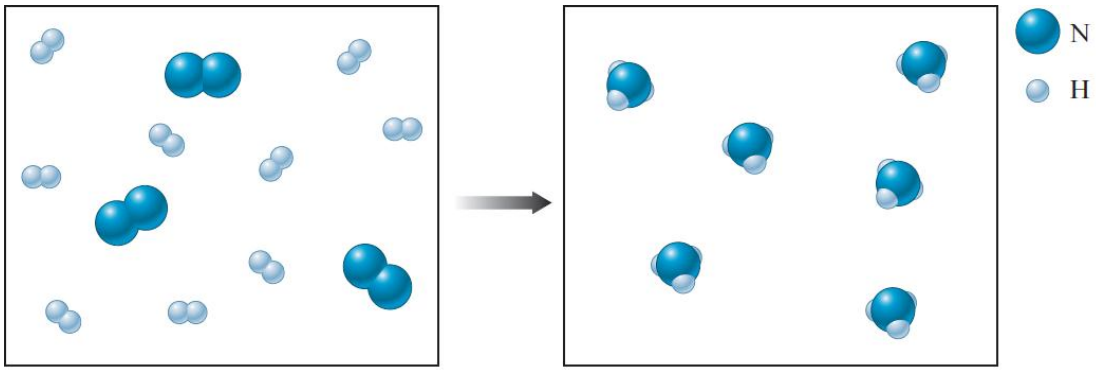
89.3 J/K·mol

Copyright ©2017 Cengage Learning. All Rights Reserved.

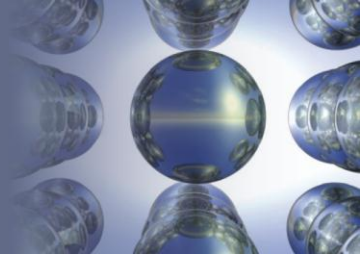
Entropy Changes and Chemical Reactions

- Positional probability determines the changes that occur in a chemical system
- Fewer the molecules, fewer the possible configurations

$$\text{Ammonia synthesis}: N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$



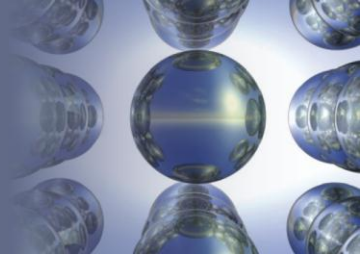
Copyright ©2017 Cengage Learning. All Rights Reserved.



Entropy Changes in Reactions That Involve Gaseous Molecules

- Change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products
  - If the number of product molecules is greater than the number of reactant molecules:
    - Positional entropy increases
    - ΔS is positive

Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.6 - Predicting the Sign of ΔS°

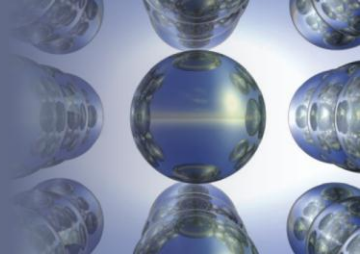
- Predict the sign of ΔS° for each of the following reactions
  a. Thermal decomposition of solid calcium carbonate

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

  b. Oxidation of SO_2 in air

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

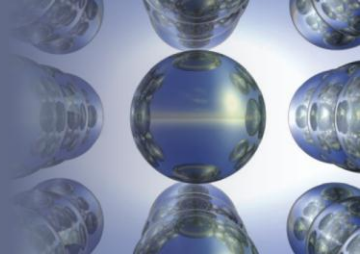


Interactive Example 17.6 - Solution

a. Since in this reaction a gas is produced from a solid reactant, the positional entropy increases, and ΔS° is positive
b. Here three molecules of gaseous reactants become two molecules of gaseous products
   - Since the number of gas molecules decreases, positional entropy decreases, and ΔS° is negative

Copyright ©2017 Cengage Learning. All Rights Reserved.

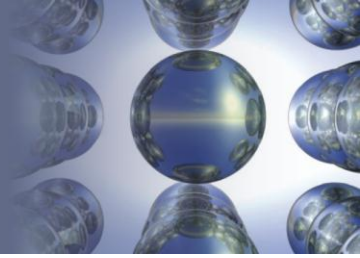
Section 17.5
Entropy Changes in Chemical Reactions



Entropy Changes

- Third law of thermodynamics
  - Entropy of a perfect crystal at 0 K is zero
- Entropy of a substance increases with temperature

Copyright ©2017 Cengage Learning. All Rights Reserved.



Entropy Values

- Standard entropy values (S°) represent increase in entropy that occurs when a substance is heated from 0 K to 298 K at 1 atm
  - More complex the molecule, the higher the standard entropy value

Copyright ©2017 Cengage Learning. All Rights Reserved.

Entropy Change for a Given Chemical Reaction

- Entropy is a state function of a chemical system
- Entropy changes can be calculated as follows:

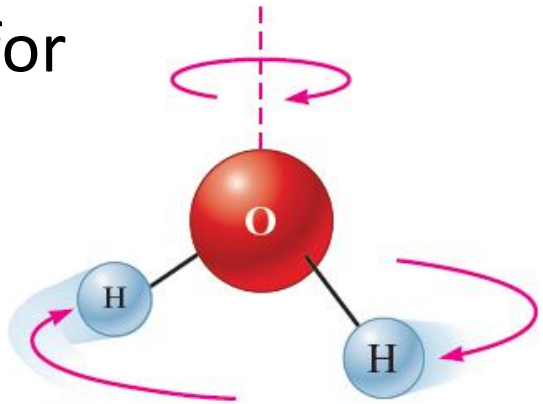
$$\Delta S^\circ_{\text{reaction}} = \sum n_{\text{p}} S^\circ_{\text{products}} - \sum n_{\text{r}} S^\circ_{\text{reactants}}$$

  - Σ - Sum of all terms
  - n_r - Number of moles of a reactant
  - n_p- Number of moles of a product

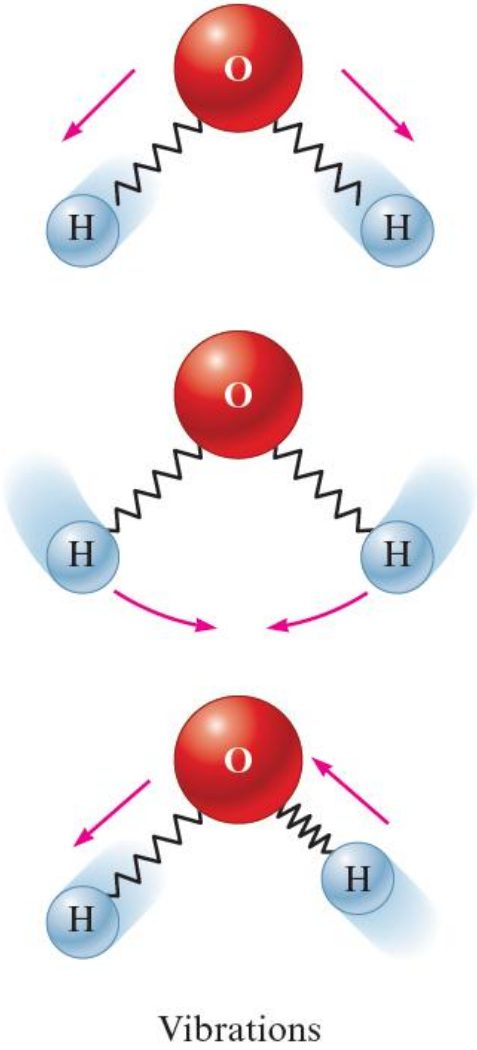
Copyright ©2017 Cengage Learning. All Rights Reserved.

Figure 17.6 - Entropy of Water

- H_2O molecule can vibrate and rotate in several ways
  - Freedom of motion leads to a higher entropy for water



Rotation



Vibrations

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.7 - Calculating ΔS°

- Calculate ΔS° at 25° C for the following reaction:

$$2\mathrm{NiS}(s) + 3\mathrm{O}_2(g) \rightarrow 2\mathrm{SO}_2(g) + 2\mathrm{NiO}(s)$$

  - The following information is given:

Substance	S° (J/K · mol)
$SO_2(g)$	248
$NiO(s)$	38
$O_2(g)$	205
$NiS(s)$	53

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.7 - Solution

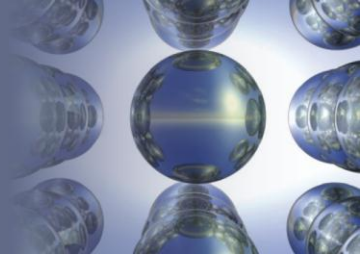
$$\Delta S^\circ = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$$

$$= 2S^\circ_{SO_2(g)} + 2S^\circ_{NiO(s)} - 2S^\circ_{NiS(s)} - 3S^\circ_{O_2(s)}$$

$$= 2\ \text{mol}\left(248\frac{\text{J}}{\text{K}\cdot\text{mol}}\right) + 2\ \text{mol}\left(38\frac{\text{J}}{\text{K}\cdot\text{mol}}\right)$$

$$-2\ \text{mol}\left(53\frac{\text{J}}{\text{K}\cdot\text{mol}}\right) - 3\ \text{mol}\left(205\frac{\text{J}}{\text{K}\cdot\text{mol}}\right)$$

Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.7 - Solution (Continued)

$$\Delta S^\circ = 496\ \text{J/K} + 76\ \text{J/K} - 106\ \text{J/K} - 615\ \text{J/K}$$

$$\Delta S^\circ = -149\ \text{J/K}$$

- We would expect ΔS° to be negative because the number of gaseous molecules decreases in this reaction

Copyright ©2017 Cengage Learning. All Rights Reserved.

Exercise

- Predict the sign of ΔS° and then calculate ΔS° for each of the following reactions:

a. $2H_2S(g) + SO_2(g) \rightarrow 3S_{rhombic}(s) + 2H_2O(g)$

Negative
$\Delta S^\circ = -186$ J/K

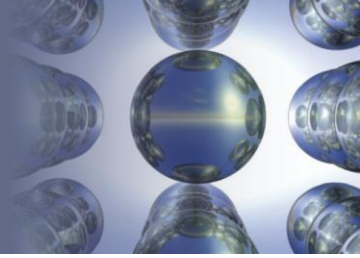
b. $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$

Positive
$\Delta S^\circ = 187$ J/K

c. $Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$

Hard to predict since $\Delta n = 0$
$\Delta S^\circ = 138$ J/K

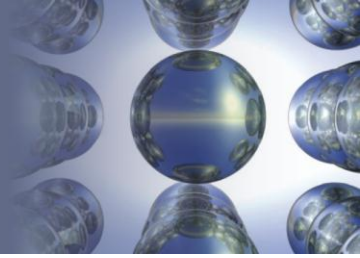
Copyright ©2017 Cengage Learning. All Rights Reserved.



Standard Free Energy Change (ΔG°)

- Change in *G* that will occur if the reactants in their standard states are converted to the products in their standard states
  - More negative the value of ΔG°, the further the reaction shifts to the right to attain equilibrium

Copyright ©2017 Cengage Learning. All Rights Reserved.



Methods for Calculating ΔG°

- Use the following formula

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

- Treat free energy as a state function and use Hess's law
- Use standard free energy of formation

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.9 - Calculating ΔH°, ΔS°, and ΔG°

- Consider the following reaction carried out at 25° C and 1 atm:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

- Calculate ΔH°, ΔS°, and ΔG° using the following data:

Substance	H_f° (kJ/mol)	S° (J/K · mol)
$SO_2(g)$	−297	248
$SO_3(g)$	−396	257
$O_2(g)$	0	205

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.9 - Solution

- The value of ΔH° can be calculated from the enthalpies of formation using the following formula:

$$\Delta H^\circ = \sum n_p \Delta H^\circ_{f\,(\text{products})} - \sum n_r \Delta H^\circ_{f\,(\text{reactants})}$$

$$\Delta H^\circ = 2\Delta H^\circ_{f\,(SO_3(g))} - 2\Delta H^\circ_{f\,(SO_2(g))} - \Delta H^\circ_{f\,(O_2(g))}$$

$$= 2\text{ mol}\left(-396\text{ kJ/mol}\right) - 2\text{ mol}\left(-297\text{ kJ/mol}\right) - 0$$

$$= -792\text{ kJ} + 594\text{ kJ} = -198\text{ kJ}$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.9 - Solution (Continued 1)

- The value of ΔS° can be calculated using the following formula:

$$\Delta S^\circ = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = 2S^\circ_{SO_3(g)} - 2S^\circ_{SO_2(g)} - 2S^\circ_{O_2(g)}$$

$$= 2\text{ mol}\,(257\text{ J/K}\cdot\text{mol}) - 2\text{ mol}\,(248\text{ J/K}\cdot\text{mol}) - 1\text{ mol}\,(205\text{ J/K}\cdot\text{mol})$$

$$= 514\text{ J/K} - 496\text{ J/K} - 205\text{ J/K} = -187\text{ J/K}$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.9 - Solution (Continued 2)

- We would expect ΔS° to be negative because three molecules of gaseous reactants give two molecules of gaseous products

- The value of ΔG° can now be calculated

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

$$\Delta G^\circ = -198\ \text{kJ} - (298\ \text{K})\left(-187\ \frac{\text{J}}{\text{K}}\right)\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$= -198\ \text{kJ} + 55.7\ \text{kJ} = -142\ \text{kJ}$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.10 - Calculating ΔG°

- Use the following data (at 25° C):

$$C_{diamond}(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta G^o = -397 \text{ kJ} \qquad (17.5)$$

$$C_{graphite}(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta G^o = -394 \text{ kJ} \qquad (17.6)$$

  - Calculate ΔG° for the following reaction:

$$C_{diamond}(s) \rightarrow C_{graphite}(s)$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.10 - Solution

- Reverse equation (17.6) to make graphite a product, as required, and then add the new equation to equation (17.5)

$$\mathrm{C_{diamond}}\left(s\right) + \mathrm{O_2}\left(g\right) \rightarrow \mathrm{CO_2}\left(g\right) \qquad \Delta G^\circ = -397\ \mathrm{kJ}$$

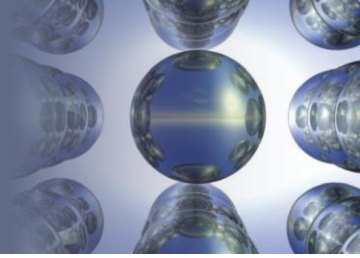
Reversed Equation (17.6)

$$\mathrm{CO_2}\left(g\right) \rightarrow \mathrm{C_{graphite}}\left(s\right) + \mathrm{O_2}\left(g\right) \qquad \Delta G^\circ = -\left(-397\ \mathrm{kJ}\right)$$

$$\mathrm{C_{diamond}}\left(s\right) \rightarrow \mathrm{C_{graphite}}\left(s\right) \qquad \Delta G^\circ = -397\ \mathrm{kJ} + 394\ \mathrm{kJ}$$

$$= -3\ \mathrm{kJ}$$

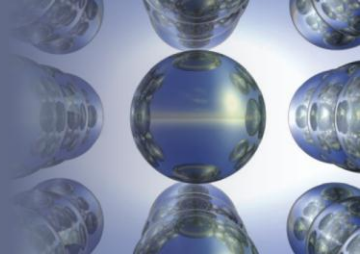
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.10 - Solution (Continued 1)

- Since ΔG° is negative for this process, diamond should spontaneously change to graphite at 25° C and 1 atm
  - However, the reaction is so slow under these conditions that we do not observe the process
  - This is another example of kinetic rather than thermodynamic control of a reaction

Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.10 - Solution (Continued 2)

- We can say that diamond is kinetically stable with respect to graphite even though it is thermodynamically unstable

Copyright ©2017 Cengage Learning. All Rights Reserved.

Standard Free Energy of Formation (ΔG_f°)

- Change in free energy that accompanies the formation of 1 mole of a substance from its constituent elements
  - All reactants and products are in their standard states
  - Used to calculate the free energy change for a reaction

$$\Delta G^\circ = \sum n_p \Delta G^\circ_{f\,(products)} - \sum n_p \Delta G^\circ_{f\,(reactants)}$$

- ΔG_f° of an element in its standard state = 0

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.11 - Calculating ΔG°

- Methanol is a high-octane fuel used in high-performance racing engines
  - Calculate ΔG° for the following reaction:

$$2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$

  - The following energies of formation are provided:

Substance	ΔG_f° (kJ/mol)
$CH_3OH(g)$	−163
$O_2(g)$	0
$CO_2(g)$	−394
$H_2O(g)$	−229

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.11 - Solution

- Use the following equation:

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

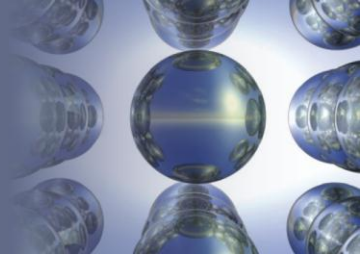
$$= 2\Delta G^\circ_{\text{f}\left(CO_2(g)\right)} + 4\Delta G^\circ_{\text{f}\left(H_2O(g)\right)} - 3\Delta G^\circ_{\text{f}\left(O_2(g)\right)} - 2\Delta G^\circ_{\text{f}\left(CH_3OH(g)\right)}$$

$$= 2\text{ mol}\left(-394\text{ kJ/mol}\right) + 4\text{ mol}\left(-229\text{ kJ/mol}\right)$$

$$-3(0) - 2\text{ mol}\left(-163\text{ kJ/mol}\right)$$

$$\Delta G^\circ = -1378\text{ kJ}$$

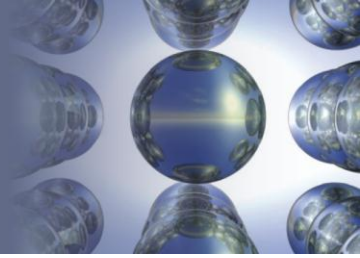
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.11 - Solution (Continued)

- The large magnitude and the negative sign of ΔG° indicate that this reaction is very favourable thermodynamically

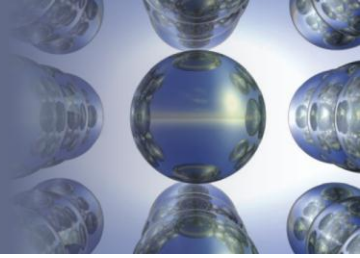
Copyright ©2017 Cengage Learning. All Rights Reserved.



Free Energy and Pressure

- System under constant *P* and *T* proceeds spontaneously in the direction that lowers its free energy
  - Free energy of a reaction system changes as the reaction proceeds
    - Dependent on the pressure of a gas or on the concentration of species in solution
- Equilibrium - Point where free energy value is at its lowest

Copyright ©2017 Cengage Learning. All Rights Reserved.

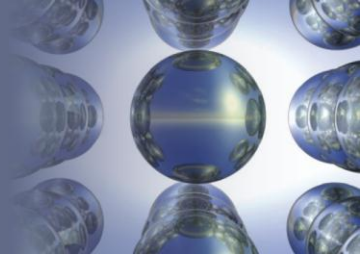


Free Energy and Pressure (Continued 1)

- For ideal gases:
  - Enthalpy is not pressure-dependent
  - Entropy depends on pressure due to its dependence on volume
- At a given temperature for 1 mole of ideal gas:
  - $S_{\text{large volume}} > S_{\text{small volume}}$

    Or,
  - $S_{\text{low pressure}} > S_{\text{high pressure}}$

Copyright ©2017 Cengage Learning. All Rights Reserved.



Free Energy and Pressure (Continued 2)

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

- G° - Free energy of a gas at 1 atm
- G - Free energy of the gas at a pressure of P atm
- R - Universal gas constant
- T - Temperature in Kelvin

Copyright ©2017 Cengage Learning. All Rights Reserved.

Free Energy and Pressure (Continued 3)

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

- Q - Reaction quotient
- T - Temperature in Kelvin
- R - Universal gas constant (8.3145 J/K·mol)
- ΔG° - Free energy change at 1 atm
- ΔG - Free energy change at specified pressures

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.13 - Calculating ΔG°

- One method for synthesizing methanol (CH_3OH) involves reacting carbon monoxide and hydrogen gases

$$\mathrm{CO}(g) + 2\mathrm{H}_2(g) \rightarrow \mathrm{CH}_3\mathrm{OH}(l)$$

  - Calculate ΔG at 25° C for this reaction where carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.13 - Solution

- To calculate ΔG for this process, use the following equation:

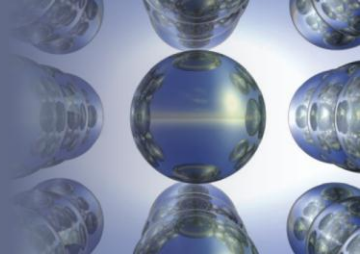
$$\Delta G = \Delta G^\circ + RT\ln(Q)$$

- First compute ΔG° from standard free energies of formation

$$\Delta G^\circ_{\mathrm{f}(\mathrm{CH_3OH}(l))} = -166\ \mathrm{kJ} \qquad \Delta G^\circ_{\mathrm{f}(\mathrm{H_2}(g))} = 0 \qquad \Delta G^\circ_{\mathrm{f}(\mathrm{CO}(g))} = -137\ \mathrm{kJ}$$

$$\Delta G^\circ = -166\ \mathrm{kJ} - (-137\ \mathrm{kJ}) - 0 = -29\ \mathrm{kJ} = -2.9\times10^4\ \mathrm{J}$$

Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.13 - Solution (Continued 1)

- One might call this the value of ΔG° for one round of the reaction or for 1 mole of the reaction
- Thus, the ΔG° value might better be written as -2.9×10^4 J/mol of reaction, or -2.9×10^4 J/mol rxn
  - Use this value to calculate the value of ΔG

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.13 - Solution (Continued 2)

- $\Delta G^\circ = -2.9 \times 10^4$ J/mol rxn
- $R = 8.3145$ J/K·mol
- $T = 273 + 25 = 298$ K

$$Q = \frac{1}{\left(P_{CO}\right)\left(P_{H_2}{}^2\right)} = \frac{1}{(5.0)(3.0)^2} = 2.2\times10^{-2}$$

- Note that the pure liquid methanol is not included in the calculation of Q

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.13 - Solution (Continued 3)

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

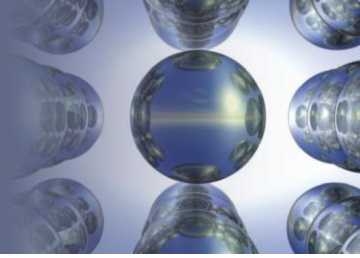
$$= \left(-2.9\times10^4 \text{ J/mol rxn}\right)$$

$$+ \left(8.3145 \text{ J/K}\cdot\text{mol rxn}\right)\left(298\text{K}\right)\ln\left(2.2\times10^{-2}\right)$$

$$= \left(-2.9\times10^4 \text{ J/mol rxn}\right) - \left(9.4\times10^3 \text{ J/mol rxn}\right)$$

$$= -3.8\times10^4 \text{ J/mol rxn} = -38 \text{ kJ/mol rxn}$$

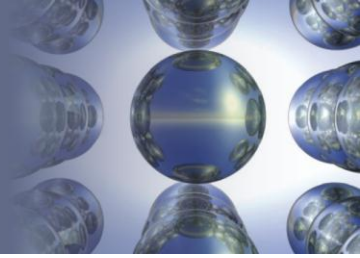
Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.13 - Solution (Continued 4)

- Note that ΔG is significantly more negative than ΔG°, implying that the reaction is more spontaneous at reactant pressures greater than 1 atm
  - This result can be expected from Le Châtelier's principle

Copyright ©2017 Cengage Learning. All Rights Reserved.



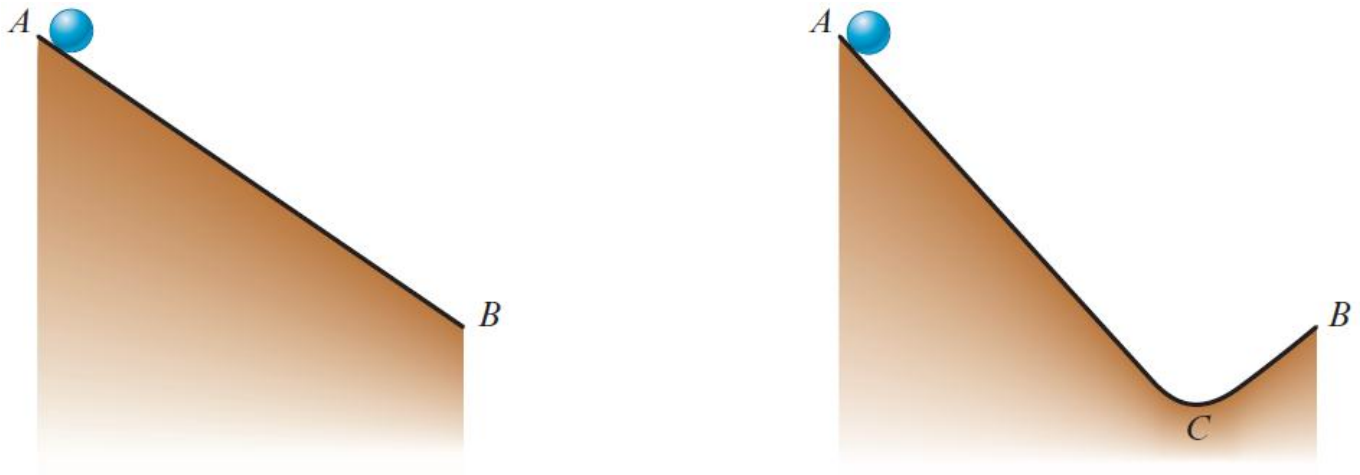
The Meaning of ΔG for a Chemical Reaction

- Even when value of ΔG provides information regarding whether the system is favored under a given set of conditions:
  - System may not proceed to pure products (if ΔG is negative)
  - System may not remain at pure reactants (if ΔG is positive)
- A system will spontaneously seek equilibrium

Copyright ©2017 Cengage Learning. All Rights Reserved.

The Meaning of ΔG for a Chemical Reaction (Continued)

- System can achieve the lowest possible free energy by going to equilibrium, not by going to completion



Copyright ©2017 Cengage Learning. All Rights Reserved.

Equilibrium Point

- Occurs at the lowest value of free energy available to the reaction system
  - Consider the following hypothetical equation where 1.0 mole of gaseous A is initially placed in a reaction vessel at 2.0 atm

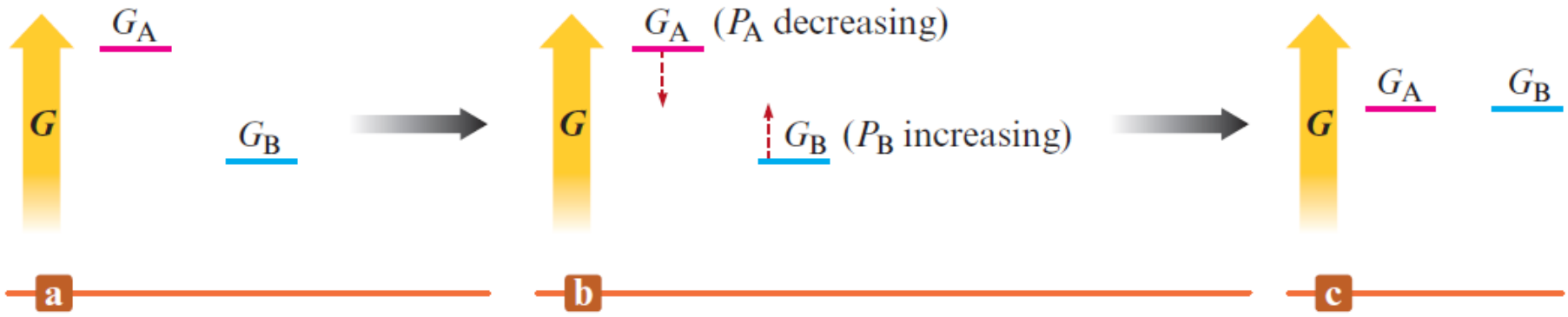
$$\mathrm{A}\,(g) \rightleftharpoons \mathrm{B}\,(g)$$

free energy of A = $G_A = G°_A + RT\ln(P_A)$ free energy of B = $G_B = G°_B + RT\ln(P_B)$

Total free energy of system = $G = G_A + G_B$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Figure 17.8 - Equilibrium Point



Copyright ©2017 Cengage Learning. All Rights Reserved.

Equilibrium Point (Continued 1)

- When substances undergo a chemical reaction, the reaction proceeds to the minimum free energy (equilibrium)
  - This corresponds to the point where:

$$G_{\text{products}} = G_{\text{reactants}}$$

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} = 0$$

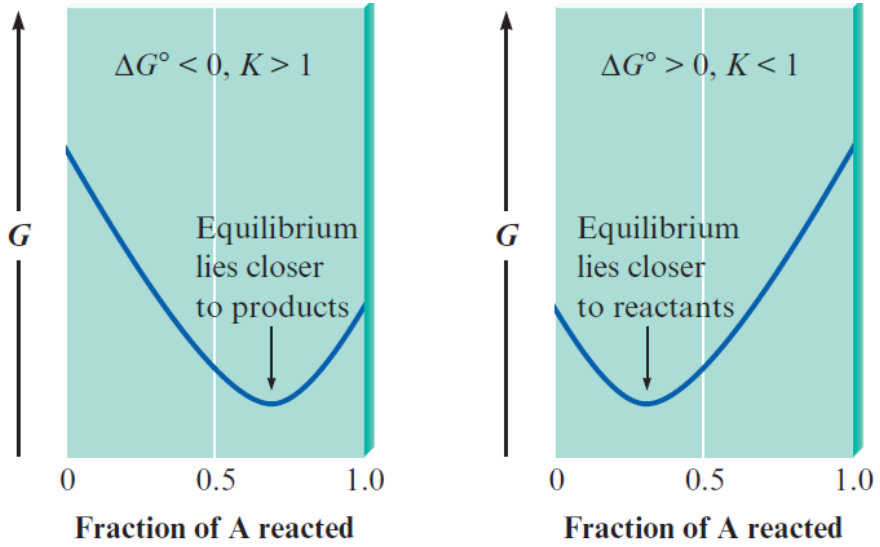
Copyright ©2017 Cengage Learning. All Rights Reserved.

Equilibrium Point (Continued 2)

- Quantitative relationship between free energy and the value of the equilibrium constant is given by:

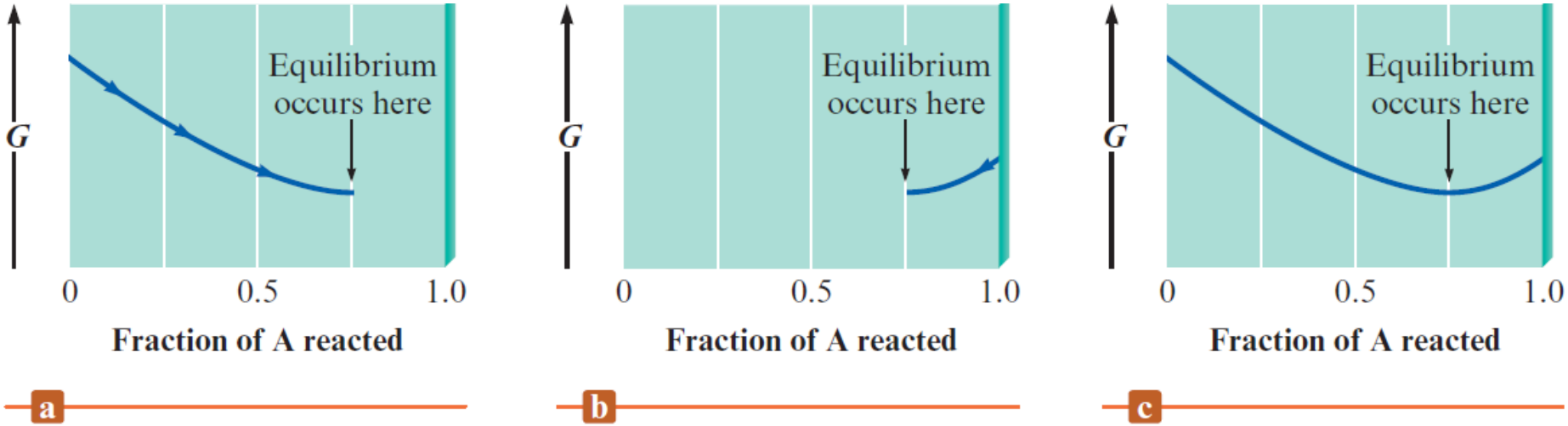
$$\Delta G = 0 = \Delta G^\circ + \mathrm{RT}\ \ln(K)$$

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



Copyright ©2017 Cengage Learning. All Rights Reserved.

Figure 17.9 - Plot of Energy versus the Mole Fraction of the reaction of A(*g*)



Copyright ©2017 Cengage Learning. All Rights Reserved.

Table 17.6 - Qualitative Relationship between the ΔG° and the K for a Given Reaction

ΔG°	K
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.15 - Free Energy and Equilibrium II

- The overall reaction for the corrosion (rusting) of iron by oxygen is as follows:

$$4\mathrm{Fe}(s) + 3\mathrm{O_2}(g) \rightleftharpoons 2\mathrm{Fe_2O_3}(s)$$

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

Substance	ΔH_f° (kJ/mol)	S° (J/K · mol)
$Fe_2O_3(s)$	−826	90
$Fe(s)$	0	27
$O_2(g)$	0	205

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.15 - Solution

- Calculate ΔG° from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta H^\circ = 2\Delta H^\circ_{f(Fe_2O_3(s))} - 3\Delta H^\circ_{f(O_2(g))} - 4\Delta H^\circ_{f(Fe(s))}$$

$$= 2\text{ mol}\left(-826\text{ kJ/mol}\right) - 0 - 0$$

$$= -1652\text{ kJ} = -1.652\times10^6\text{ J}$$

$$\Delta S^\circ = 2S^\circ_{Fe_2O_3} - 3S^\circ_{O_2} - 4S^\circ_{Fe}$$

$$= 2\text{ mol}\left(90\text{ J/K}\cdot\text{mol}\right) - 3\text{ mol}\left(205\text{ J/K}\cdot\text{mol}\right)$$

$$- \ 4\text{ mol}\left(27\text{ J/K}\cdot\text{mol}\right) = -543\text{ J/K}$$

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

Copyright ©2017 Cengage Learning. All Rights Reserved.

Interactive Example 17.15 - Solution (Continued 1)

- Therefore,

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

$$= (-1.652 \times 10^6 \text{ J}) - (298 \text{ K})\ (-543 \text{ J/K})$$

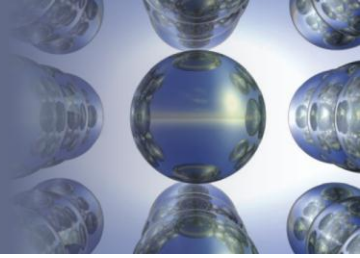
$$= -1.490 \times 10^6 \text{ J}$$

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

$$= -(8.3145 \text{ J/K} \cdot \text{mol})(298\text{K}) \ln(K)$$

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

Copyright ©2017 Cengage Learning. All Rights Reserved.



Interactive Example 17.15 - Solution (Continued 2)

- Therefore,

$$K = e^{601}$$

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

Copyright ©2017 Cengage Learning. All Rights Reserved.

The Temperature Dependence of *K*

- Quantitative dependence of *K* on temperature is given by:

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

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

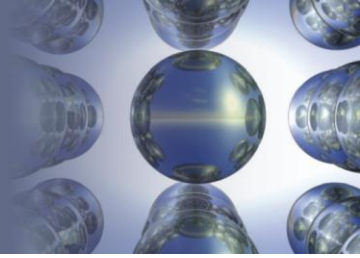
$$\boldsymbol{y = mx + b}$$

Copyright ©2017 Cengage Learning. All Rights Reserved.

The Temperature Dependence of *K* (Continued)

- If the values of *K* are determined at various levels of *T*:
  - Plot of ln(*K*) versus 1/*T* will be linear
  - Slope = $-\Delta H^\circ / R$
  - Intercept = $\Delta S^\circ / R$
- Assume that ΔH° and ΔS° are independent of *T*

Copyright ©2017 Cengage Learning. All Rights Reserved.



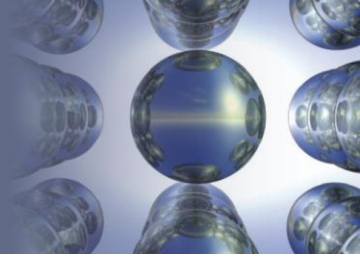
Relationship Between Free Energy and Work

- Maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy

$$w_{\max} = \Delta G$$

- Achieving the maximum work available from a spontaneous process can occur only via a hypothetical pathway
  - Any real pathway wastes energy

Copyright ©2017 Cengage Learning. All Rights Reserved.

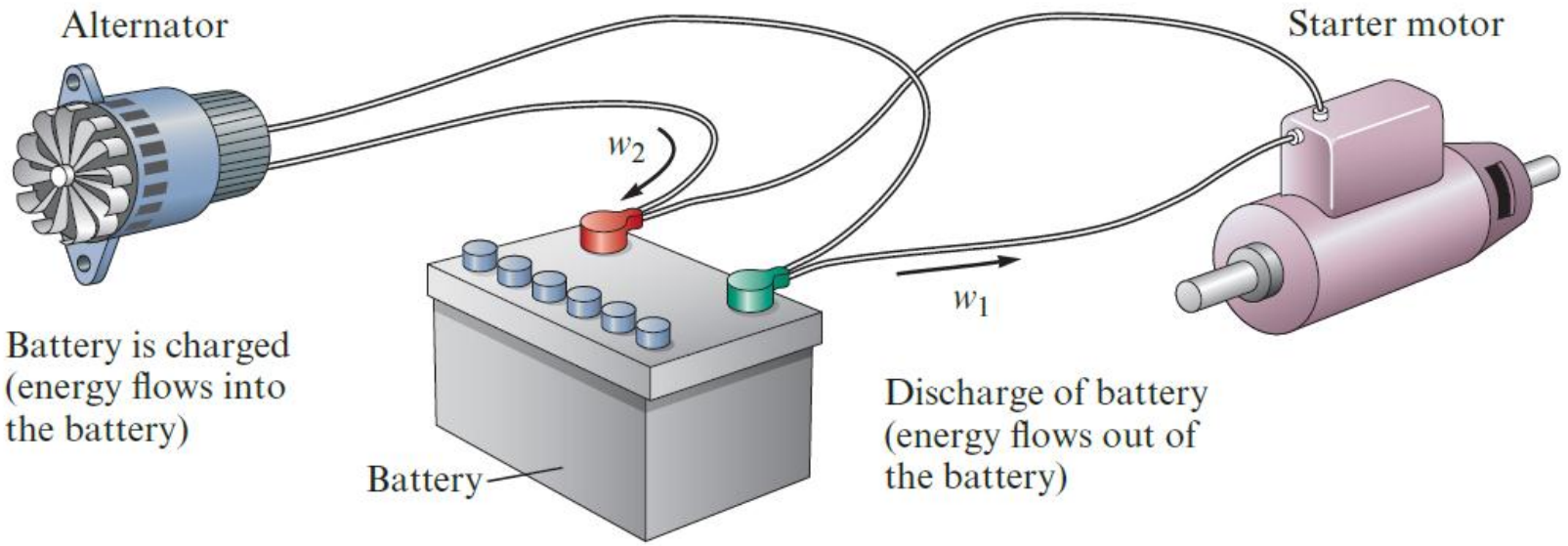


Reversible and Irreversible Processes

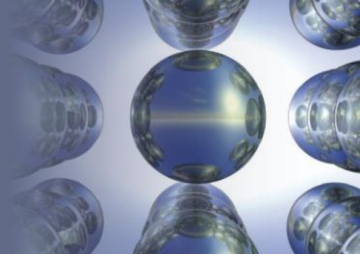
- **Reversible process**: Universe is exactly the same as it was before a cyclic process
- **Irreversible process**: Universe is different after a cyclic process
  - All real processes are irreversible
- Characteristics of a real cyclic process
  - Work is changed to heat
  - Entropy of the universe increases

Copyright ©2017 Cengage Learning. All Rights Reserved.

Figure 17.11 - Reversible Process as Seen in a Battery



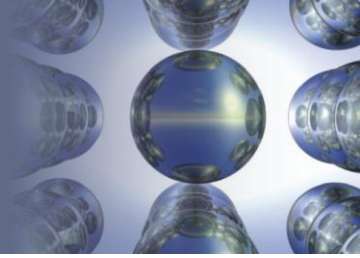
Copyright ©2017 Cengage Learning. All Rights Reserved.



Revisiting the Laws of Thermodynamics

- First law
  - You can't win; you can only break even
- Second law
  - You can't break even
- As we use energy, we degrade its usefulness

Copyright ©2017 Cengage Learning. All Rights Reserved.



Critical Thinking

- What if the first law of thermodynamics was true but the second law was not?
  - How would the world be different?

Copyright ©2017 Cengage Learning. All Rights Reserved.