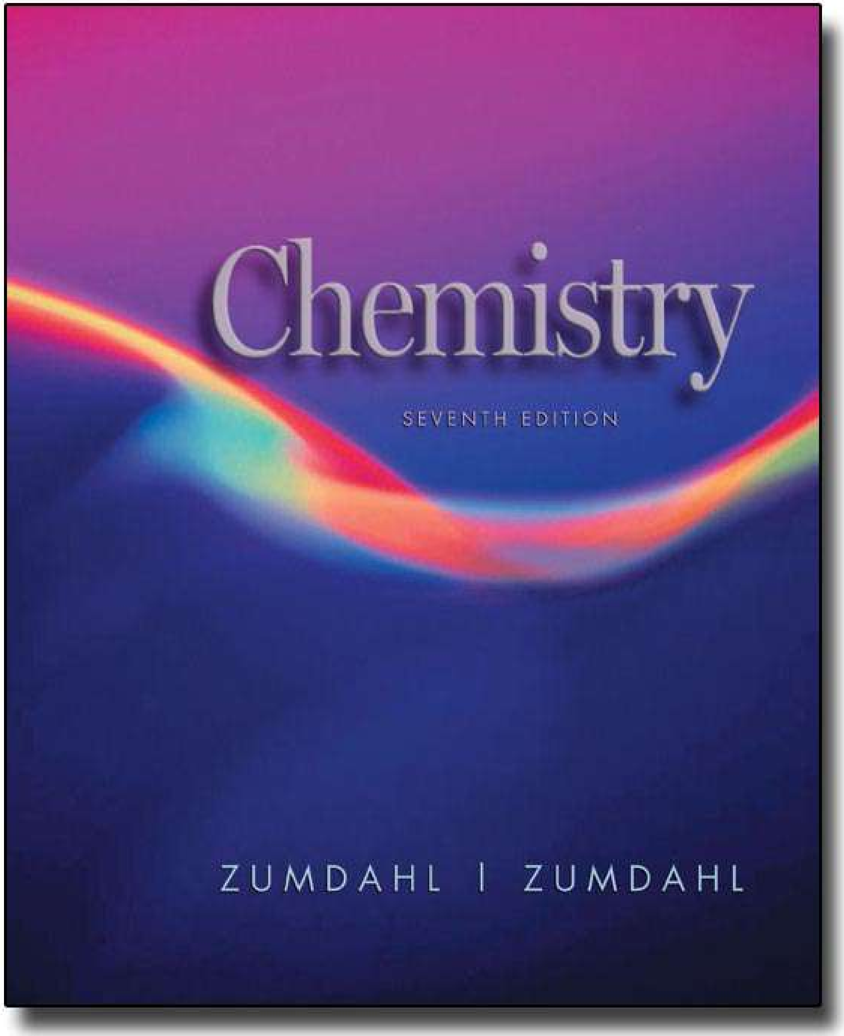
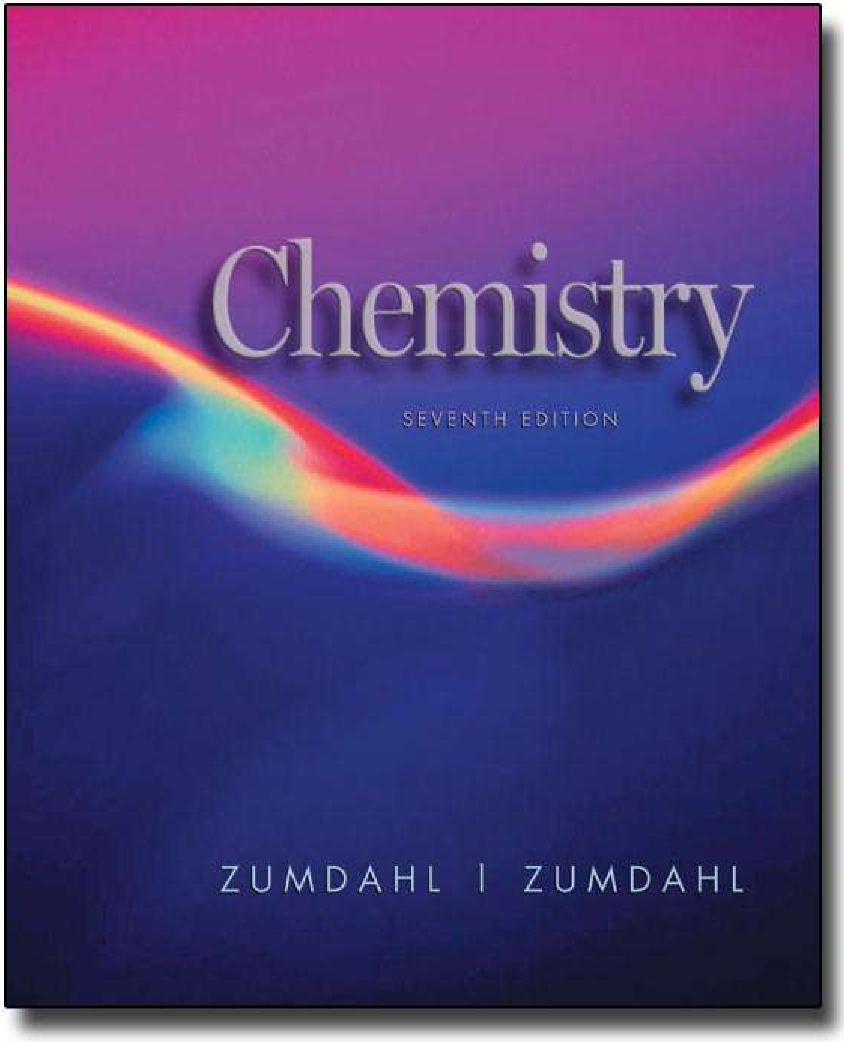


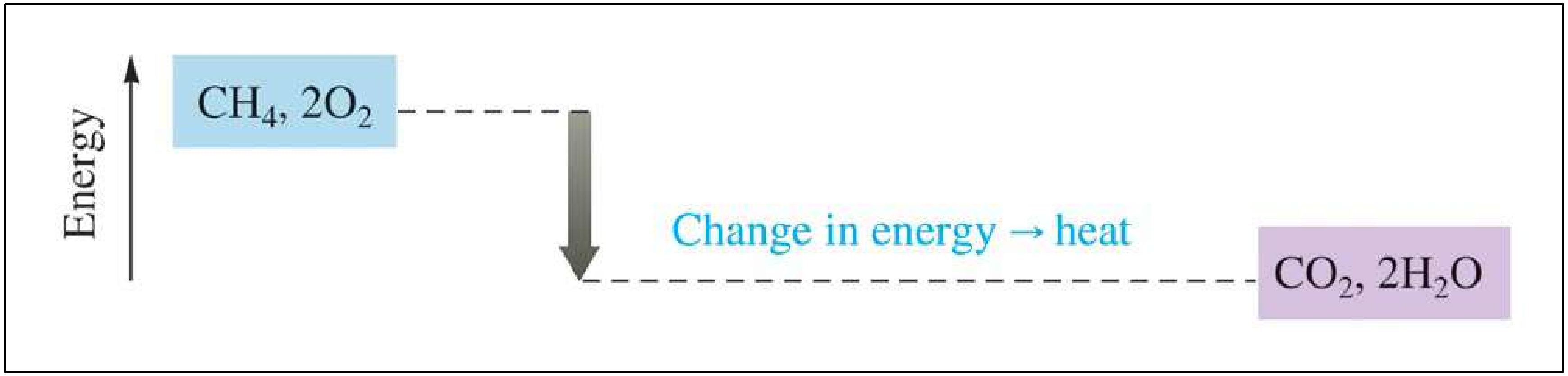
Chapter Sixteen:

SPONTANEITY, ENTROPY, AND FREE ENERGY

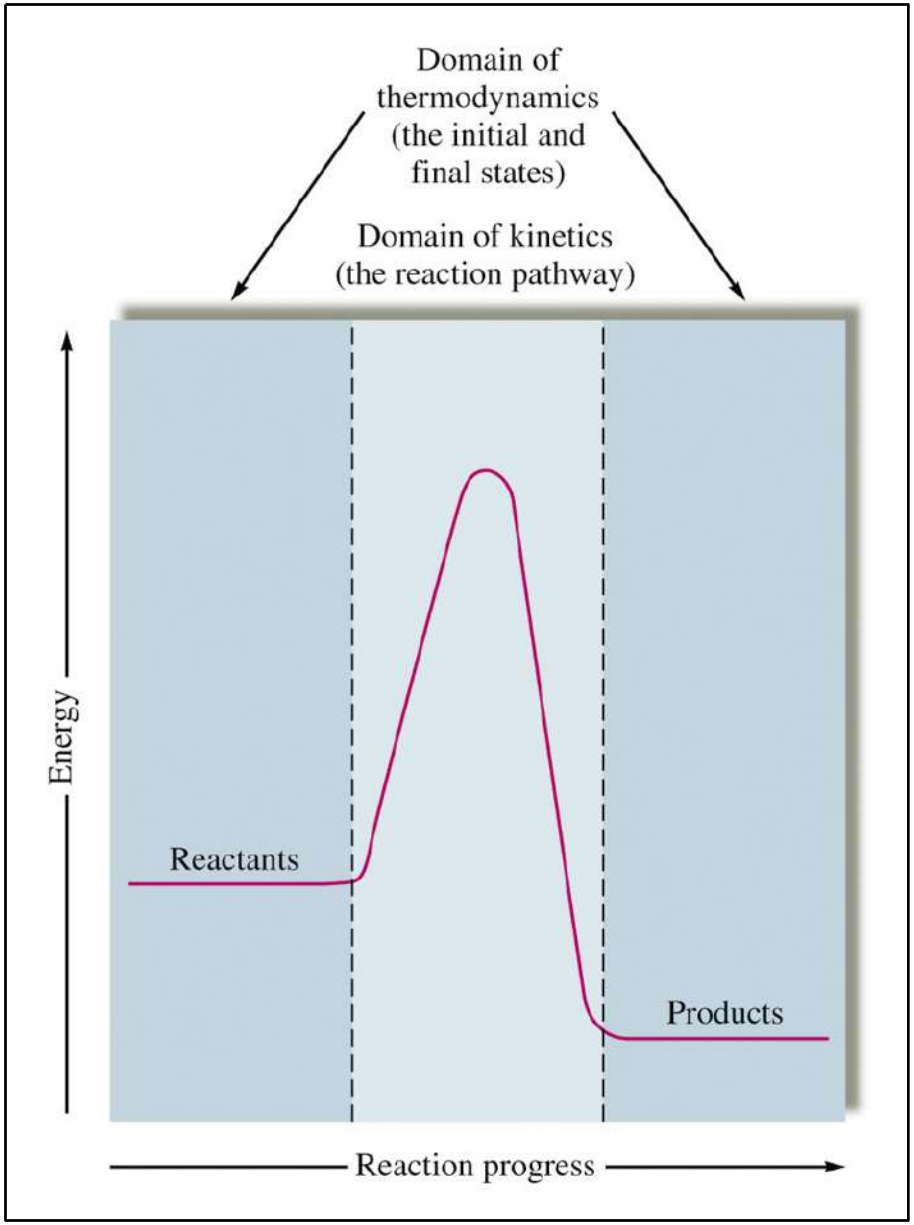


Spontaneous Processes and Entropy

Figure 16.1 The products have lower potential energy than the reactants. This change in potential energy results in energy flow (heat) to the surroundings



Thermodynamics vs. Kinetics



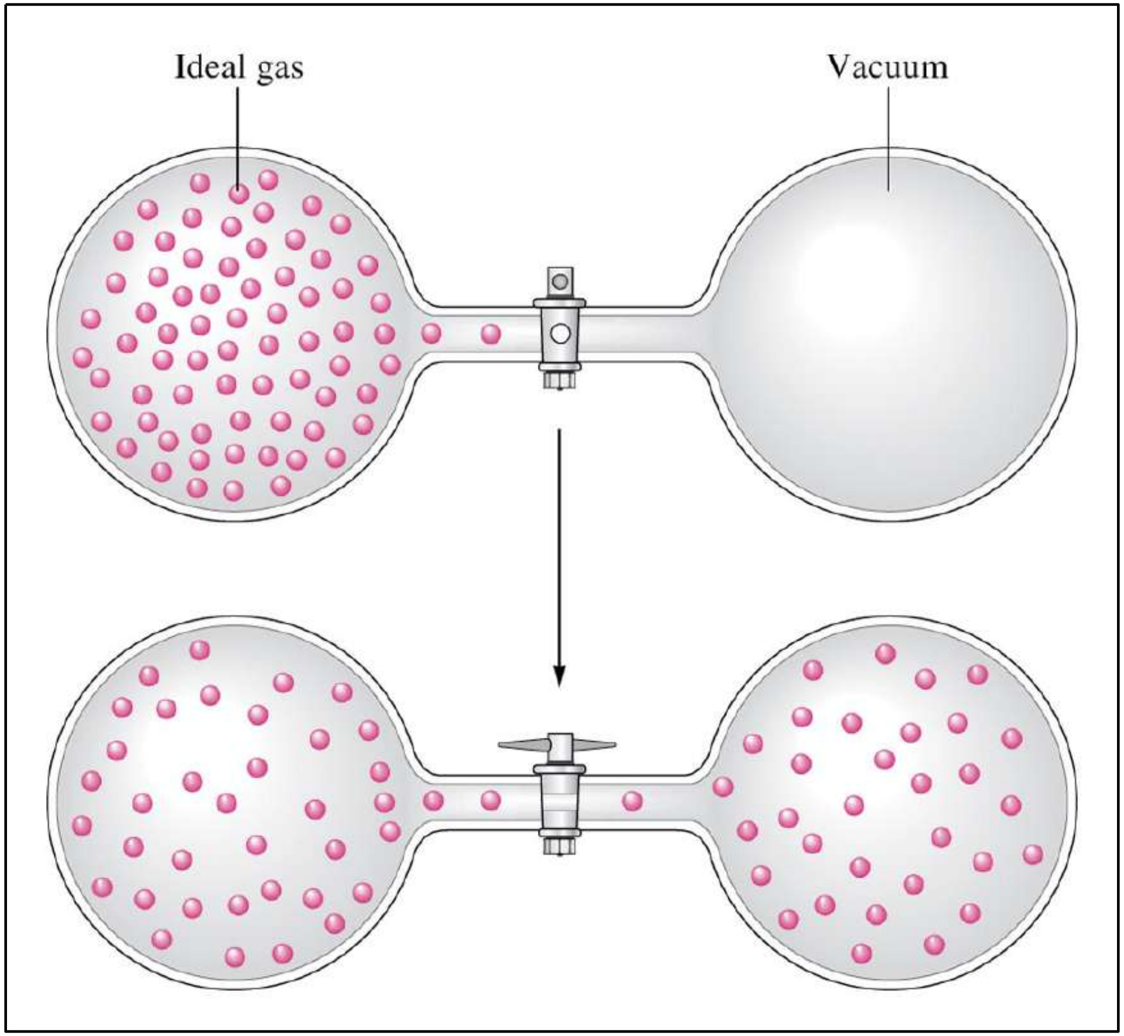
Plant materials burn to form CO_2 and H_2O

Spontaneous Processes and Entropy

- Thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process.
- A spontaneous process is one that occurs without outside intervention.

A Disordered Pile of Playing Cards

Figure 16.3 The expansion of an ideal gas into an evacuated bulb.



React 1

Consider 2.4 moles of a gas contained in a 4.0 L bulb at a constant temperature of 32°C. This bulb is connected to an evacuated 20.0 L sealed bulb with a valve. Assume the temperature is constant.

a) What should happen to the gas when you open the valve?

React 1

Consider 2.4 moles of a gas contained in a 4.0 L bulb at a constant temperature of 32°C. This bulb is connected to an evacuated 20.0 L sealed bulb with a valve. Assume the temperature is constant.

b) Calculate ΔH, ΔE, q, and w for the process you described above.

React 1

Consider 2.4 moles of a gas contained in a 4.0 L bulb at a constant temperature of 32°C. This bulb is connected to an evacuated 20.0 L sealed bulb with a valve. Assume the temperature is constant.

c) Given your answer to part b, what is the driving force for the process?

The Expansion of An Ideal Gas Into an Evacuated Bulb

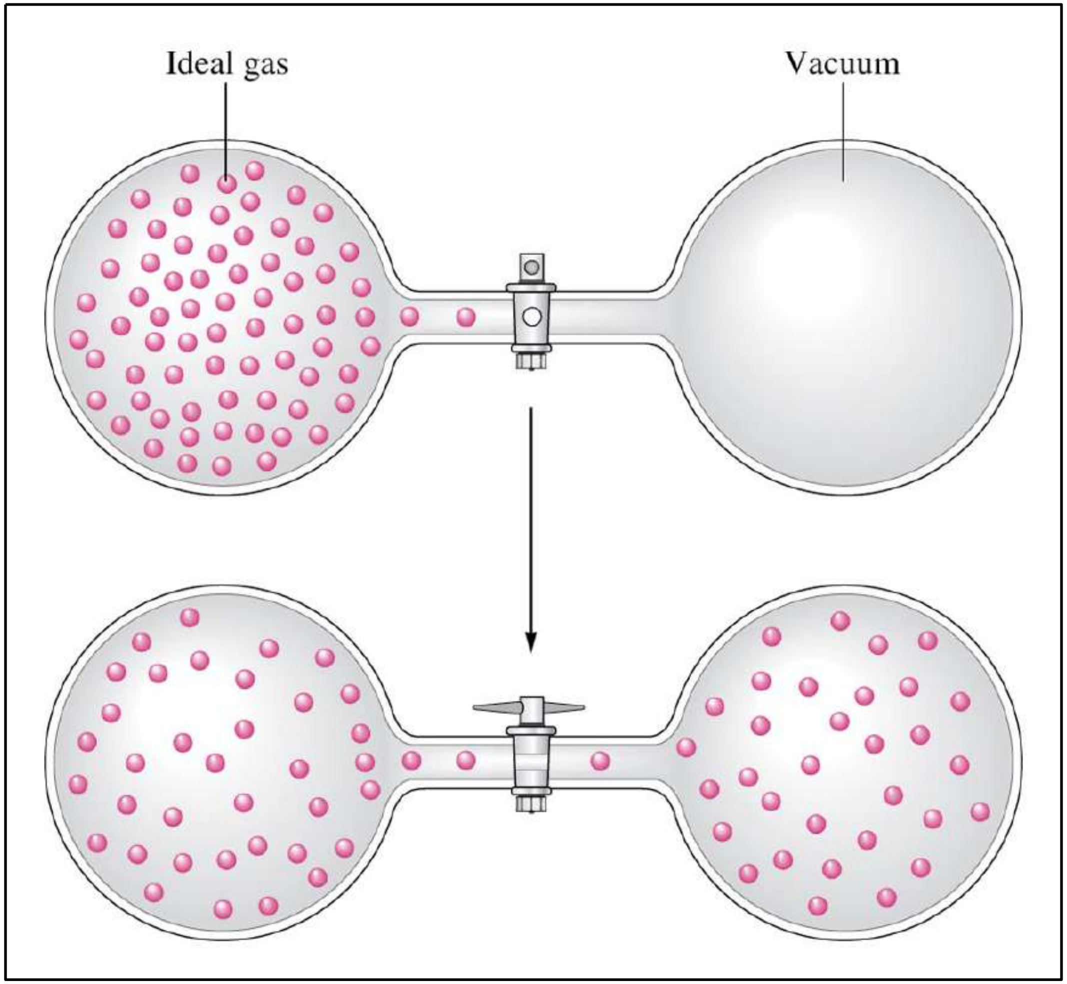
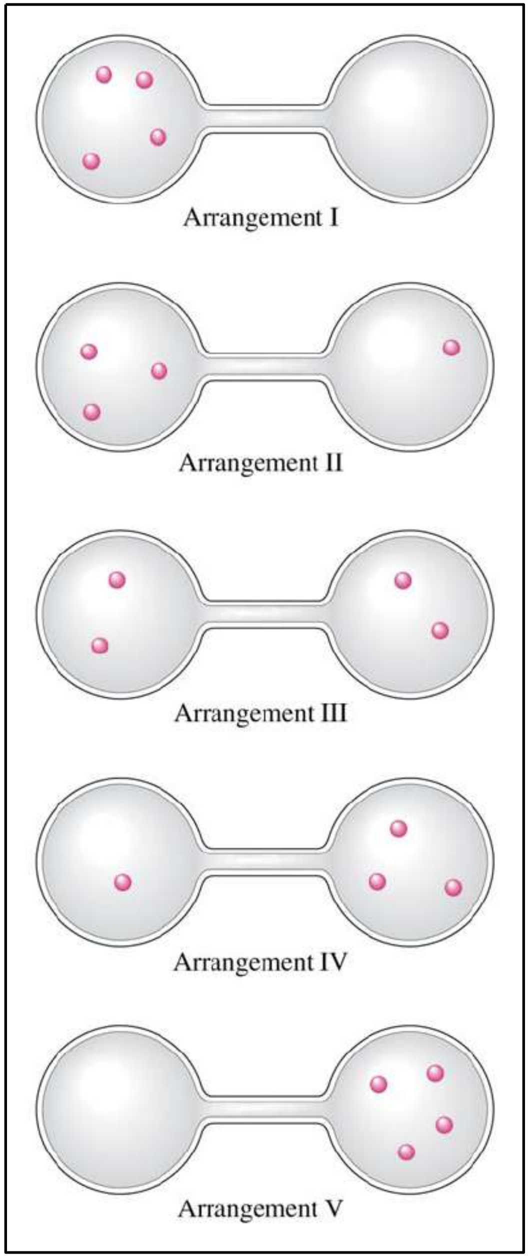


Figure 16.4 Possible arrangements (states) of four molecules in a two-bulbed flask.



The Microstates That Give a Particular Arrangement (State)

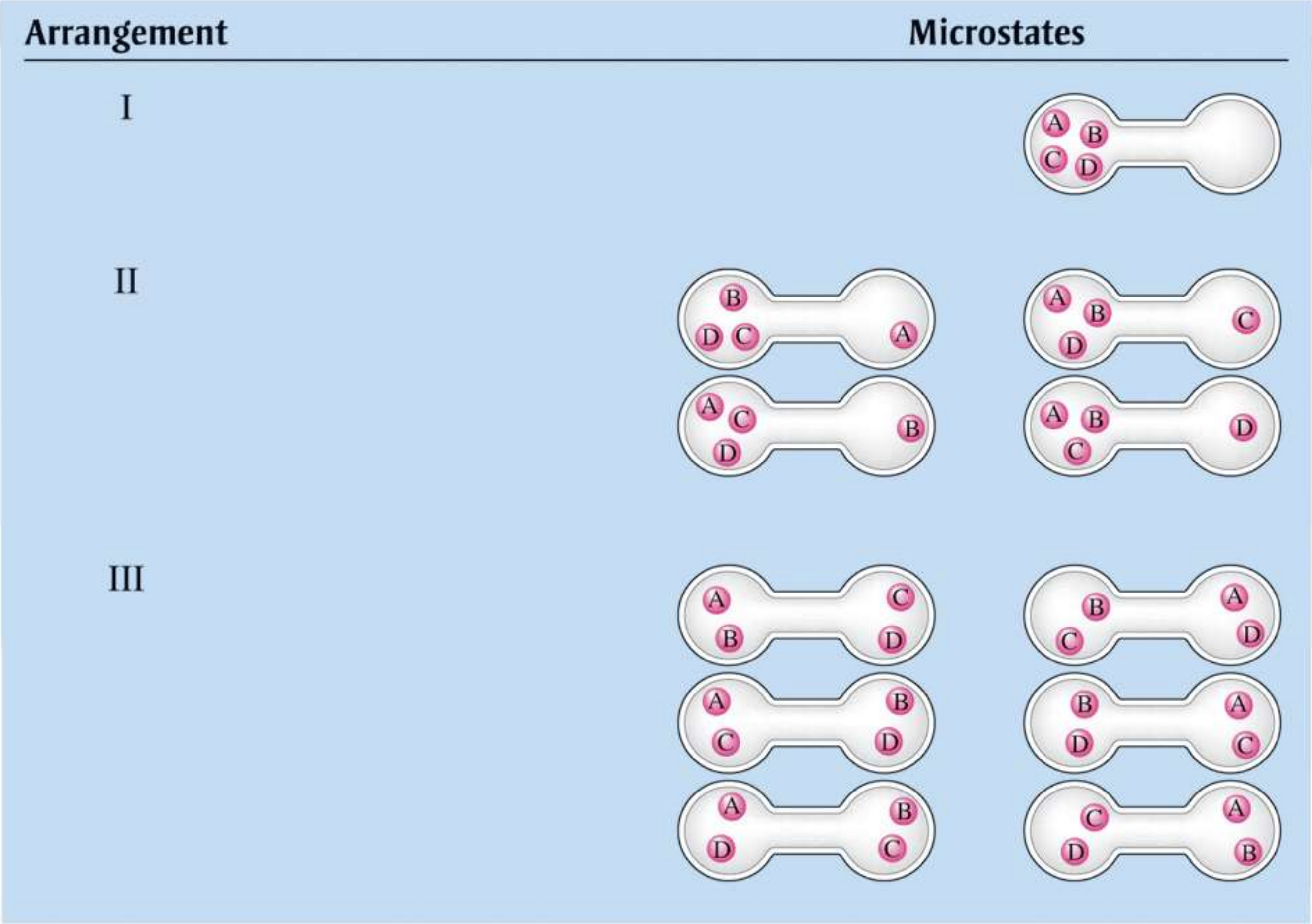


Table 16.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

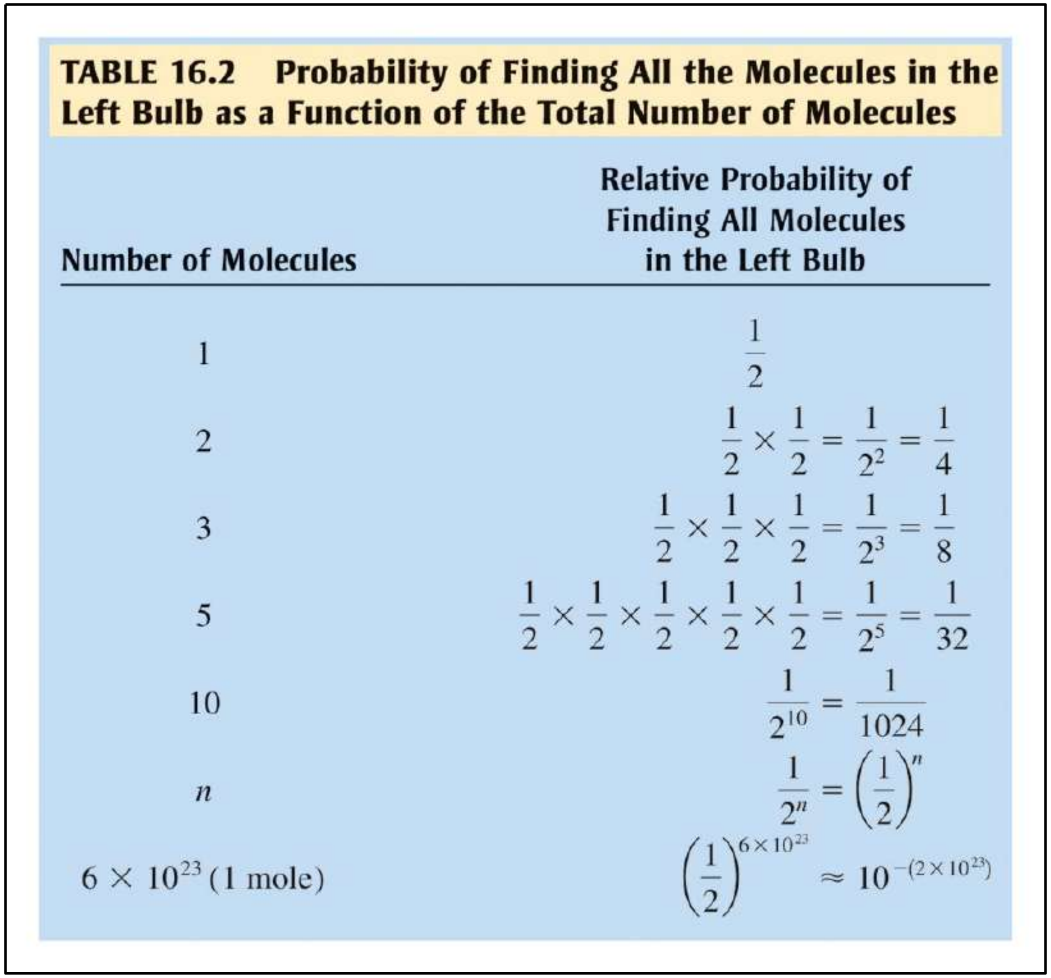
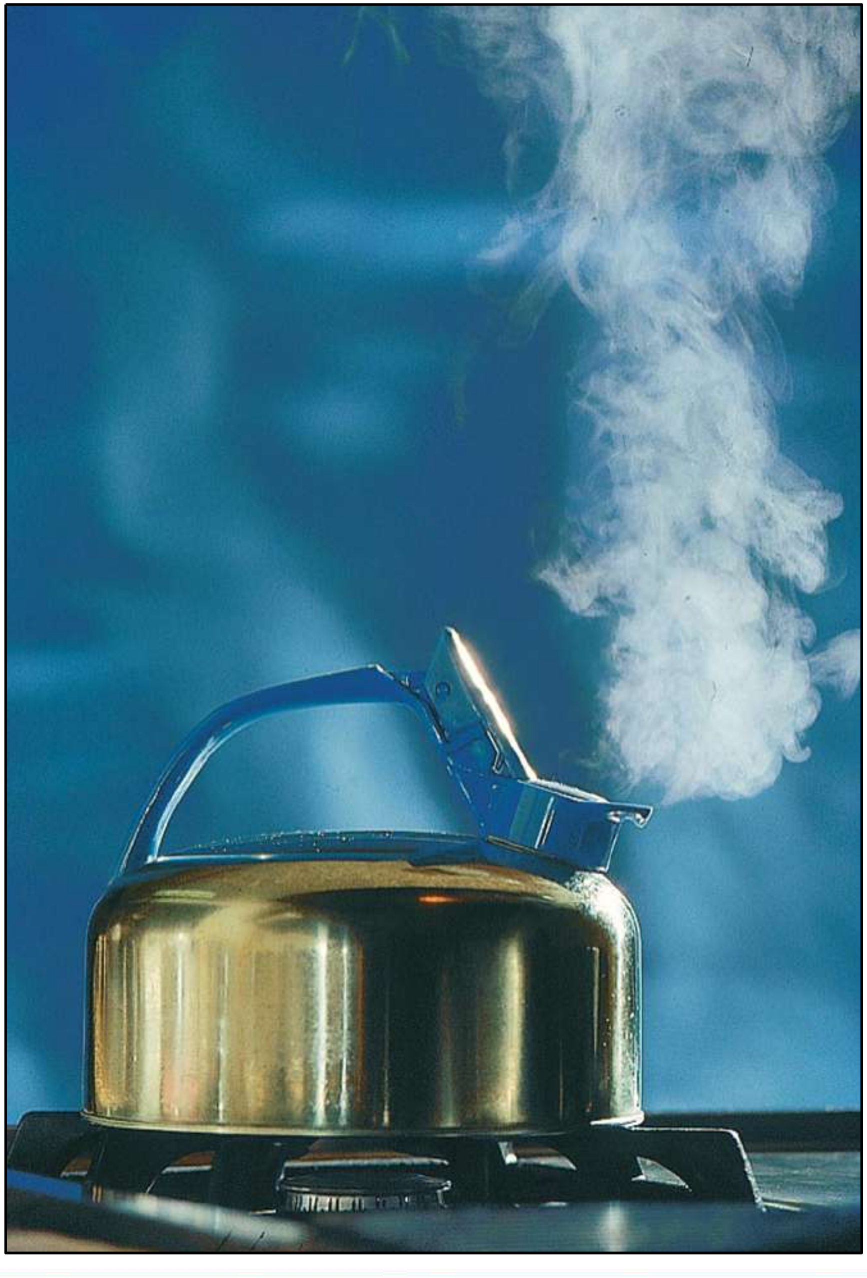


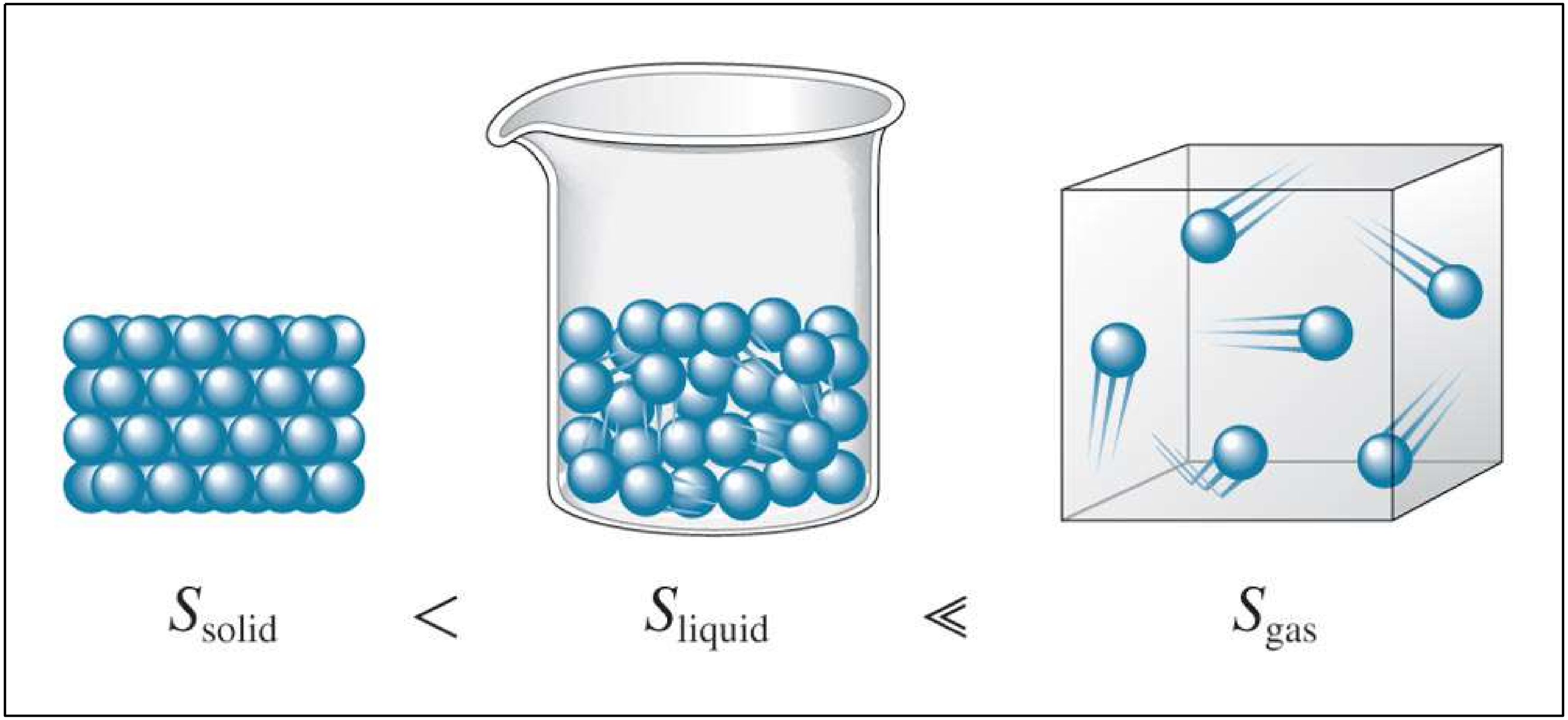
TABLE 16.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

Number of Molecules	Relative Probability of Finding All Molecules in the Left Bulb
1	$\frac{1}{2}$
2	$\frac{1}{2} \times \frac{1}{2} = \frac{1}{2^2} = \frac{1}{4}$
3	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^3} = \frac{1}{8}$
5	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^5} = \frac{1}{32}$
10	$\frac{1}{2^{10}} = \frac{1}{1024}$
n	$\frac{1}{2^n} = \left(\frac{1}{2}\right)^n$
6×10^{23} (1 mole)	$\left(\frac{1}{2}\right)^{6 \times 10^{23}} \approx 10^{-(2 \times 10^{23})}$

Boiling Water to Form Steam Increases Its Volume and Thus Its Entropy



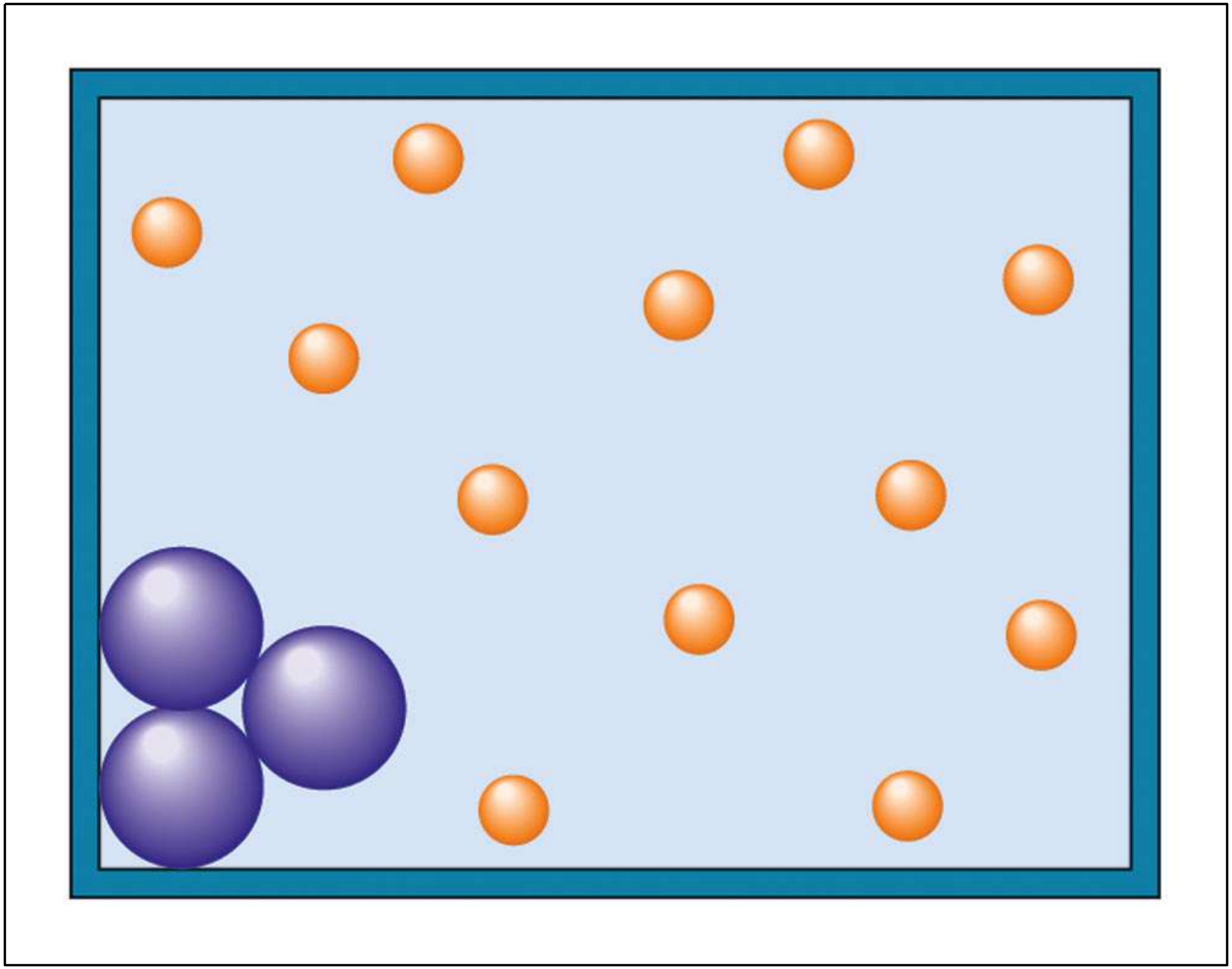
Probabilities of microstate processes.



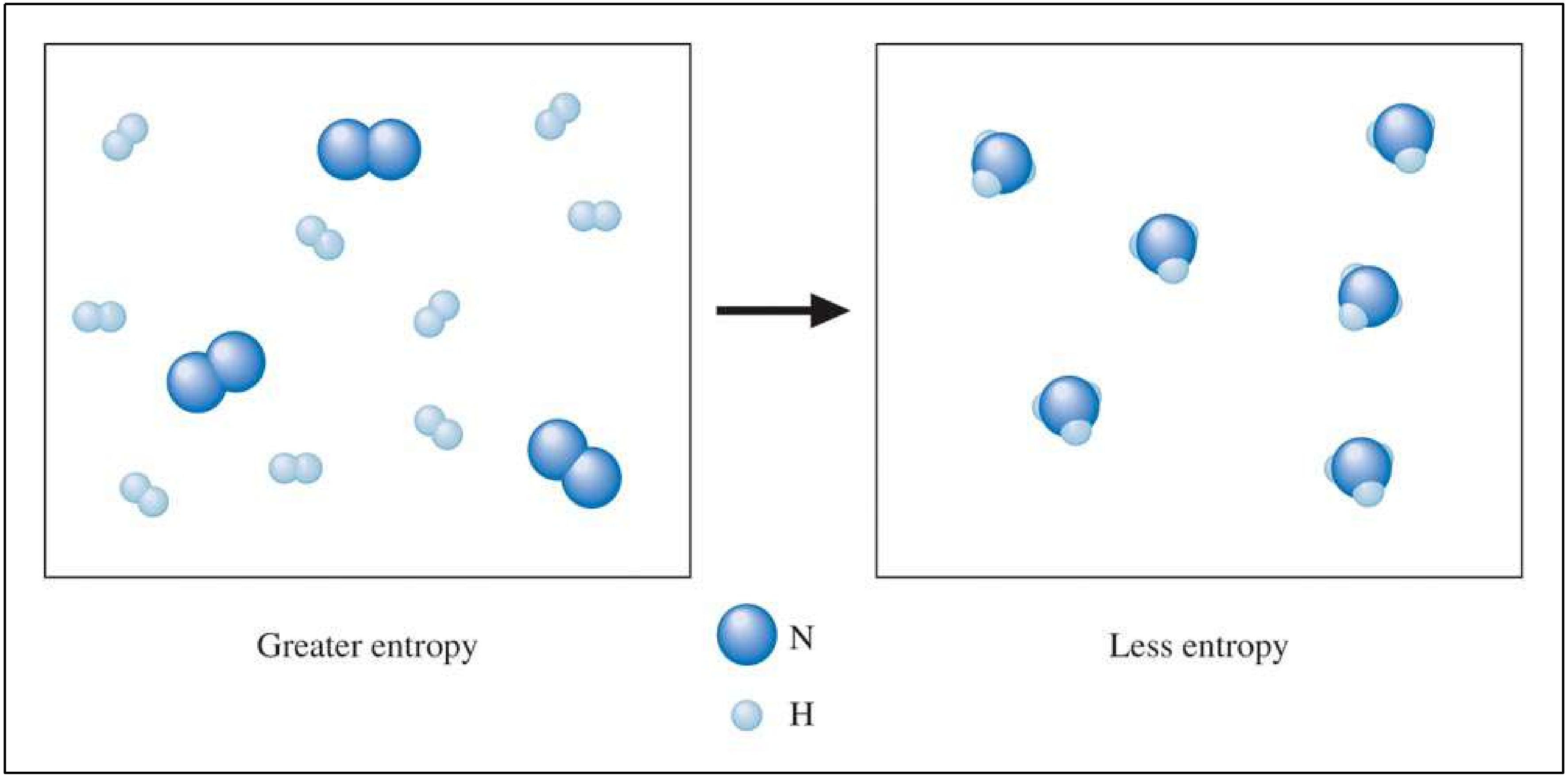
Positional Entropy

- A gas expands into a vacuum because the expanded state has the highest positional probability of states available to the system.
- Therefore, $S_{solid} < S_{liquid} \ll S_{gas}$

Molecule positioning.



Maximizing entropy.



React 2

Predict the sign of ΔS for each of the following, and explain:

a) the evaporation of alcohol
b) the freezing of water
c) compressing an ideal gas at constant temperature
d) heating an ideal gas at constant pressure
e) dissolving NaCl in water

Figure 16.5 a-b The entropy of a perfect crystal at 0K is zero. As the temperature is raised, entropy increases.

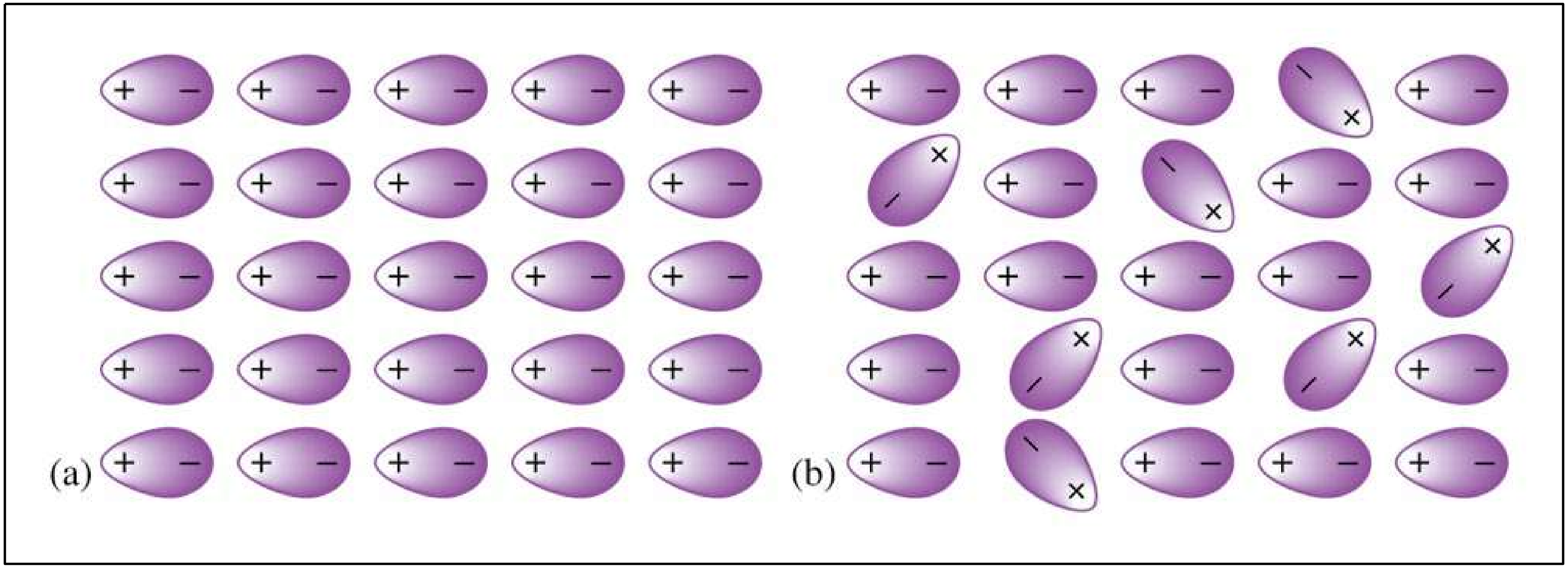
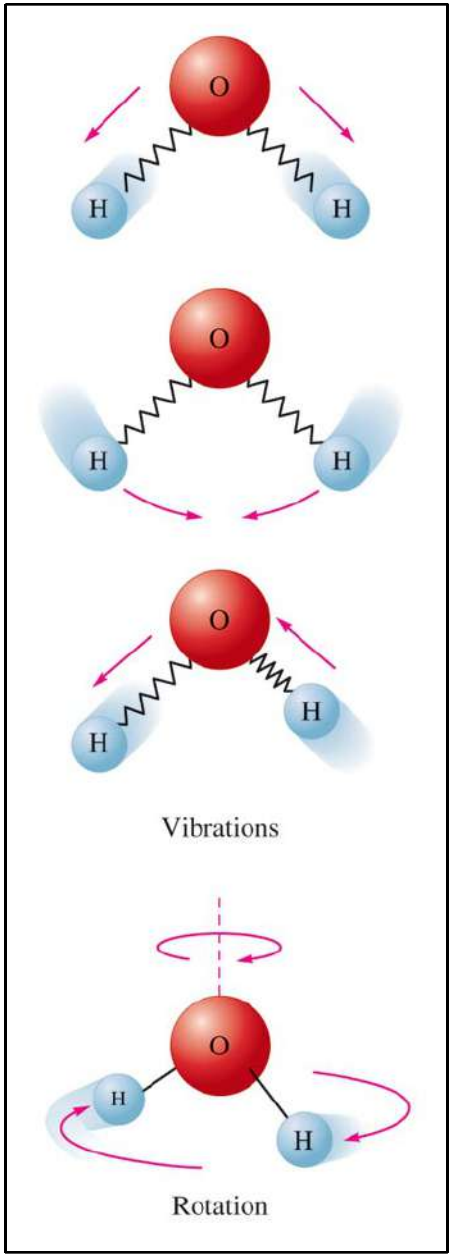
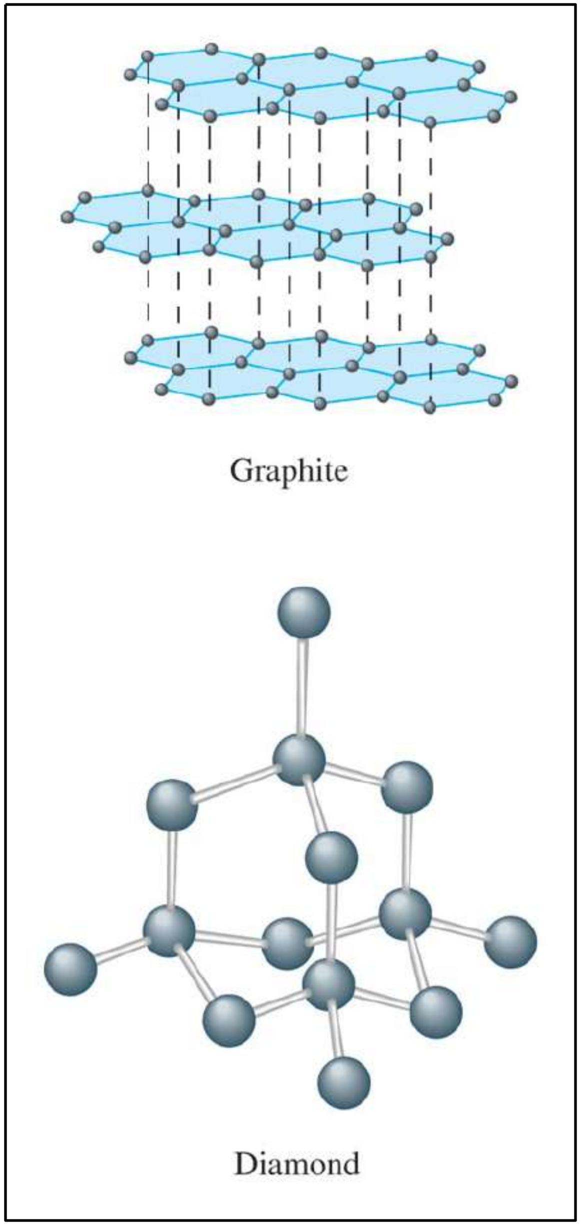
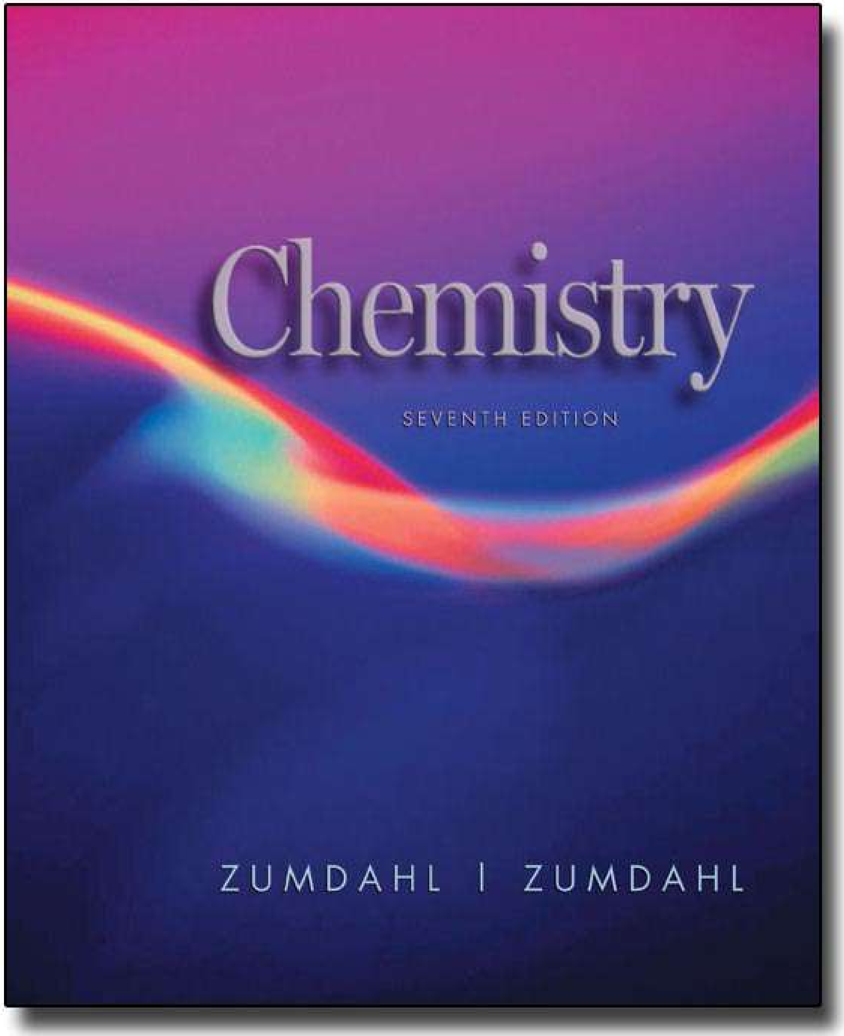


Figure 16.6 a-d H_2O has rotational and Vibrational motions.



Graphite; Diamond





The Effects of Temperature on Spontaneity

React 3

- For the process $A(l) \rightarrow A(s)$, which direction involves an increase in energy randomness? Positional randomness? Explain your answer.
- As temperature increases/decreases (answer for both), which takes precedence? Why?
- At what temperature is there a balance between energy randomness and positional randomness?

React 4

- Describe the following as spontaneous/ non-spontaneous/cannot tell, and explain.
- A reaction that is
  a) Exothermic and becomes more positionally random
  b) Exothermic and becomes less positionally random
  c) Endothermic and becomes more positionally random
  d) Endothermic and becomes less positionally random
  e) Explain how temperature affects your answers.

Provide a real example of two of the items above.

React 5

Use the ideas of energy randomness and positional randomness in your discussion of the following:

a) Under what conditions is the freezing of water spontaneous? Why?

b) Under what conditions is the melting of water spontaneous? Why?

c) Under what conditions is the freezing of water as likely as the melting of water? Why?

React 6

A liquid is vaporized at its boiling point. Predict the signs of w, q, ΔH, ΔS, ΔS_{surr} and ΔG.

Explain your answers.

Now Try These

Consider the process $H_2O(l) \rightarrow H_2O(g)$ at a constant P of 1 atm

- At a constant T of 95°C, what are the signs of w, q, ΔH, ΔS, ΔS_{univ}, and ΔG? Explain.
- At a constant T of 105°C, what are the signs of w, q, ΔH, ΔS, ΔS_{univ}, and ΔG? Explain.

Now Try These

Consider the process $H_2O(l) \rightarrow H_2O(s)$ at a constant P of 1 atm

- At a constant T of 10°C, what are the signs of *w*, *q*, ΔH, ΔS, ΔS_{univ}, and ΔG? Explain.
- At a constant T of −10°C, what are the signs of *w*, *q*, ΔH, ΔS, ΔS_{univ}, and ΔG? Explain.

React 7

Rubidium has a heat of vaporization of 69.0 kJ/mol at its boiling point (686°C). For the process (1 atm, 686°C)

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

Calculate:

- a) ΔE (in kJ/mol)

b) ΔS (in J/K mol)
c) ΔG (in kJ/mol)

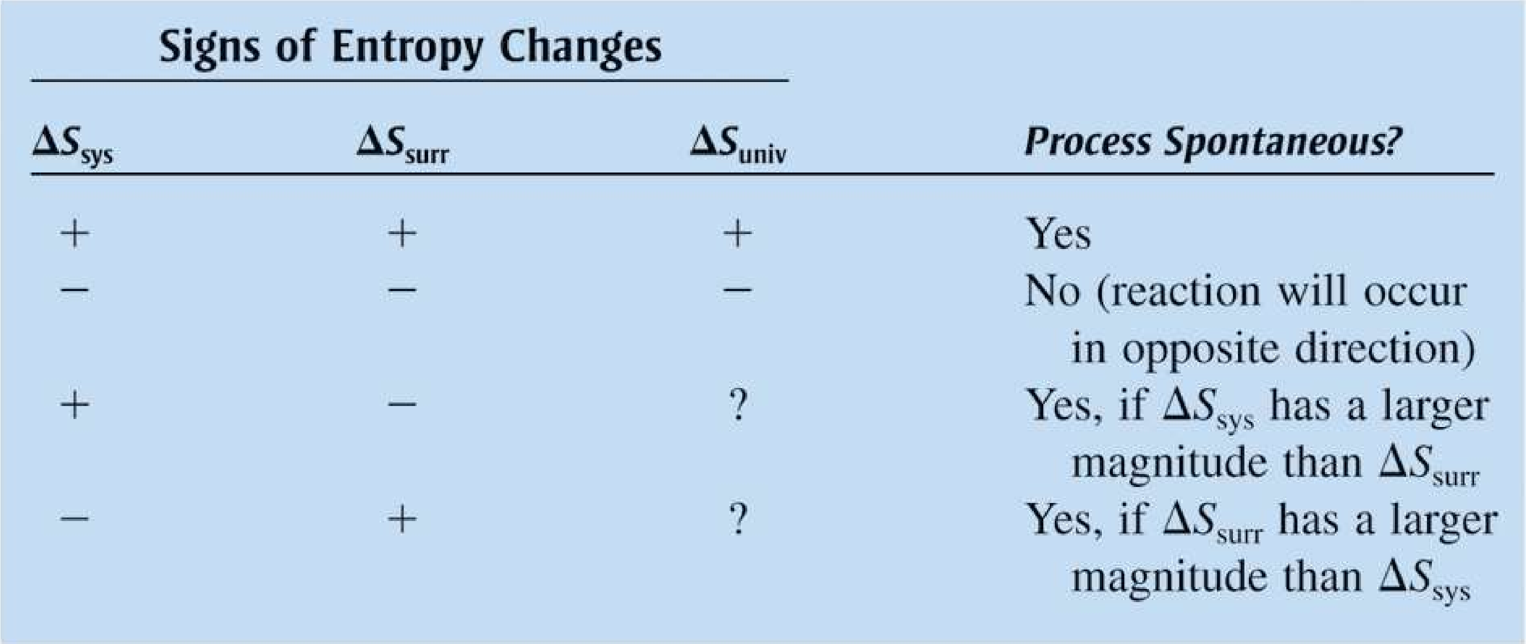
React 8

The value of $\Delta H_{vaporization}$ of substance X is 45.7 kJ/mol, and its normal boiling point is 72.5°C.

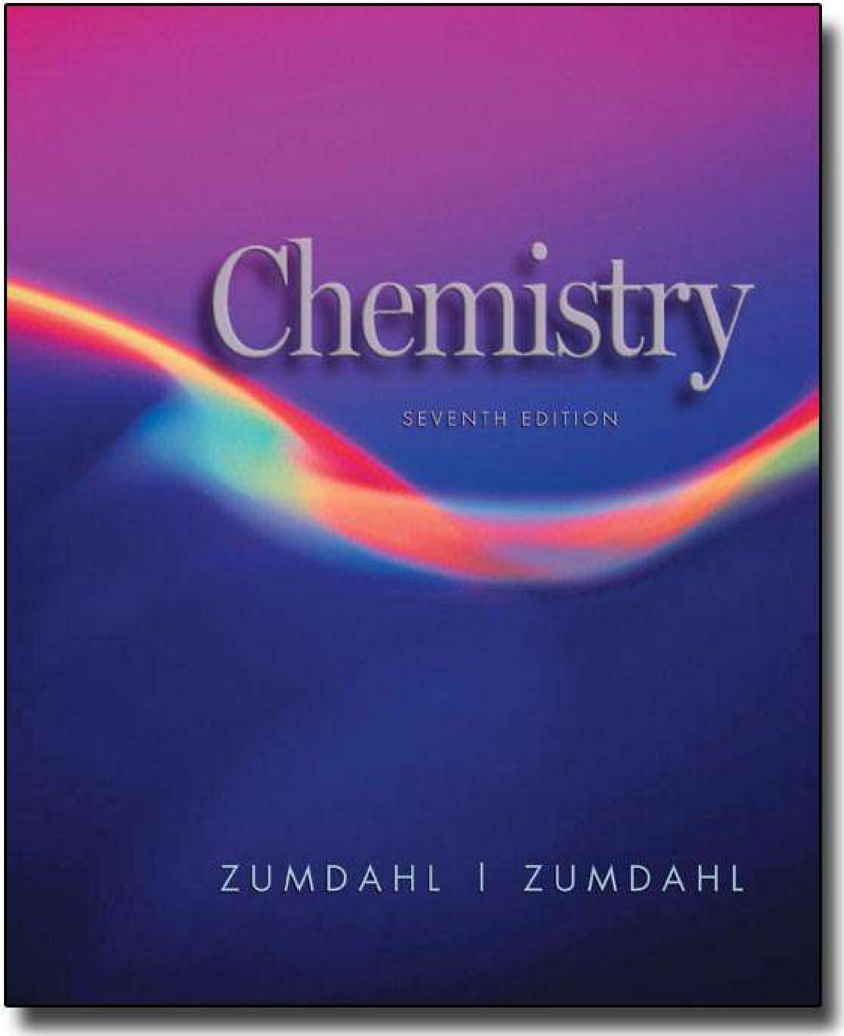
Calculate ΔS, ΔS_{surr}, and ΔG for the vaporization of one mole of this substance at 72.5°C and 1 atm.

The Mineral Stibnite Contains Sb_2S_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}



Free Energy

Spontaneous Reactions

Table 16.4 Results of the Calculation of ΔS_{univ} and $\Delta G°$ for the Process $H_2O \Rightarrow H_2O(l)$ at -10°C, 0°C, and 10°C

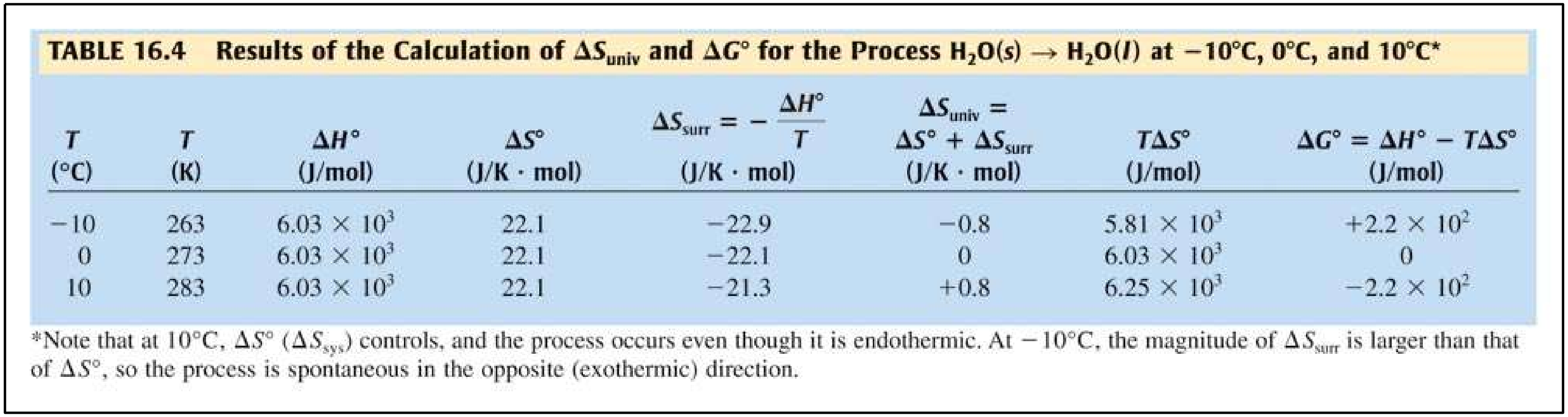


TABLE 16.4 Results of the Calculation of ΔS_{univ} and $\Delta G°$ for the Process $H_2O(s) \rightarrow H_2O(l)$ at −10°C, 0°C, and 10°C*

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

*Note that at 10°C, $\Delta S°$ (ΔS_{sys}) controls, and the process occurs even though it is endothermic. At −10°C, the magnitude of ΔS_{surr} is larger than that of $\Delta S°$, so the process is spontaneous in the opposite (exothermic) direction.

Table 16.5 Various Possible Combinations of ΔH and Δs for a Process and the Resulting Dependence of Spontaneity on Temperature

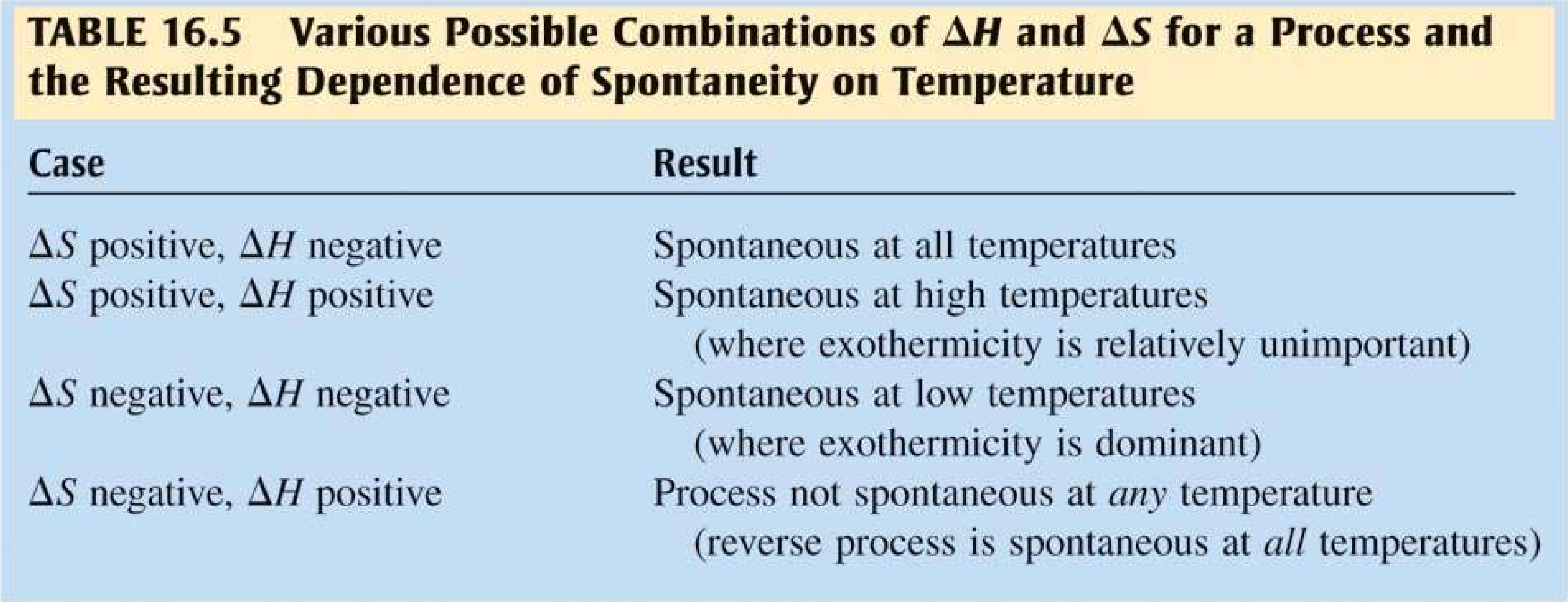
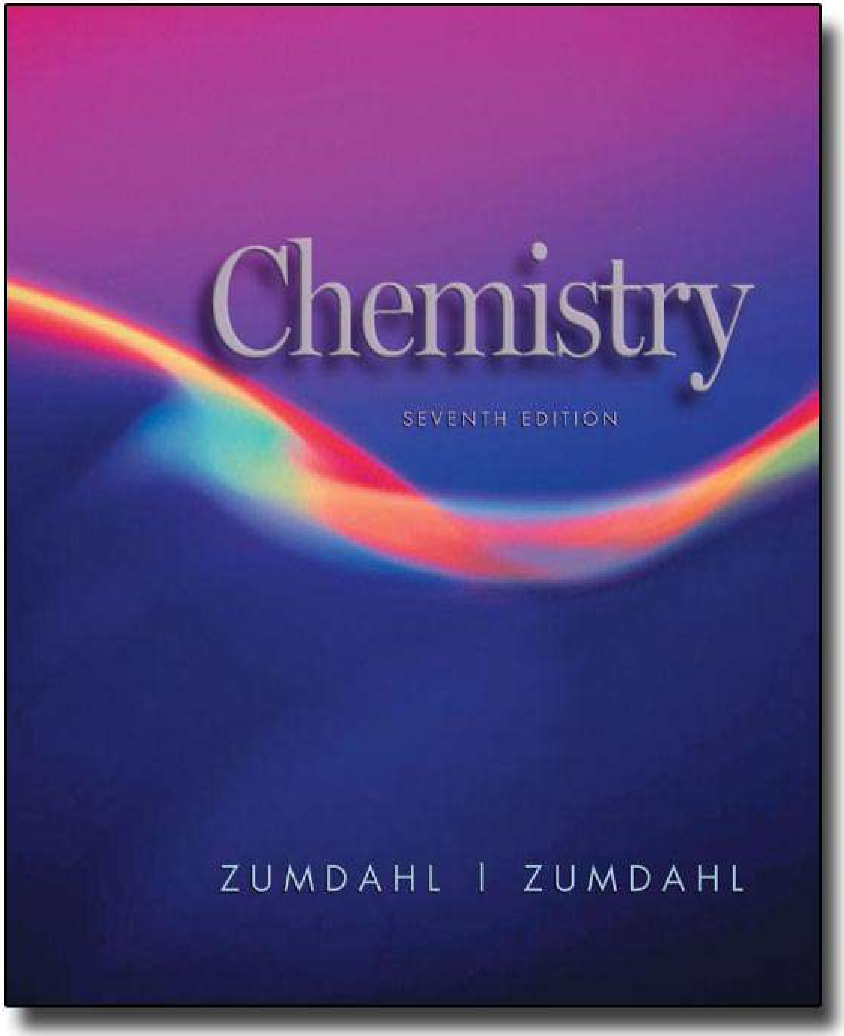


TABLE 16.5 Various Possible Combinations of Δ*H* and Δ*S* for a Process and the Resulting Dependence of Spontaneity on Temperature

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

Effect of ΔH and ΔS on Spontaneity

ΔH	ΔS	Result
–	+	spontaneous at all temps
+	+	spontaneous at high temps
–	–	spontaneous at low temps
+	–	not spontaneous at any temp



Entropy Changes and Free Energy in Chemical Reactions

React 9

Gas A_2 reacts with gas B_2 to form gas AB at constant temperature and pressure. The bond energy of AB is much greater than that of either reactant.

Predict the signs of:

$\Delta H \Delta S_{surr} \Delta S \Delta S_{univ}$

Explain.

React 10

A stable diatomic molecule spontaneously forms from its atoms.

Predict the signs of

$\Delta H^\circ \Delta S^\circ \Delta G^\circ$

Explain.

React 11

Consider the following system at equilibrium at 25°C.

$$PCl_3(g) + Cl_2 \rightleftharpoons PCl_5(g)$$

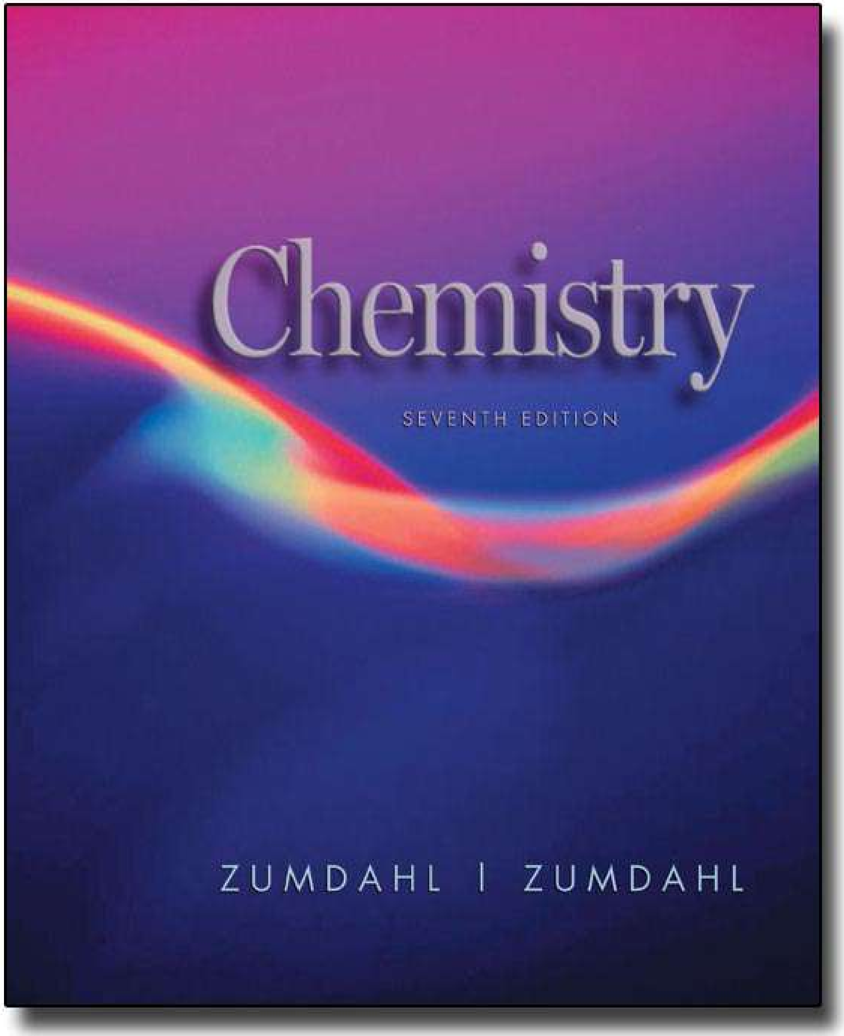
$$\Delta G° = -92.50 \text{ kJ}$$

- What will happen to the ratio of partial pressure of PCl_5 to partial pressure of PCl_3 if the temperature is raised?
- Explain.

React 12

Sketch graphs of

1. G vs. P
2. H vs. P
3. ln(K) vs. 1/T (for both endothermic and exothermic cases)



Free Energy and Equilibrium

Figure 16.7 a-b Like the Ball, a Chemical System will Seek the Lowest Possible Free Energy

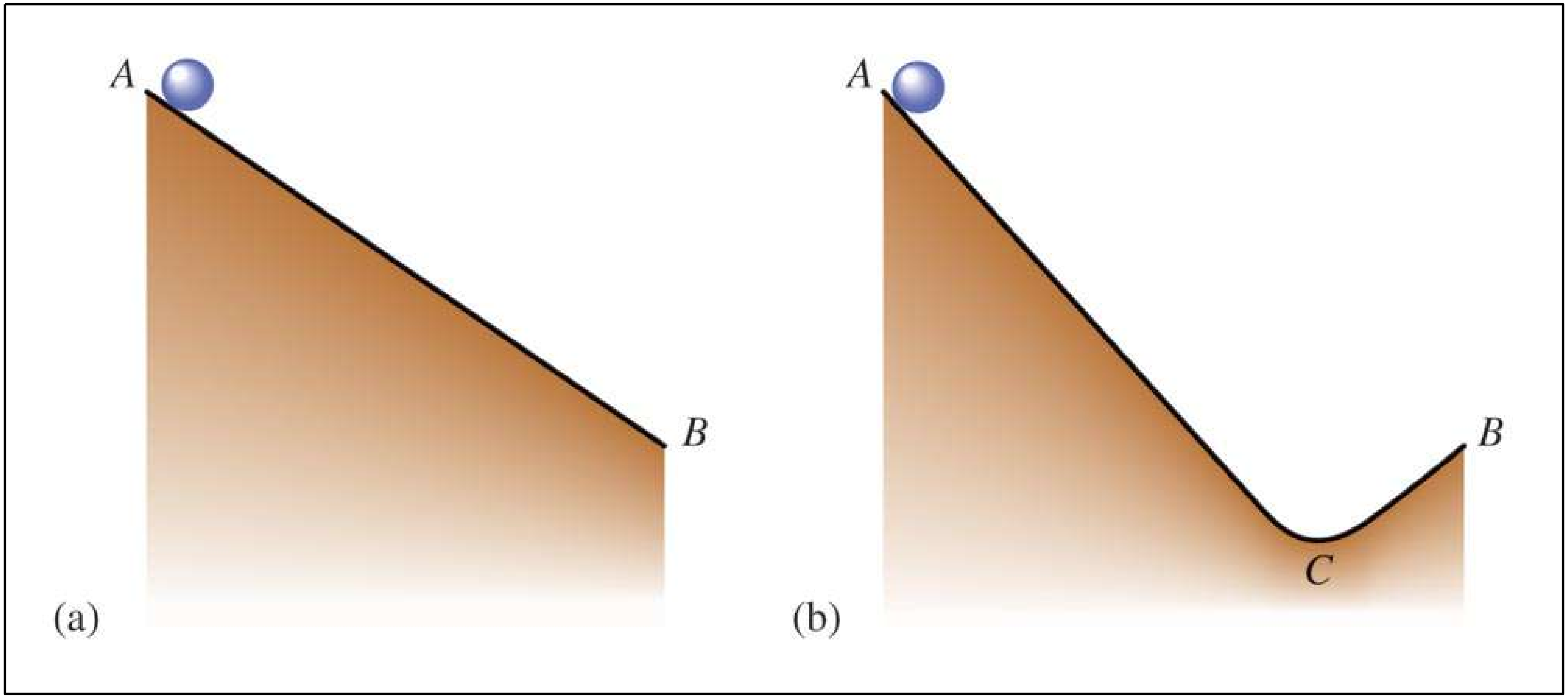
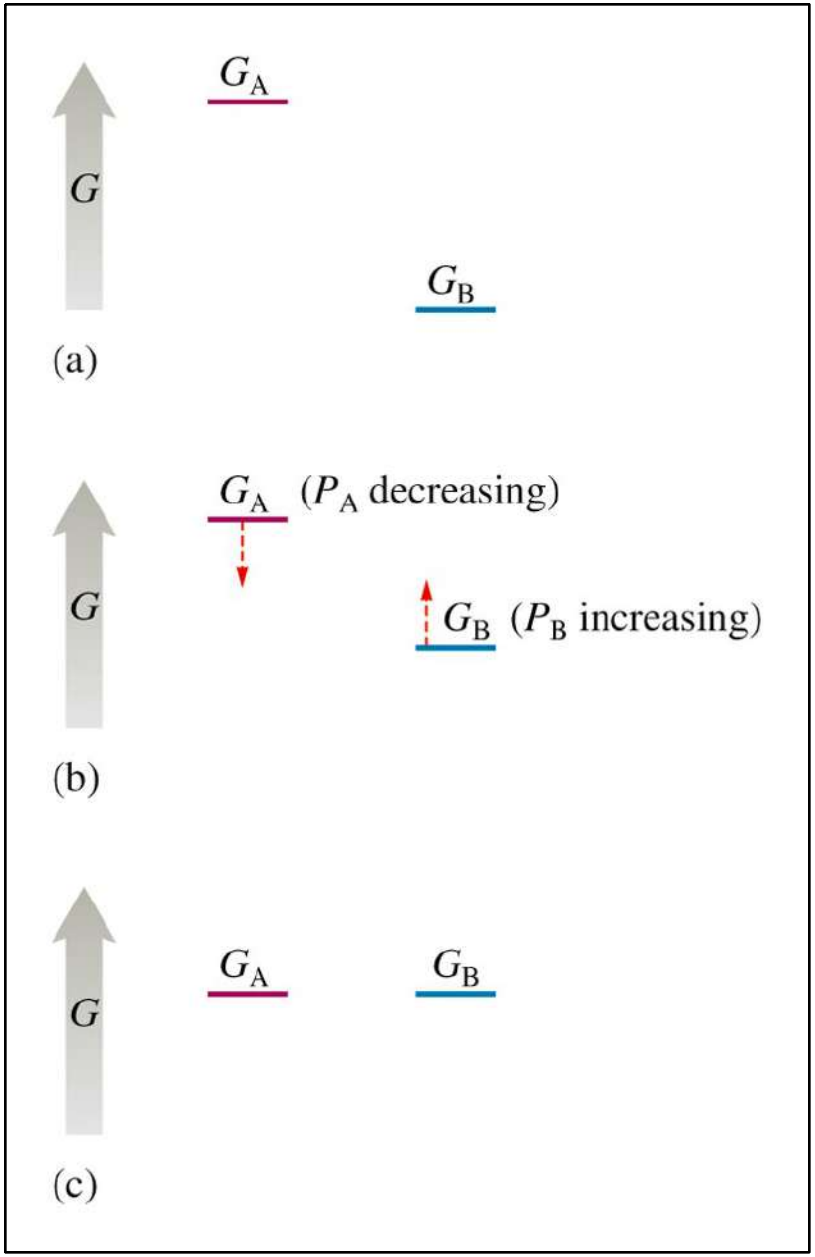


Figure 16.8 a-c (a) The initial free energies of A and B. (b) As A(g) changes to B(g), the free energy of A decreases and that of B increases. (c) Eventually, pressures of A and B are achieved such that $G_A = G_B$, the equilibrium position



Change in Free Energy to Reach Equilibrium

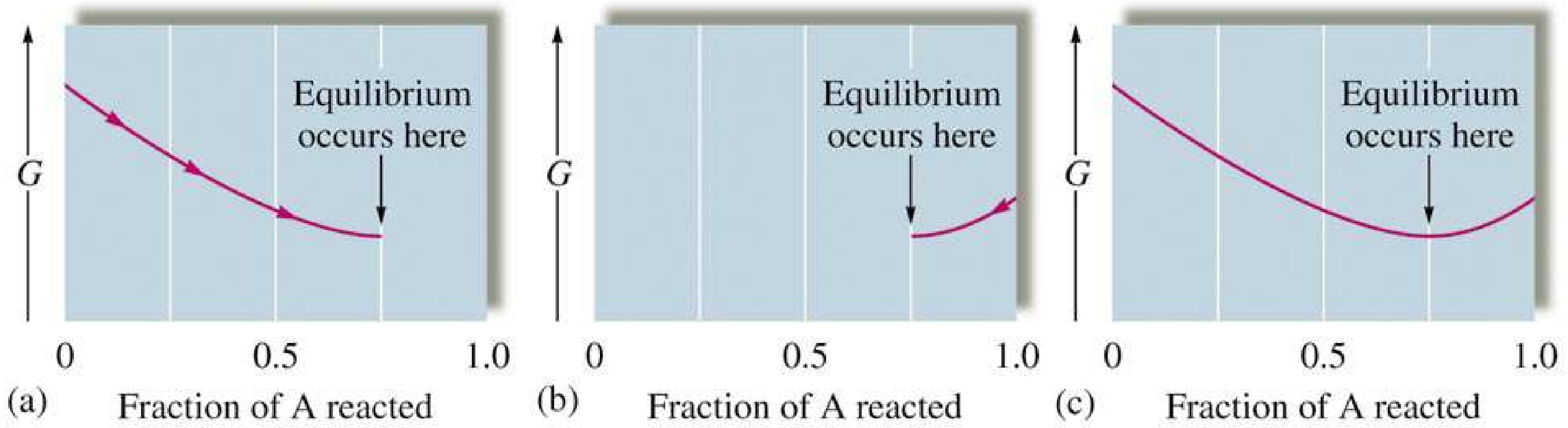
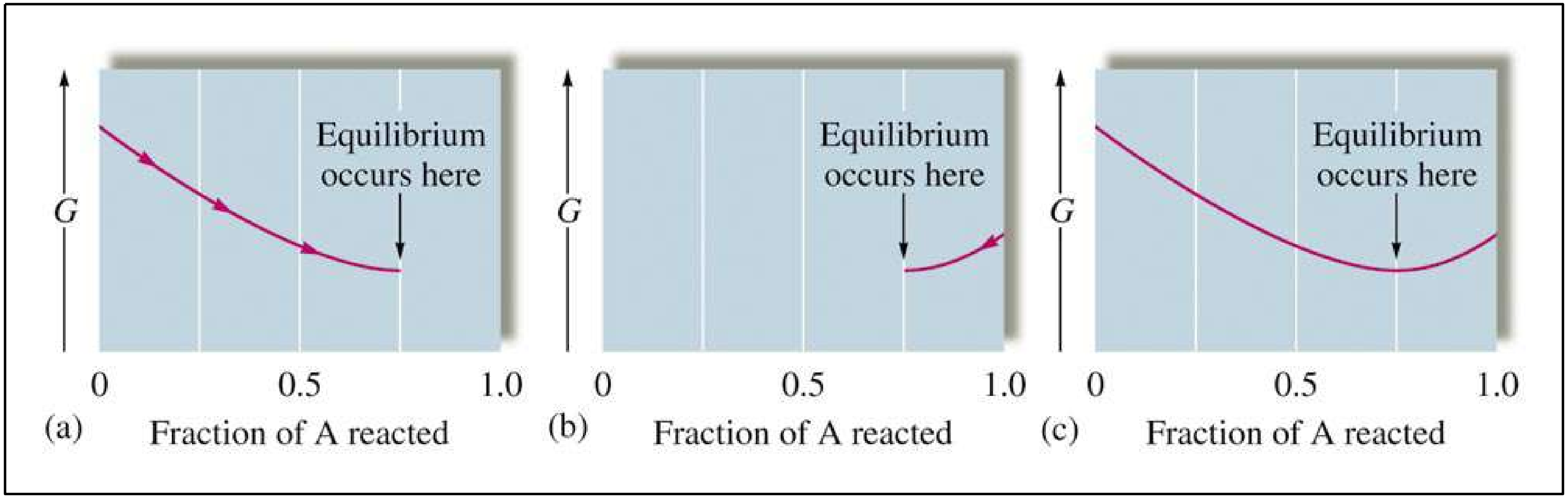
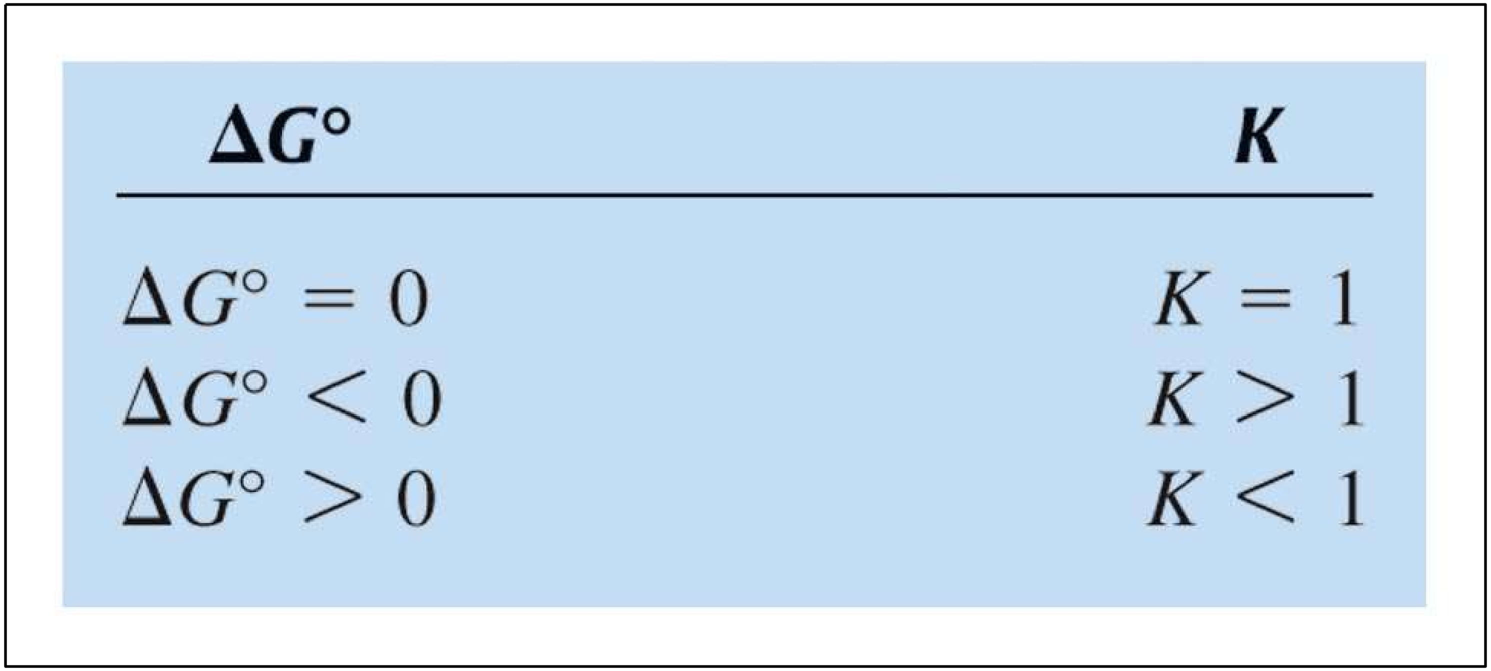


Figure 16.9 a-c Minimum free energy is reached when 75% of A has been changed to B



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



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

Formation of Rust on Bare Steel is a Spontaneous Process

Figure 16.10 Reversible Process of a Car Battery