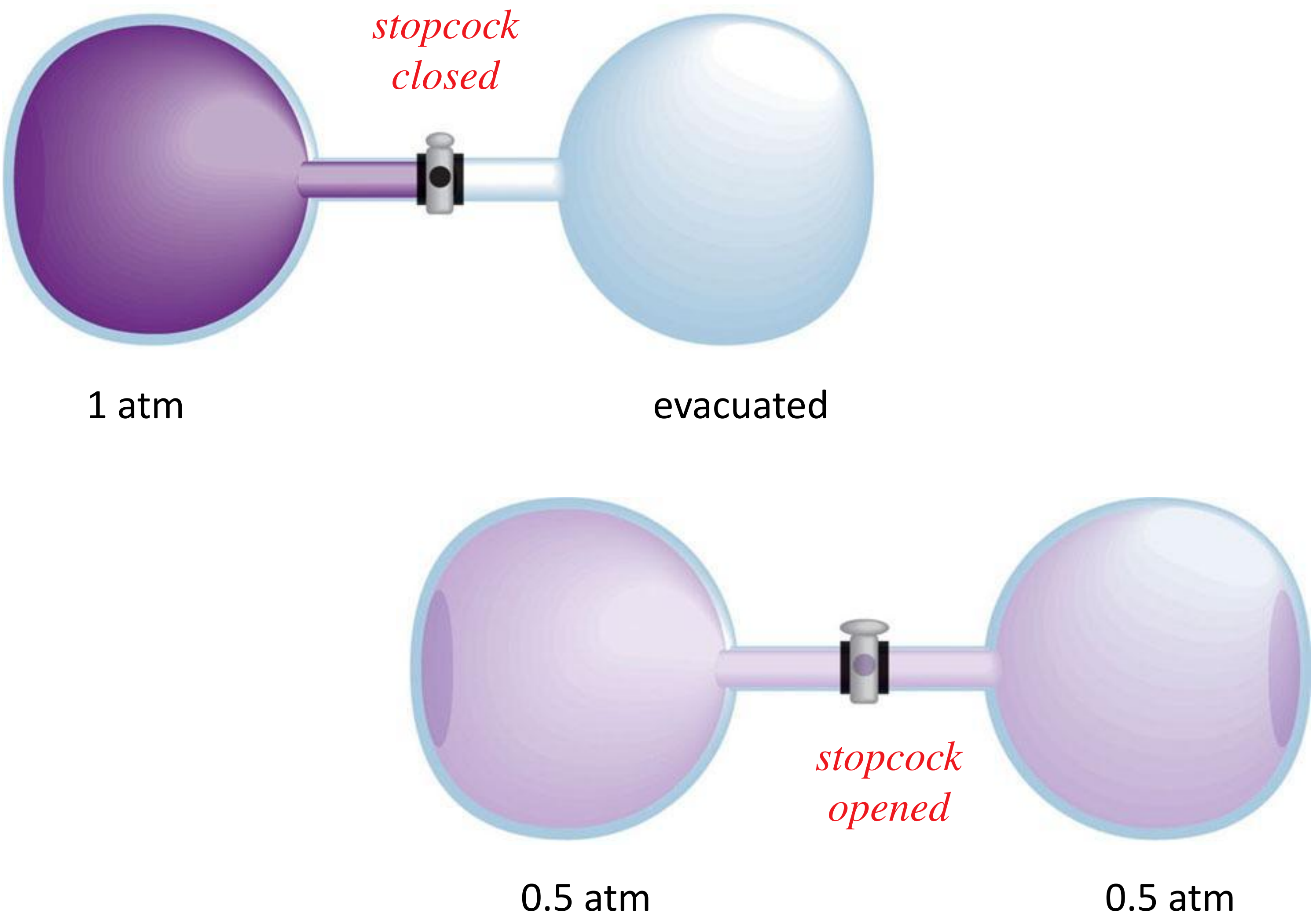
Chapter 20 – Thermodynamics

- 20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change
- 20.2 – Calculating the Change in Entropy of a Reaction
- 20.3 – Entropy, Free Energy, and Work
- 20.4 – Free Energy, Equilibrium, and Reaction Direction

20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

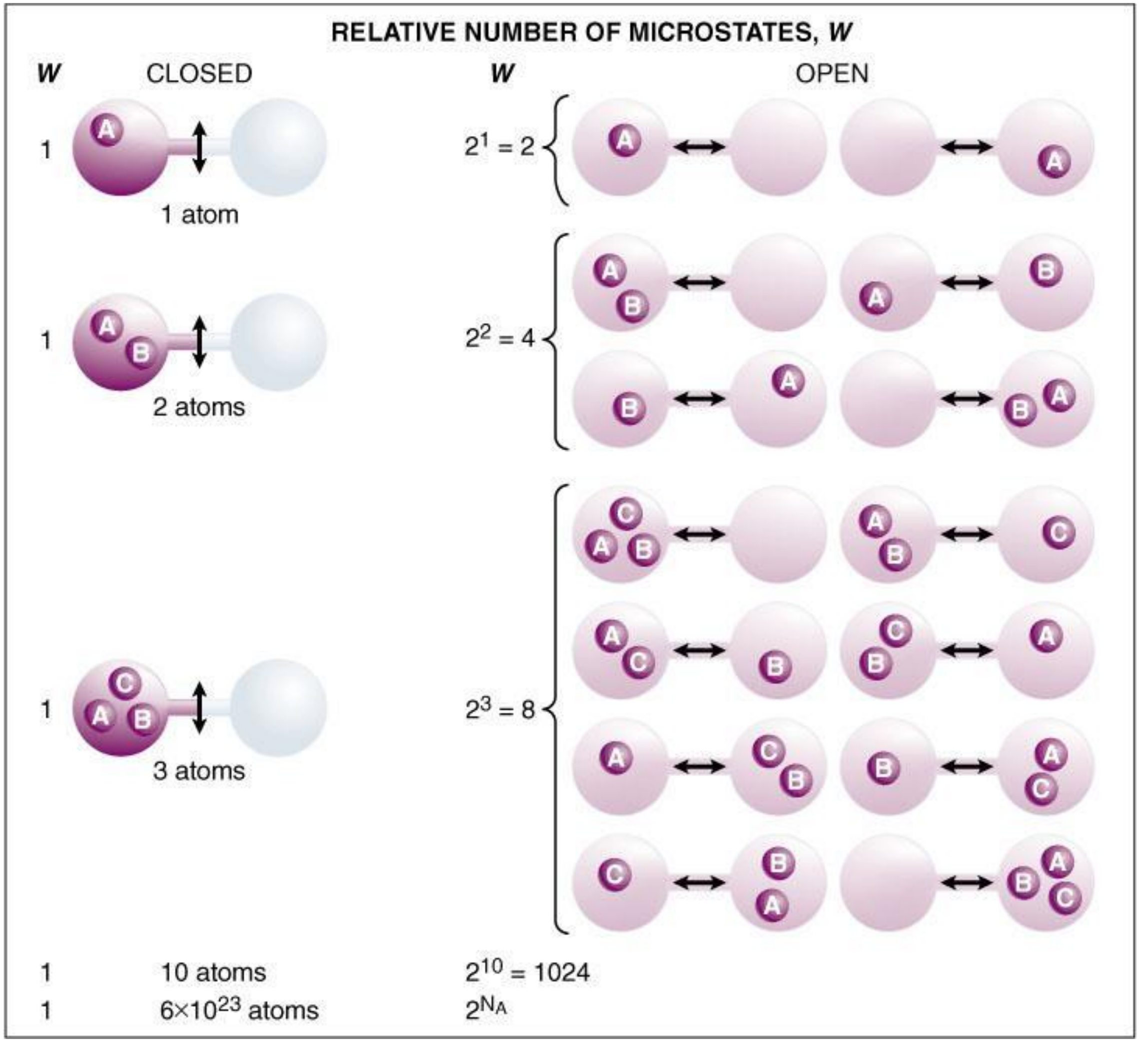
Figure 20.2 **Spontaneous expansion of a gas**



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

Figure 20.3

Expansion of a gas and the increase in number of microstates.



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

1877 Ludwig Boltzman

$$S = k \ln W$$

where S is entropy, W is the number of ways of arranging the components of a system, and k is a constant (the Boltzman constant), R/N_A (R = universal gas constant, N_A = Avogadro's number.

- A system with relatively few equivalent ways to arrange its components (smaller W) has relatively less disorder and low entropy.

- A system with many equivalent ways to arrange its components (larger W) has relatively more disorder and high entropy.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

*The **second law of thermodynamics.***

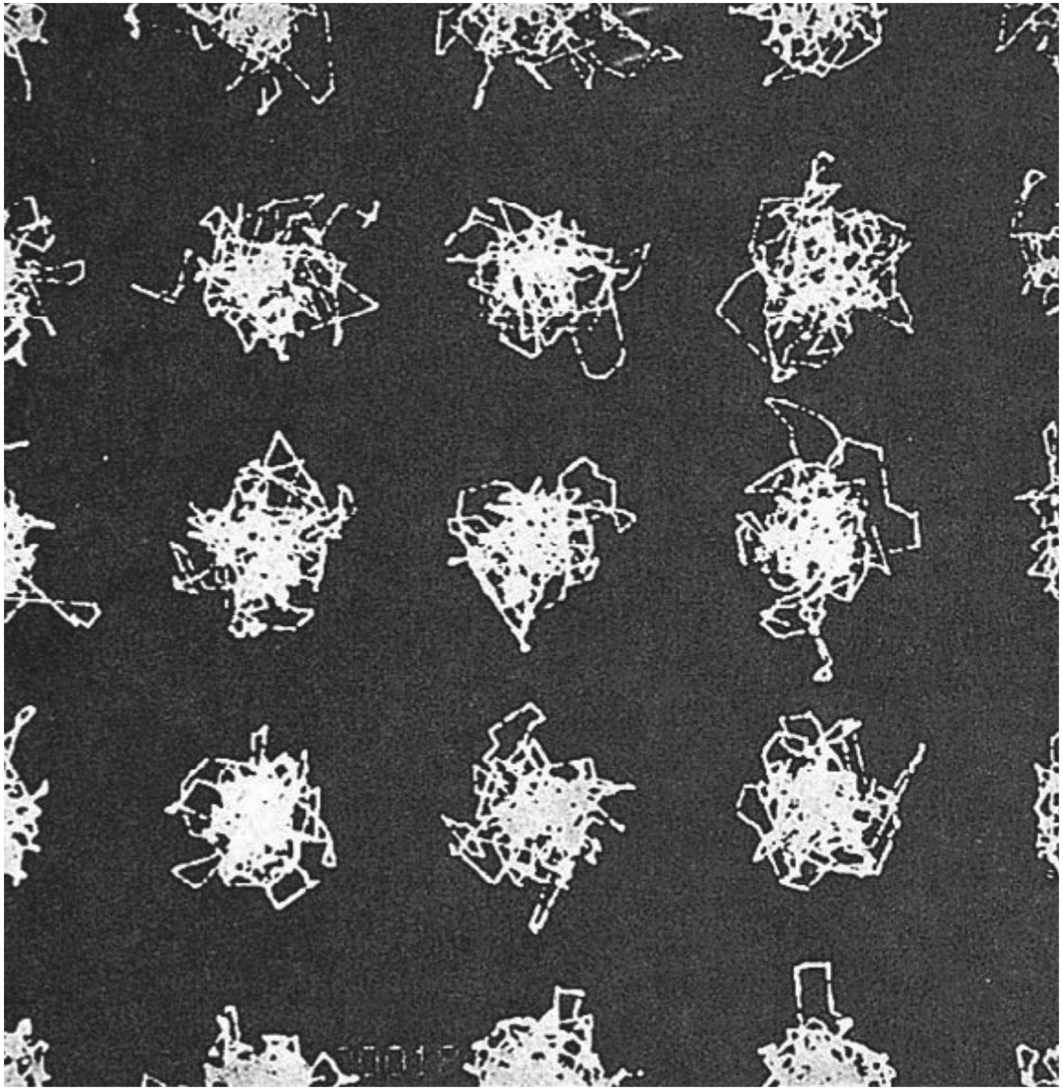
20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

Figure 20.4 **Random motion in a crystal**

The ***third law of thermodynamics*****.**

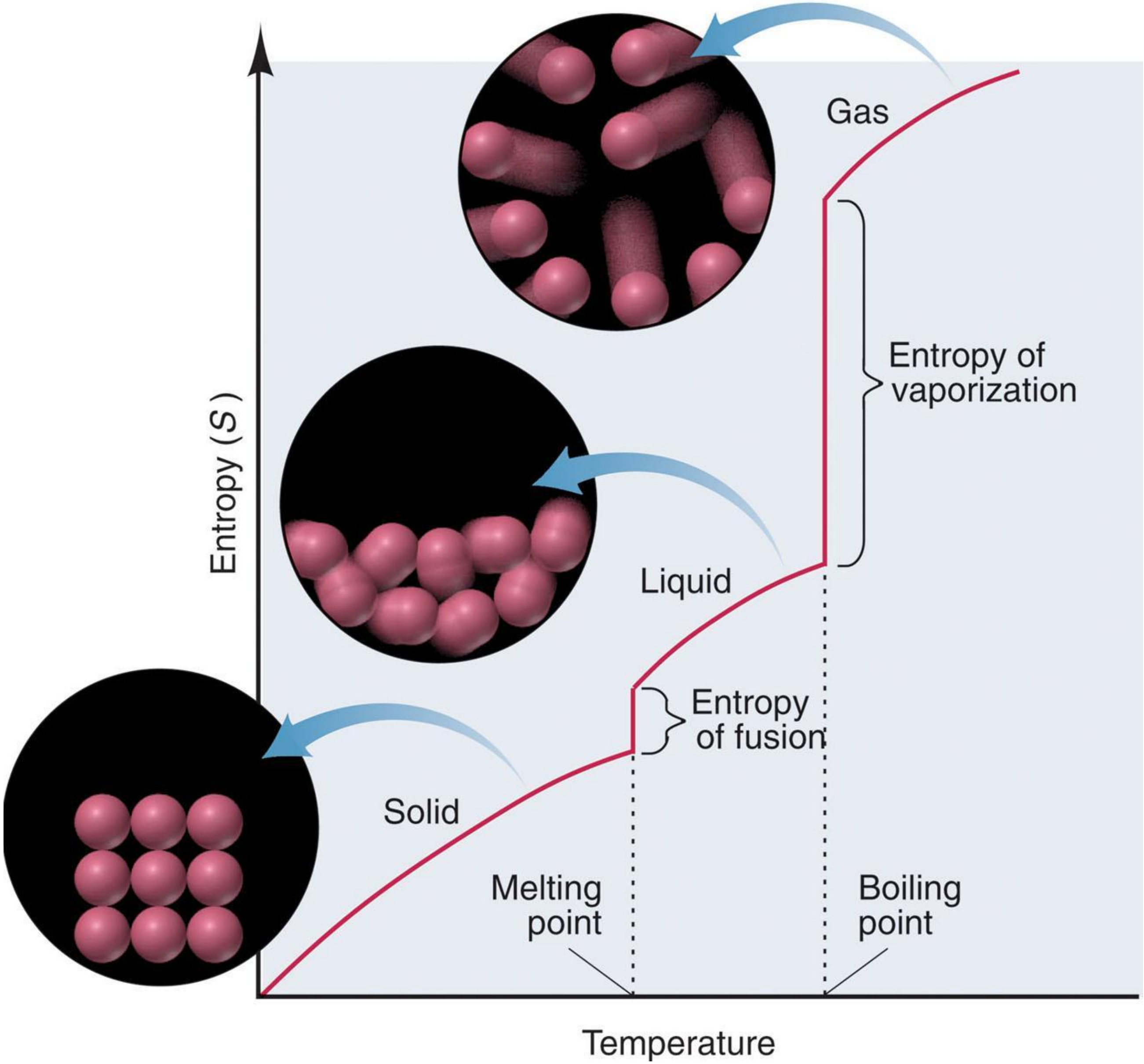
A perfect crystal has zero entropy at a temperature of *absolute zero.*

S_{system} = 0 at 0 K



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

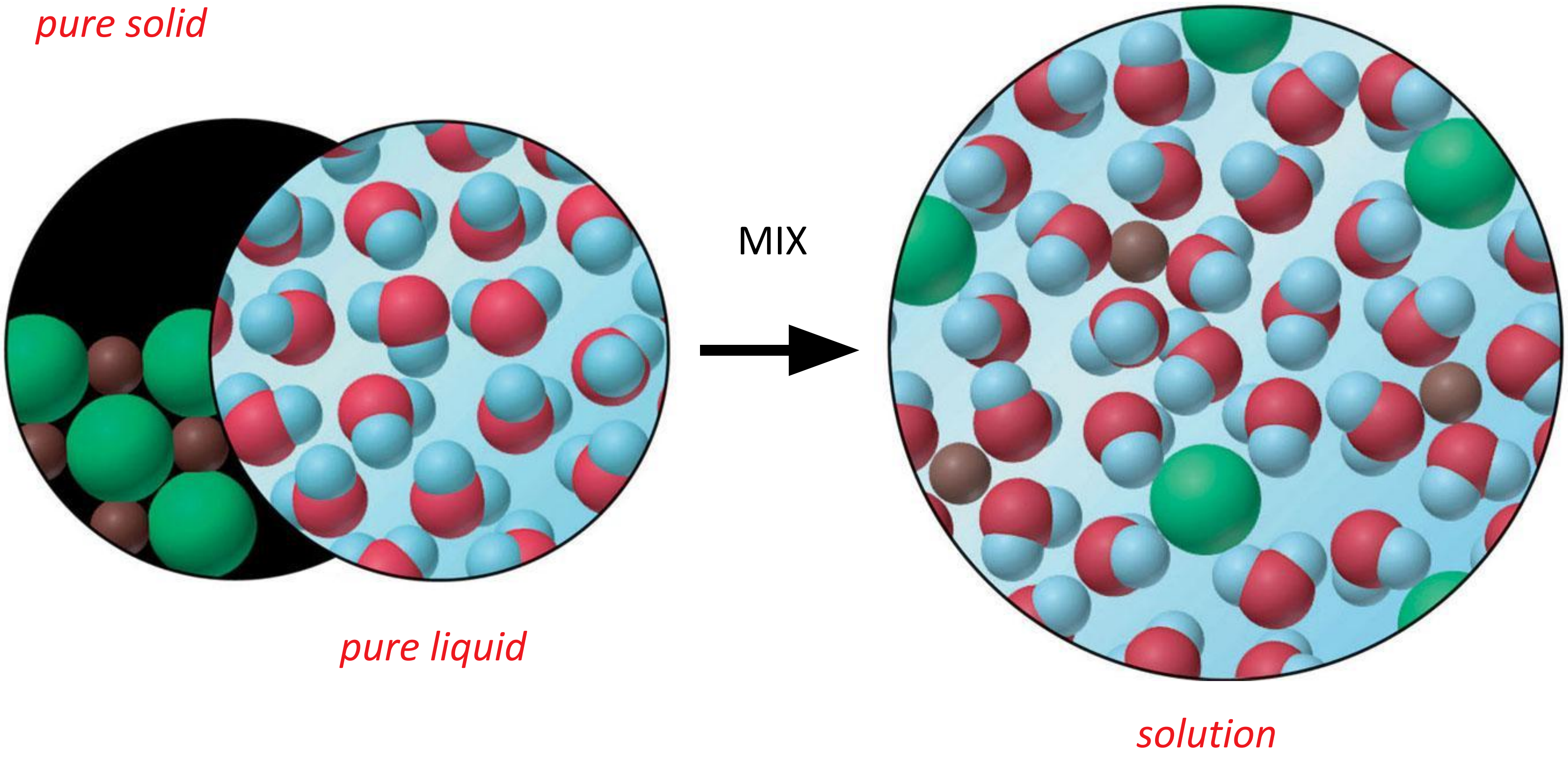
Figure 20.5 **The increase in entropy from solid to liquid to gas.**



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

Figure 20.6

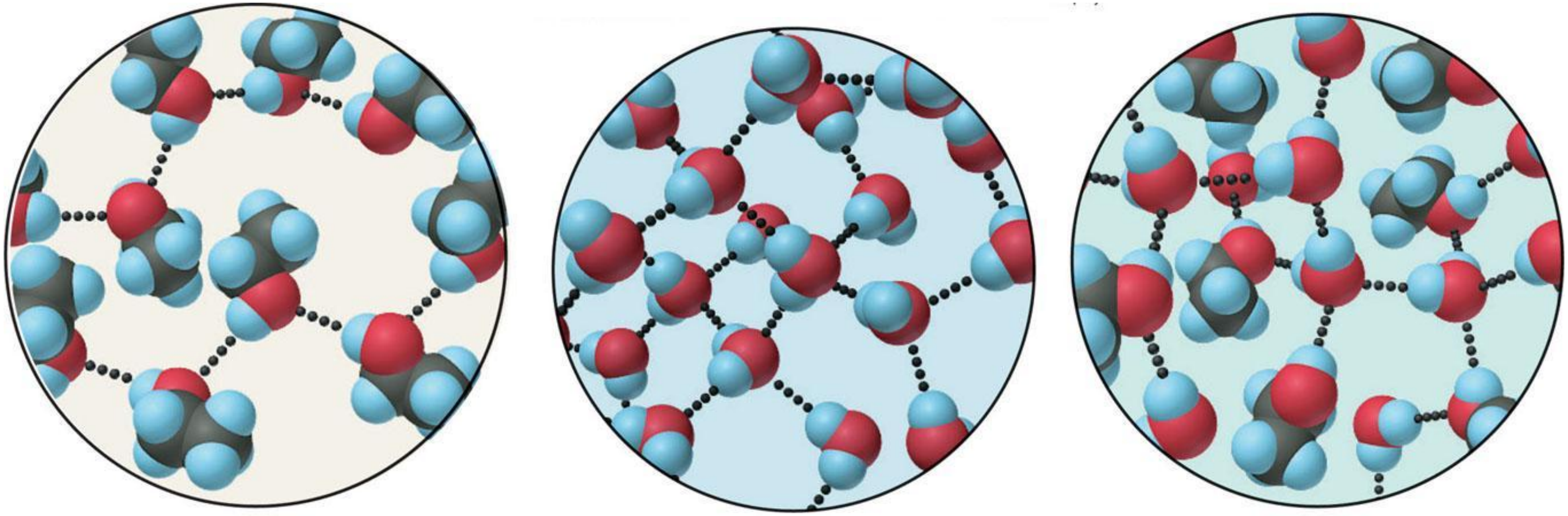
The entropy change accompanying the dissolution of a salt.



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

Figure 20.7

The small increase in entropy when ethanol dissolves in water.



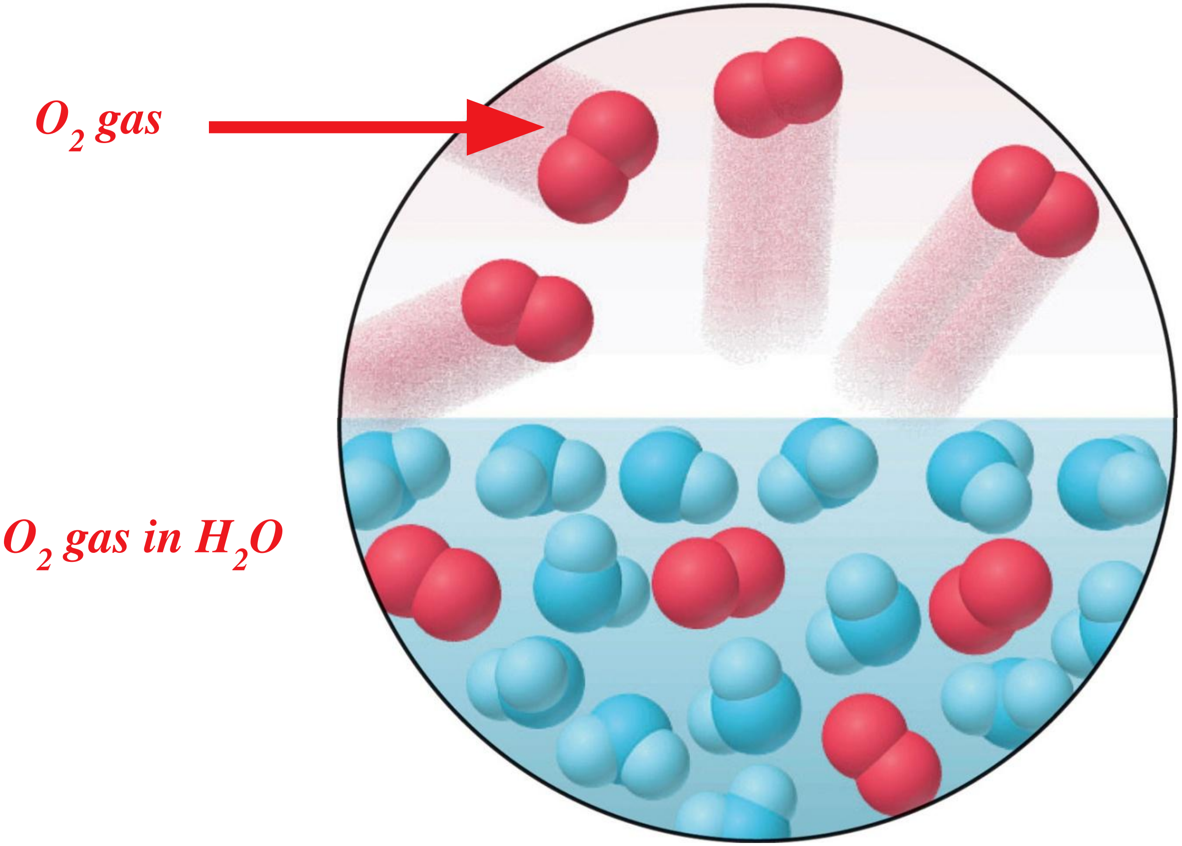
Ethanol

Water

Solution of
ethanol and
water

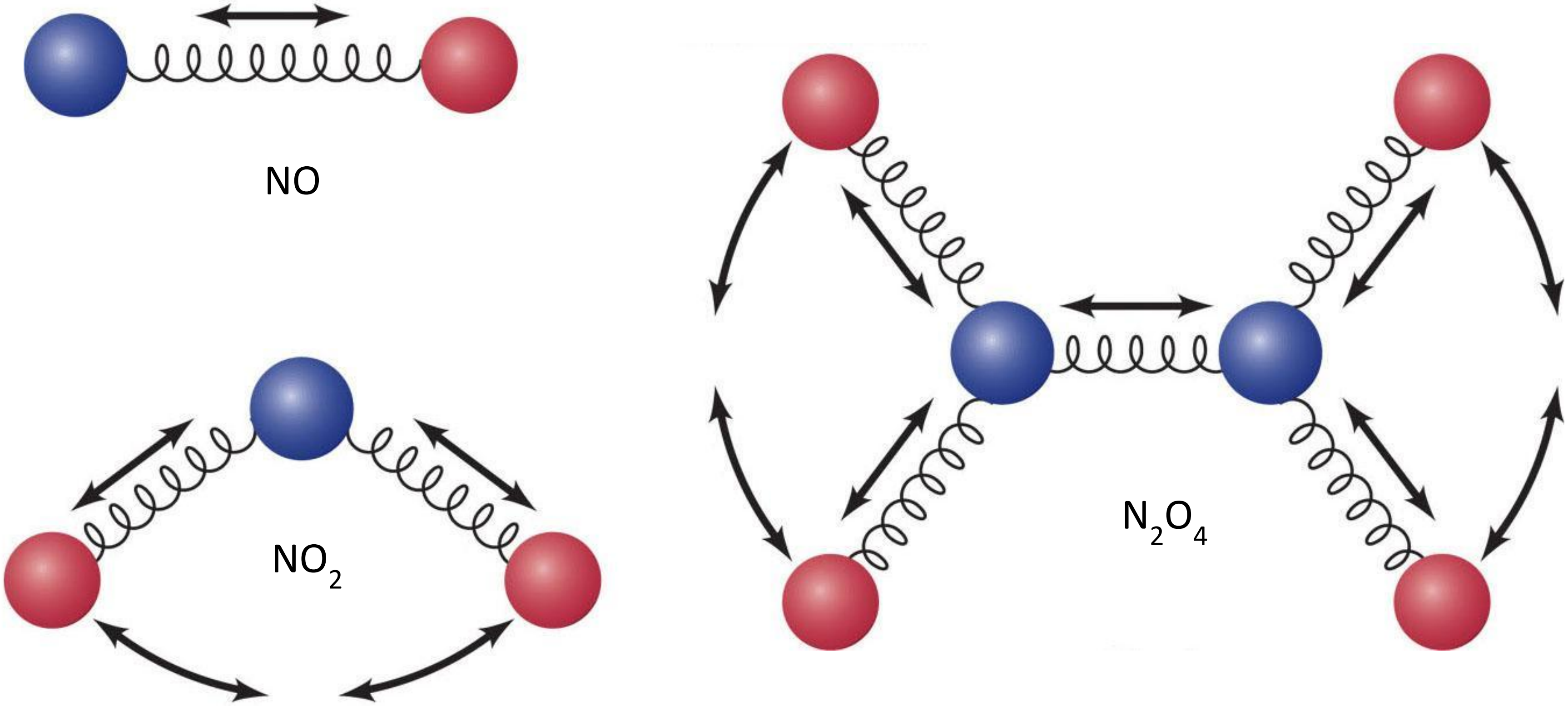
Figure 20.8

The large decrease in entropy when a gas dissolves in a liquid.



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

Figure 20.9 **Entropy and vibrational motion.**



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

Sample Problem 20.1: Predicting Relative Entropy Values

PROBLEM: Choose the member with the higher entropy in each of the following pairs, and justify your choice [assume constant temperature, except in part (e)]:

(a) 1mol of $SO_2(g)$ or 1mol of $SO_3(g)$
(b) 1mol of $CO_2(s)$ or 1mol of $CO_2(g)$
(c) 3mol of oxygen gas (O_2) or 2mol of ozone gas (O_3)
(d) 1mol of $KBr(s)$ or 1mol of $KBr(aq)$
(e) Seawater in midwinter at 2^0C or in midsummer at 23^0C
(f) 1mol of $CF_4(g)$ or 1mol of $CCl_4(g)$

PLAN: In general less ordered systems have higher entropy than ordered systems and entropy increases with an increase in temperature.

SOLUTION:

(a) 1mol of $SO_3(g)$ - more atoms

(b) 1mol of $CO_2(g)$ - gas > solid

(c) 3mol of $O_2(g)$ - larger #mols

(d) 1mol of $KBr(aq)$ - solution > solid

(e) 23^0C - higher temperature

(f) CCl_4 - larger mass

20.2 – Calculating the Change in Entropy of a Reaction

Sample Problem 20.2: Calculating the Standard Entropy of Reaction, ΔS^0_{rxn}

PROBLEM: Calculate ΔS^0_{rxn} for the combustion of 1mol of propane at 25^0C.

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

PLAN: Use summation equations. It is obvious that entropy is being lost because the reaction goes from 6 mols of gas to 3 mols of gas.

SOLUTION: Find standard entropy values in the Appendix or other table.

$\Delta S = [(3\ mol)(S^0\ CO_2) + (4\ mol)(S^0\ H_2O)] - [(1\ mol)(S^0\ C_3H_8) + (5\ mol)(S^0\ O_2)]$

$\Delta S = [(3\ mol)(213.7 J/mol*K) + (4\ mol)(69.9 J/mol*K)] - [(1\ mol)(269.9 J/mol*K) + (5\ mol)(205.0 J/mol*K)]$

$\Delta S = -\ 374\ J/K$

20.2 – Calculating the Change in Entropy of a Reaction

Sample Problem 20.3: Determining Reaction Spontaneity

PROBLEM: At 298K, the formation of ammonia has a negative ΔS^0_{sys};

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta S^0_{sys} = -197\ J/K$$

Calculate ΔS^0_{rxn}, and state whether the reaction occurs spontaneously at this temperature.

PLAN: $\Delta S^0_{universe}$ must be > 0 in order for this reaction to be spontaneous, so $\Delta S^0_{surroundings}$ must be > 197 J/K. To find ΔS^0_{surr}, first find ΔH_{sys}; $\Delta H_{sys} = \Delta H_{rxn}$ which can be calculated using ΔH^0_f values from tables. $\Delta S^0_{universe} = \Delta S^0_{surr} + \Delta S^0_{sys}$.

SOLUTION:

$$\Delta H^0_{rx} = [(2\ mol)(\Delta H^0_f NH_3)] - [(1\ mol)(\Delta H^0_f N_2) + (3\ mol)(\Delta H^0_f H_2)]$$

$$\Delta H^0_{rx} = -91.8\ kJ$$

$$\Delta S^0_{surr} = -\Delta H^0_{sys}/T = -(-91.8x10^3 J/298K) = 308\ J/K$$

$$\Delta S^0_{universe} = \Delta S^0_{surr} + \Delta S^0_{sys} = 308\ J/K + (-197\ J/K) = 111\ J/K$$

$\Delta S^0_{universe}$ > 0 so the reaction is spontaneous.

Sample Problem 20.4: Calculating ΔG^0 from Enthalpy and Entropy Values

PROBLEM: Potassium chlorate, a common oxidizing agent in fireworks and matchheads, undergoes a solid-state disproportionation reaction when heated.

Note that the oxidation number of Cl in the reactant is higher in one of the products and lower in the other (disproportionation).

$$\overset{+5}{4KClO_3}(s) \xrightarrow{\Delta} \overset{+7}{3KClO_4}(s) + \overset{-1}{KCl}(s)$$

Use ΔH^0_f and S^0 values to calculate ΔG^0_{sys} (ΔG^0_{rxn}) at 25^{0}C for this reaction.

PLAN: Use Appendix B values for thermodynamic entities; place them into the Gibbs Free Energy equation and solve.

SOLUTION:

$$\Delta H^0_{rxn} = \Sigma\, m\Delta H^0_{products} - \Sigma\, n\Delta H^0_{reactants}$$

$$\Delta H^0_{rxn} = (3\text{ mol})(-432.8\text{ kJ/mol}) + (1\text{ mol})(-436.7\text{ kJ/mol}) - (4\text{ mol})(-397.7\text{ kJ/mol})$$

$$\Delta H^0_{rxn} = -144\text{ kJ}$$

Sample Problem 20.4: **Calculating ΔG^0 from Enthalpy and Entropy Values**

continued

$$\Delta S^0_{rxn} = \Sigma\, m\Delta S^0_{products} - \Sigma\, n\Delta S^0_{reactants}$$

$$\Delta S^0_{rxn} = (3\text{ mol})(151\text{ J/mol*K}) + (1\text{ mol})(82.6\text{ J/mol*K}) - (4\text{ mol})(143.1\text{ J/mol*K})$$

$$\Delta S^0_{rxn} = -36.8\text{ J/K}$$

$$\Delta G^0_{rxn} = \Delta H^0_{rxn} - T\,\Delta S^0_{rxn}$$

$$\Delta G^0_{rxn} = -144\text{ kJ} - (298\text{K})(-36.8\text{ J/K})(\text{kJ}/10^3\text{ J})$$

$$\Delta G^0_{rxn} = -133\text{ kJ}$$

Sample Problem 20.5: Calculating ΔG^0_{rxn} from ΔG^0_f Values

PROBLEM: Use ΔG^0_f values to calculate ΔG_{rxn} for the reaction in Sample Problem 20.4:

$$4KClO_3(s) \xrightarrow{\Delta} 3KClO_4(s) + KCl(s)$$

PLAN: Use the ΔG summation equation.

SOLUTION:

$$\Delta G^0_{rxn} = \Sigma\, m\Delta G^0_{products} - \Sigma\, n\Delta G^0_{reactants}$$

$$\Delta G^0_{rxn} = (3mol)(-303.2kJ/mol) + (1mol)(-409.2kJ/mol) - (4mol)(-296.3kJ/mol)$$

$$\Delta G^0_{rxn} = -134kJ$$

Sample Problem 20.6: Determining the Effect of Temperature on ΔG^0

PROBLEM: An important reaction in the production of sulfuric acid is the oxidation of $SO_2(g)$ to $SO_3(g)$:

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

At 298K, $\Delta G^0 = -141.6kJ$; $\Delta H^0 = -198.4kJ$; and $\Delta S^0 = -187.9J/K$

(a) Use the data to decide if this reaction is spontaneous at 25^0C, and predict how ΔG^0 will change with increasing T.

(b) Assuming ΔH^0 and ΔS^0 are constant with increasing T, is the reaction spontaneous at $900.^0$C?

PLAN: The sign of ΔG^0 tells us whether the reaction is spontaneous and the signs of ΔH^0 and ΔS^0 will be indicative of the T effect. Use the Gibbs free energy equation for part (b).

SOLUTION: **(a)** The reaction is spontaneous at 25^0C because ΔG^0 is (-). Since ΔH^0 is (-) but ΔS^0 is also (-), ΔG^0 will become less spontaneous as the temperature increases.

Sample Problem 20.6: Determining the Effect of Temperature on ΔG^0

continued

(b) $\Delta G^0_{rxn} = \Delta H^0_{rxn} - T\,\Delta S^0_{rxn}$

ΔG^0_{rxn} = -198.4kJ - (1173K)(-187.9J/mol*K)(kJ/10^3J)

ΔG^0_{rxn} = 22.0 kJ; the reaction will be nonspontaneous at 900.^{0}C

20.3 – Entropy, Free Energy, and Work

Figure B20.3

The coupling of a nonspontaneous reaction to the hydrolysis of ATP.

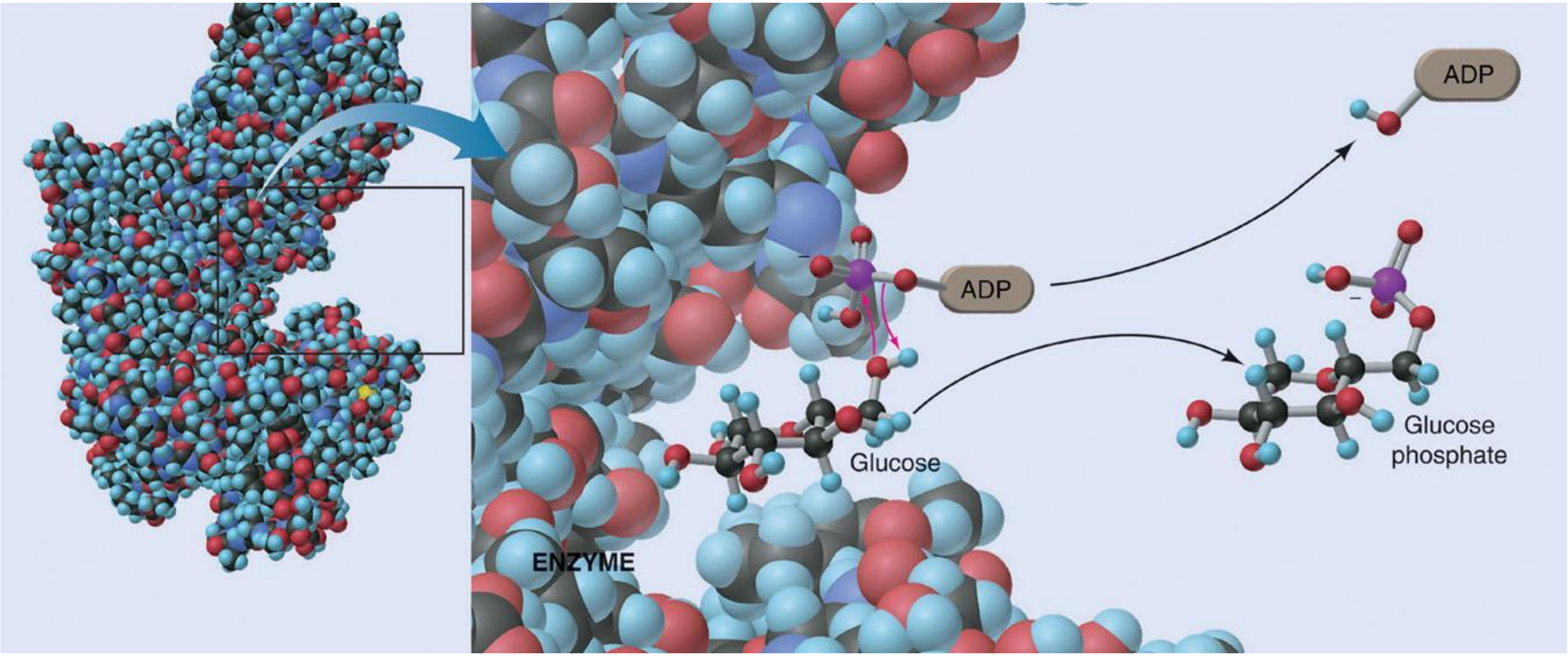
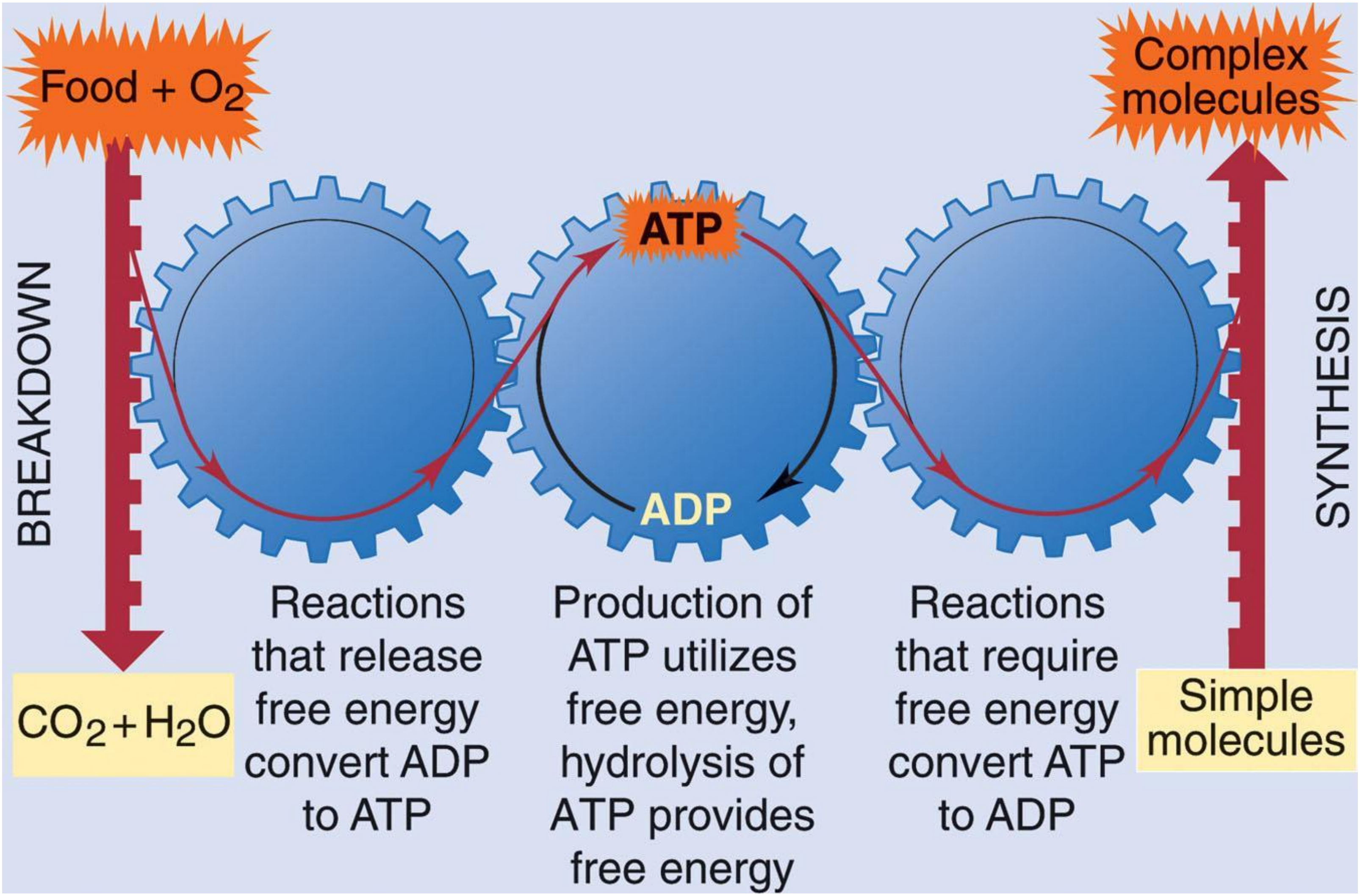


Figure B20.4 **The cycling of metabolic free enery through ATP**



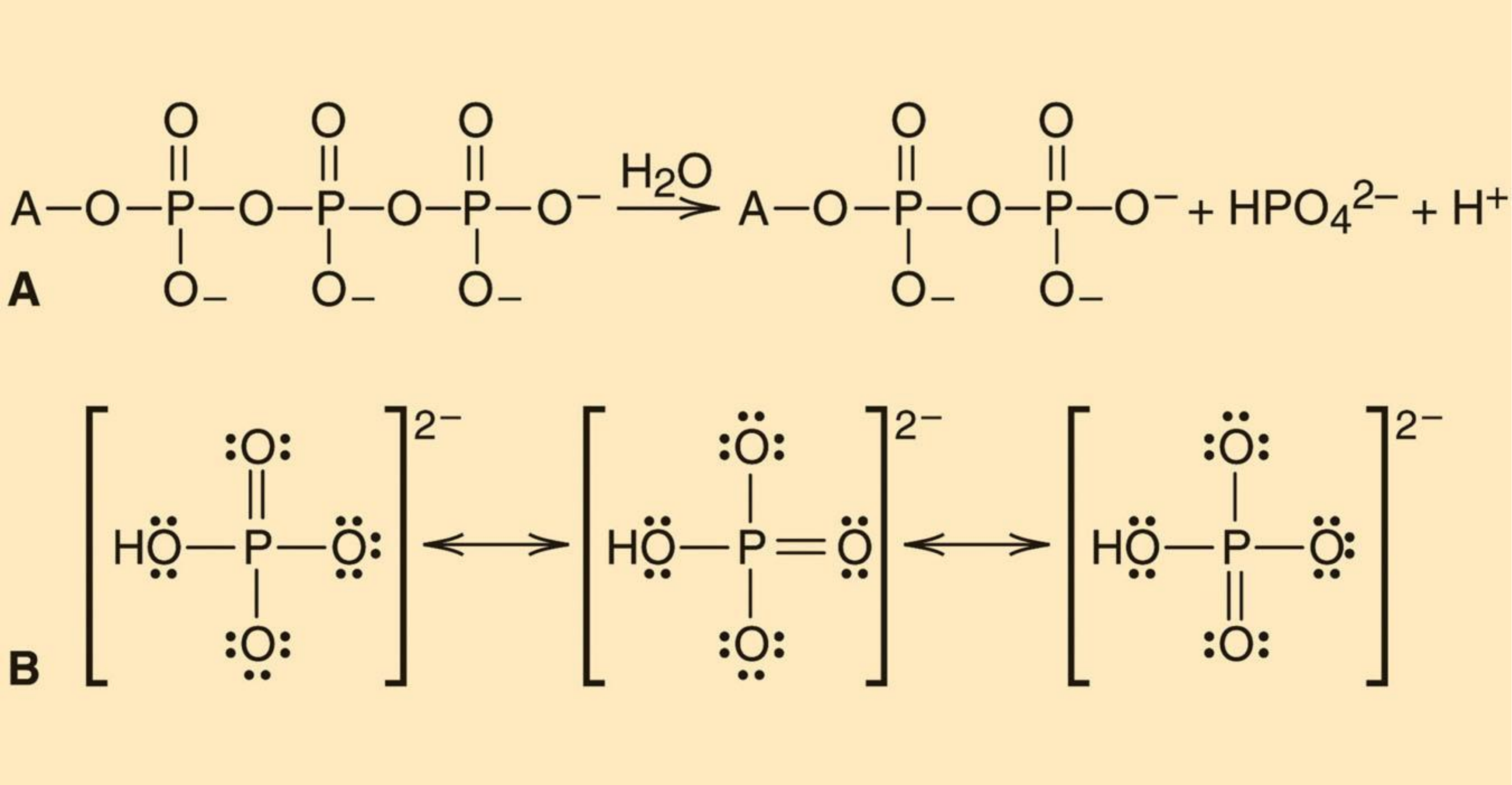
Reactions that release free energy convert ADP to ATP

Production of ATP utilizes free energy, hydrolysis of ATP provides free energy

Reactions that require free energy convert ATP to ADP

Figure B20.5

Why is ATP a high-energy molecule?



Free Energy, Equilibrium and Reaction Direction

- If $Q/K < 1$, then $\ln Q/K < 0$; the reaction proceeds to the right ($\Delta G < 0$)
- If $Q/K > 1$, then $\ln Q/K > 0$; the reaction proceeds to the left ($\Delta G > 0$)
- If $Q/K = 1$, then $\ln Q/K = 0$; the reaction is at equilibrium ($\Delta G = 0$)

$$\Delta G = RT \ln Q/K = RT \ln Q - RT \ln K$$

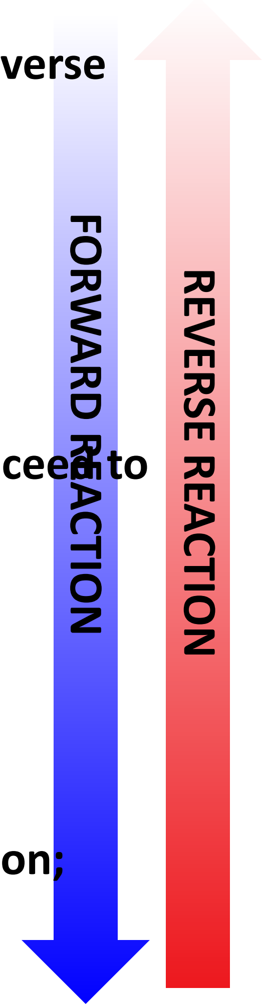
Under standard conditions (1M concentrations, 1atm for gases), $Q = 1$ and $\ln Q = 0$ so

$$\Delta G^0 = - RT \ln K$$

20.4 – Free Energy, Equilibrium, and Reaction Direction

Table 20.2 The Relationship Between ΔG^0 and K at 25^0C

ΔG^0(kJ)	K	Significance
200	$9x10^{-36}$	Essentially no forward reaction; reverse reaction goes to completion
100	$3x10^{-18}$	
50	$2x10^{-9}$	
10	$2x10^{-2}$	
1	$7x10^{-1}$	Forward and reverse reactions proceed to same extent
0	1	
-1	1.5	
-10	$5x10^{1}$	
-50	$6x10^{8}$	
-100	$3x10^{17}$	Forward reaction goes to completion; essentially no reverse reaction
-200	$1x10^{35}$	



Sample Problem 20.7: **Calculating ΔG at Nonstandard Conditions**

PROBLEM: The oxidation of SO_2, which we considered in Sample Problem 20.6

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

is too slow at 298K to be useful in the manufacture of sulfuric acid. To overcome this low rate, the process is conducted at an elevated temperature.

(a) Calculate K at 298K and at 973K. (ΔG^0_{298} = -141.6kJ/mol of reaction as written using ΔH^0 and ΔS^0 values at 973K. ΔG^0_{973} = -12.12kJ/mol of reaction as written.)

(b) In experiments to determine the effect of temperature on reaction spontaneity, two sealed containers are filled with 0.500atm of SO_2, 0.0100atm of O_2, and 0.100atm of SO_3 and kept at 25^0C and at $700.^0$C. In which direction, if any, will the reaction proceed to reach equilibrium at each temperature?

(c) Calculate ΔG for the system in part (b) at each temperature.

Sample Problem 20.7: Calculating ΔG at Nonstandard Conditions

continued (2 of 3)

SOLUTION: **(a)** Calculating K at the two temperatures:

$\Delta G^0 = -RT\ln K$ so $K = e^{-(\Delta G^\circ/RT)}$

At 298, the exponent is $-\Delta G^0/RT$ $= -\dfrac{(-141.6\text{kJ/mol})(10^3\text{J/kJ})}{(8.314\text{J/mol*K})(298\text{K})} = 57.2$

$K = e^{-(\Delta G^\circ/RT)} = e^{57.2}$ $= 7\text{x}10^{24}$

At 973, the exponent is $-\Delta G^0/RT$ $\dfrac{(-12.12\text{kJ/mol})(10^3\text{J/kJ})}{(8.314\text{J/mol*K})(973\text{K})} = 1.50$

$K = e^{-(\Delta G^\circ/RT)} = e^{1.50}$ $= 4.5$

Sample Problem 20.7: Calculating ΔG at Nonstandard Conditions

continued (3 of 3)

(b) The value of Q =

$$\frac{p_{SO_3}{}^2}{(p_{SO_2})^2(p_{O_2})} = \frac{(0.100)^2}{(0.500)^2(0.0100)} = 4.00$$

Since Q is < K at both temperatures the reaction will shift right; for 298K there will be a dramatic shift while at 973K the shift will be slight.

(c) The nonstandard ΔG is calculated using $\Delta G = \Delta G^0 + RT\ln Q$

$$\Delta G_{298} = -141.6\text{kJ/mol} + (8.314\text{J/mol*K})(\text{kJ}/10^3\text{J})(298\text{K})(\ln 4.00)$$

$$\Delta G_{298} = -138.2\text{kJ/mol}$$

$$\Delta G_{973} = -12.12\text{kJ/mol} + (8.314\text{J/mol*K})(\text{kJ}/10^3\text{J})(973\text{K})(\ln 4.00)$$

$$\Delta G_{298} = -0.9\text{kJ/mol}$$