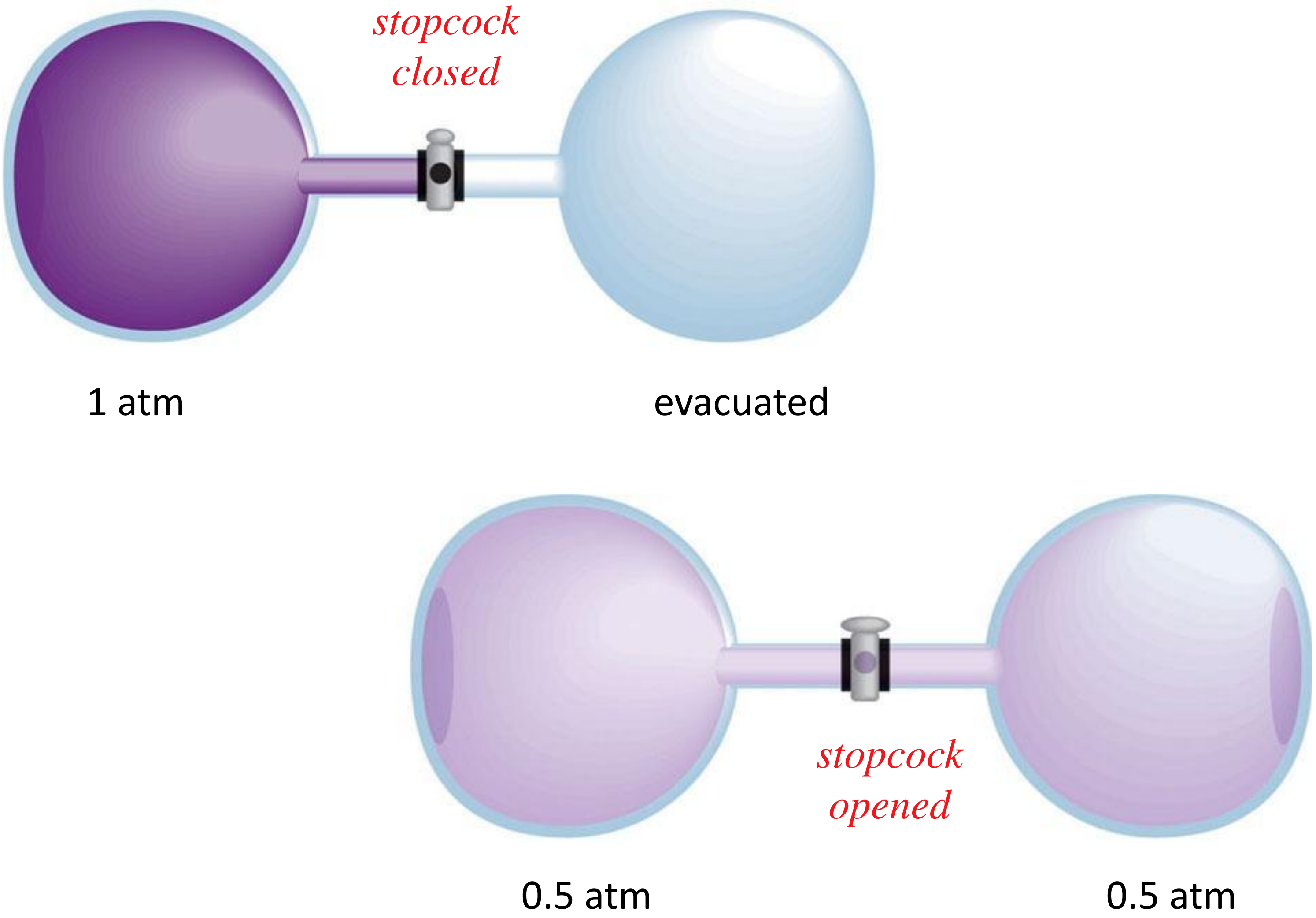
Chapter 20 – Thermodynamics

- 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

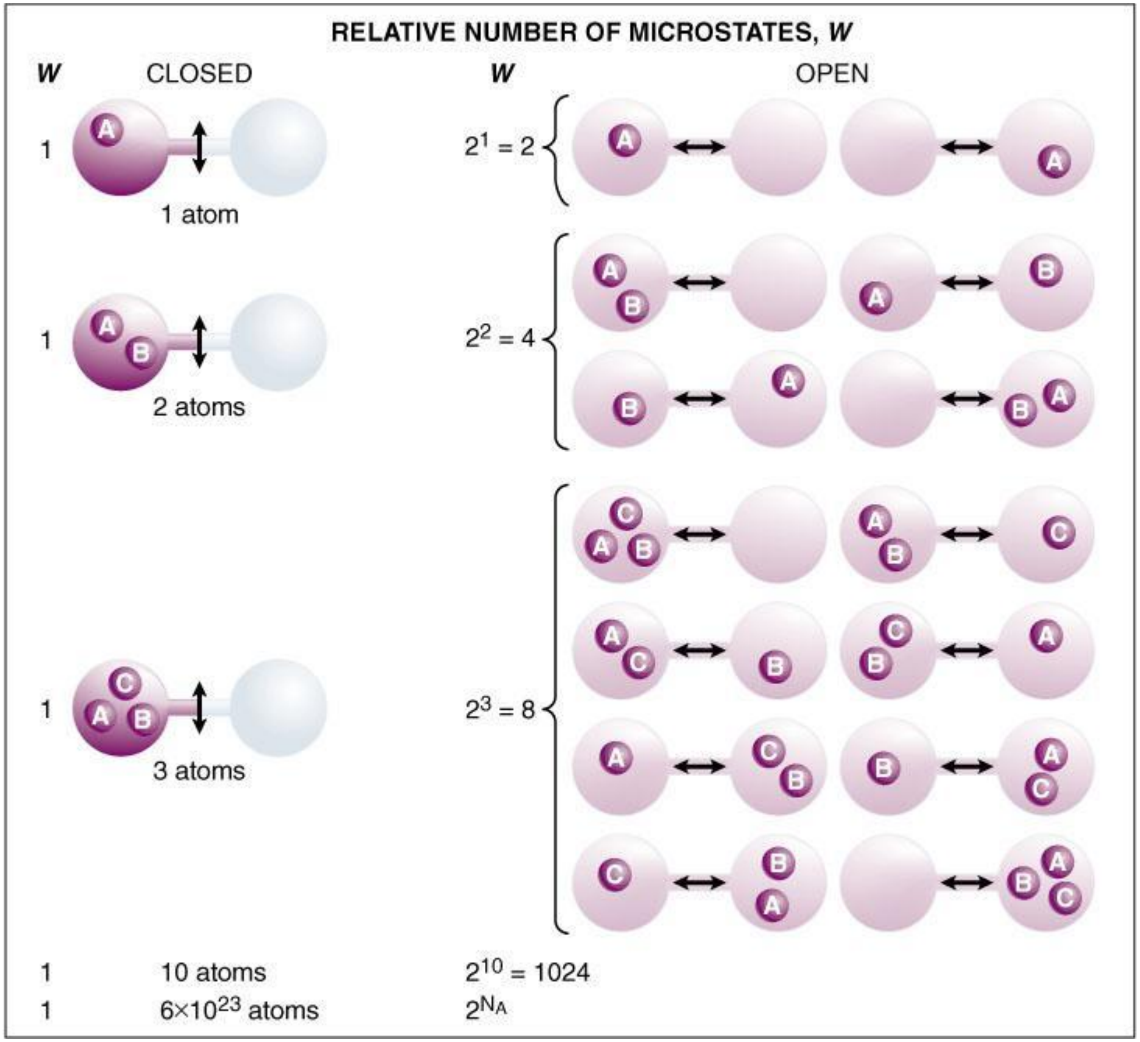
Figure 20.2 **Spontaneous expansion of a gas**



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.

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

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

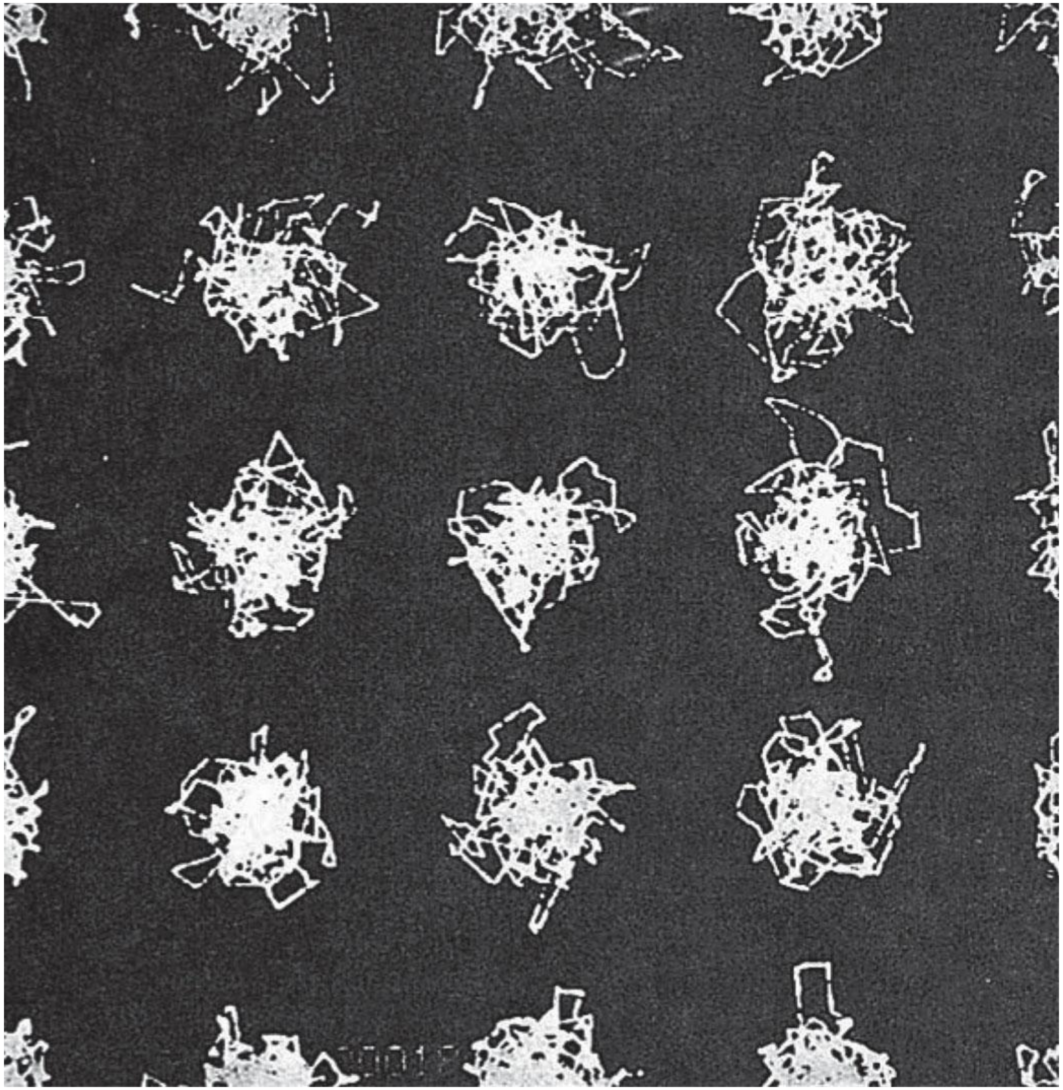
20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

Figure 20.4 **Random motion in a crystal**

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

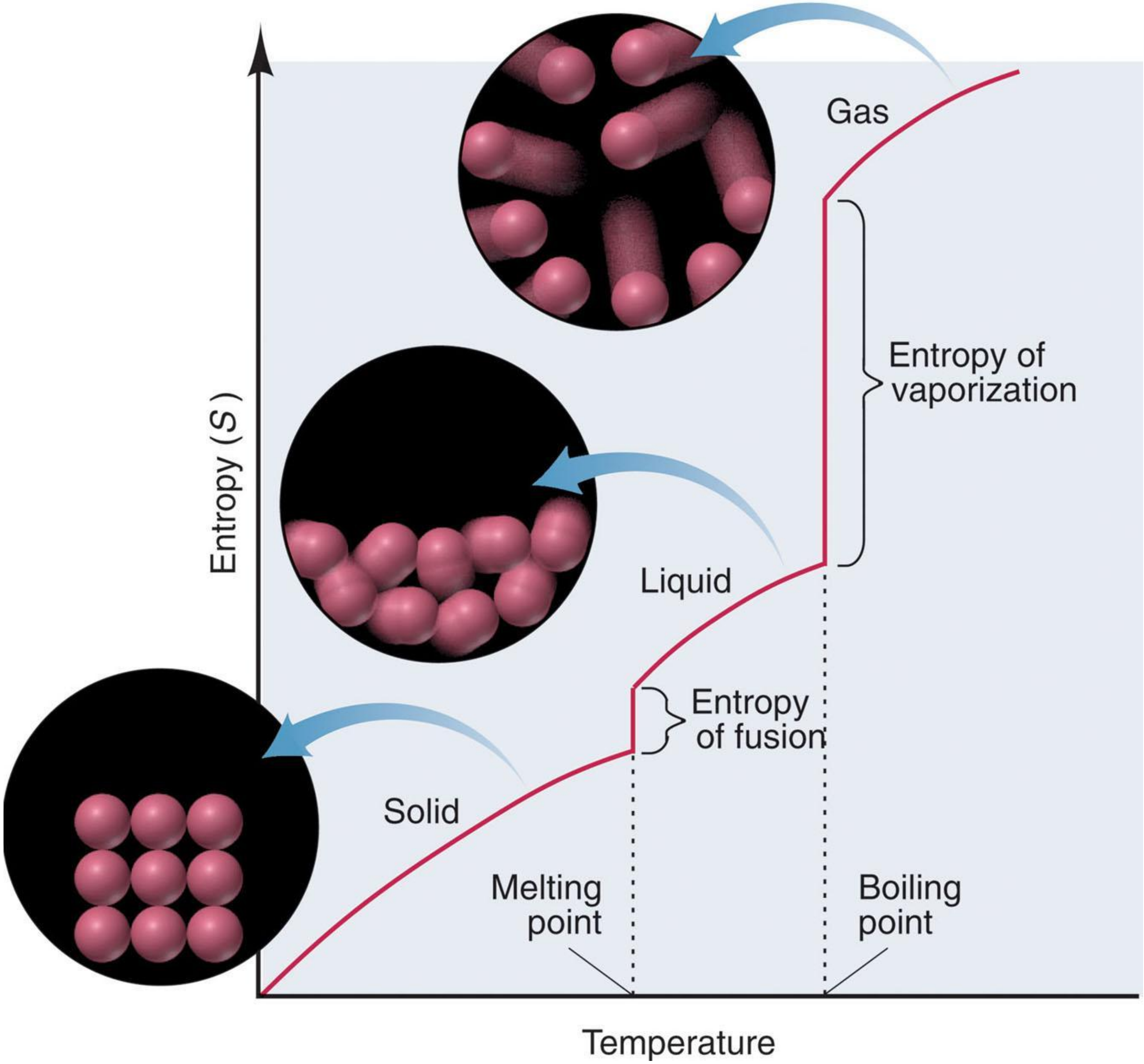
A perfect crystal has zero entropy at a temperature of *absolute zero.*

S_{system} = 0 at 0 K



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

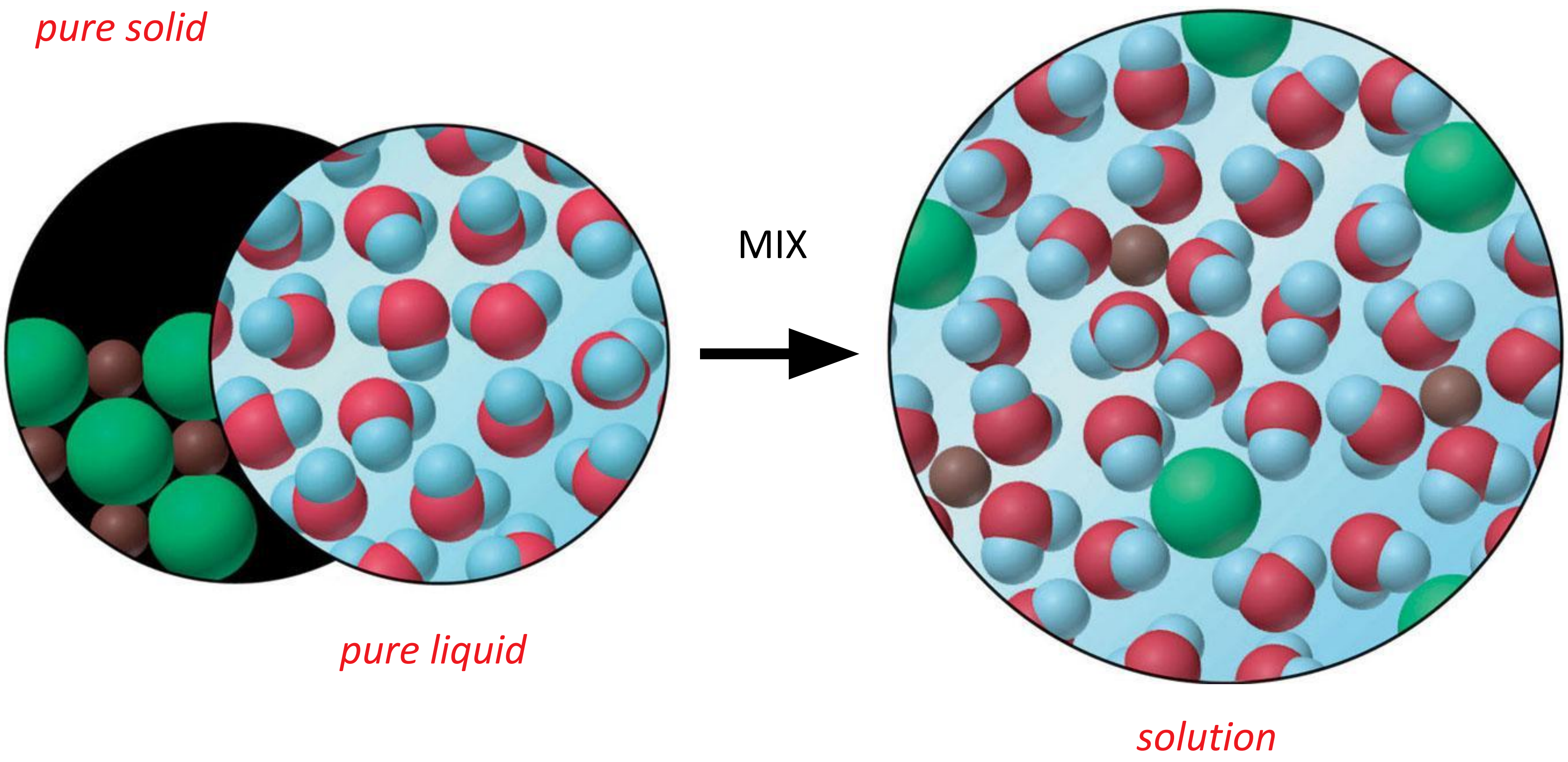
Figure 20.5 **The increase in entropy from solid to liquid to gas.**



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

Figure 20.6

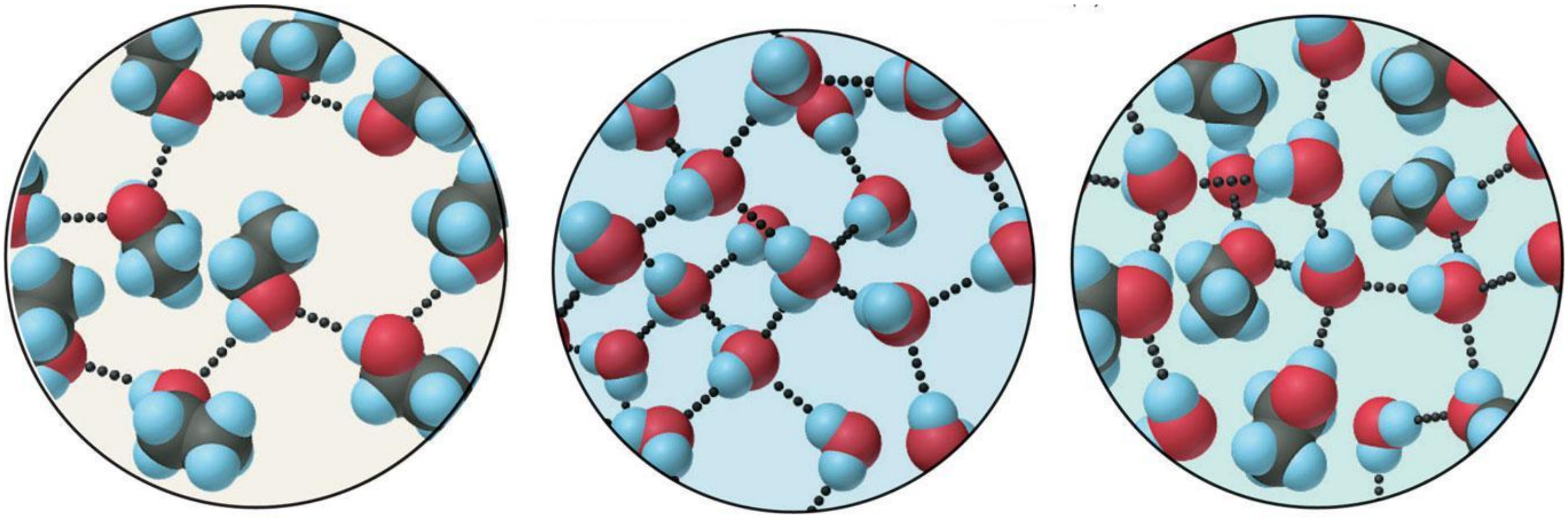
The entropy change accompanying the dissolution of a salt.



20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

Figure 20.7

The small increase in entropy when ethanol dissolves in water.



Ethanol

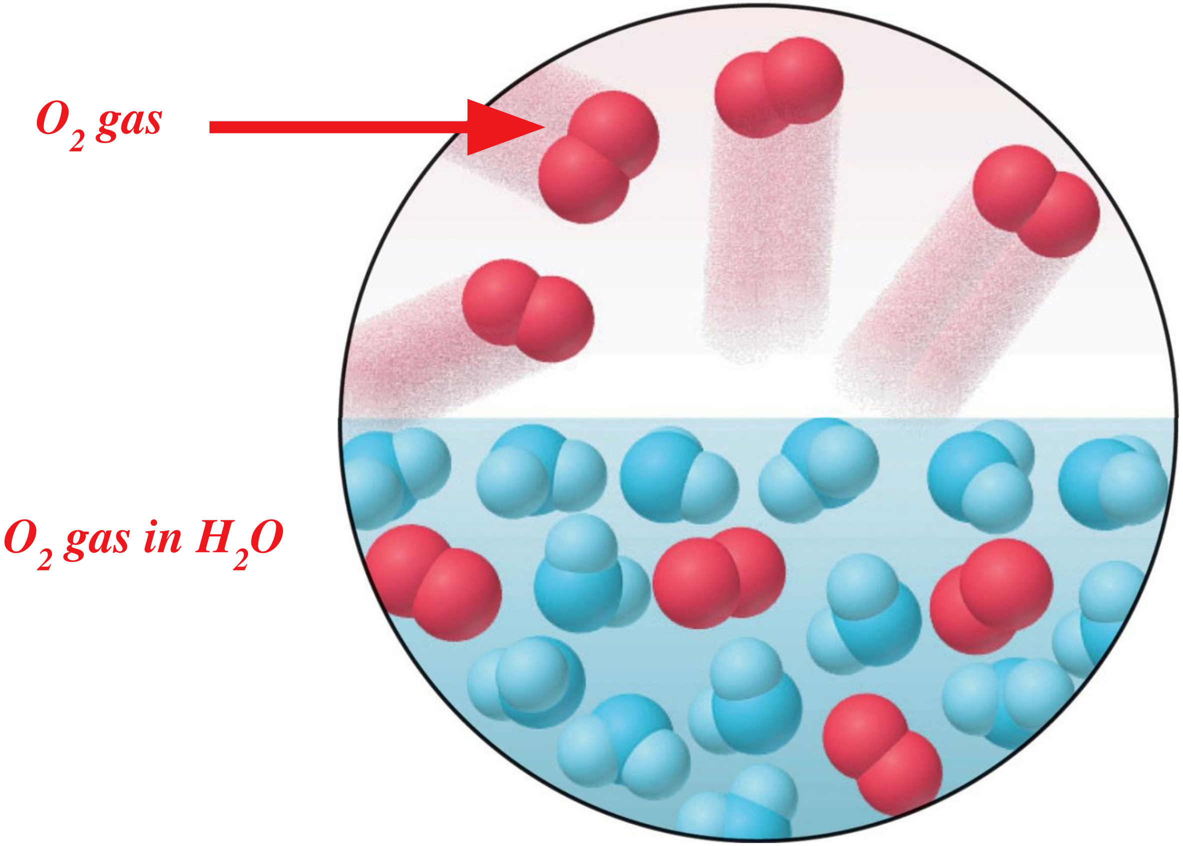
Water

Solution of ethanol and water

20.1 – The Second Law of Thermodynamics: Predicting Spontaneous Change

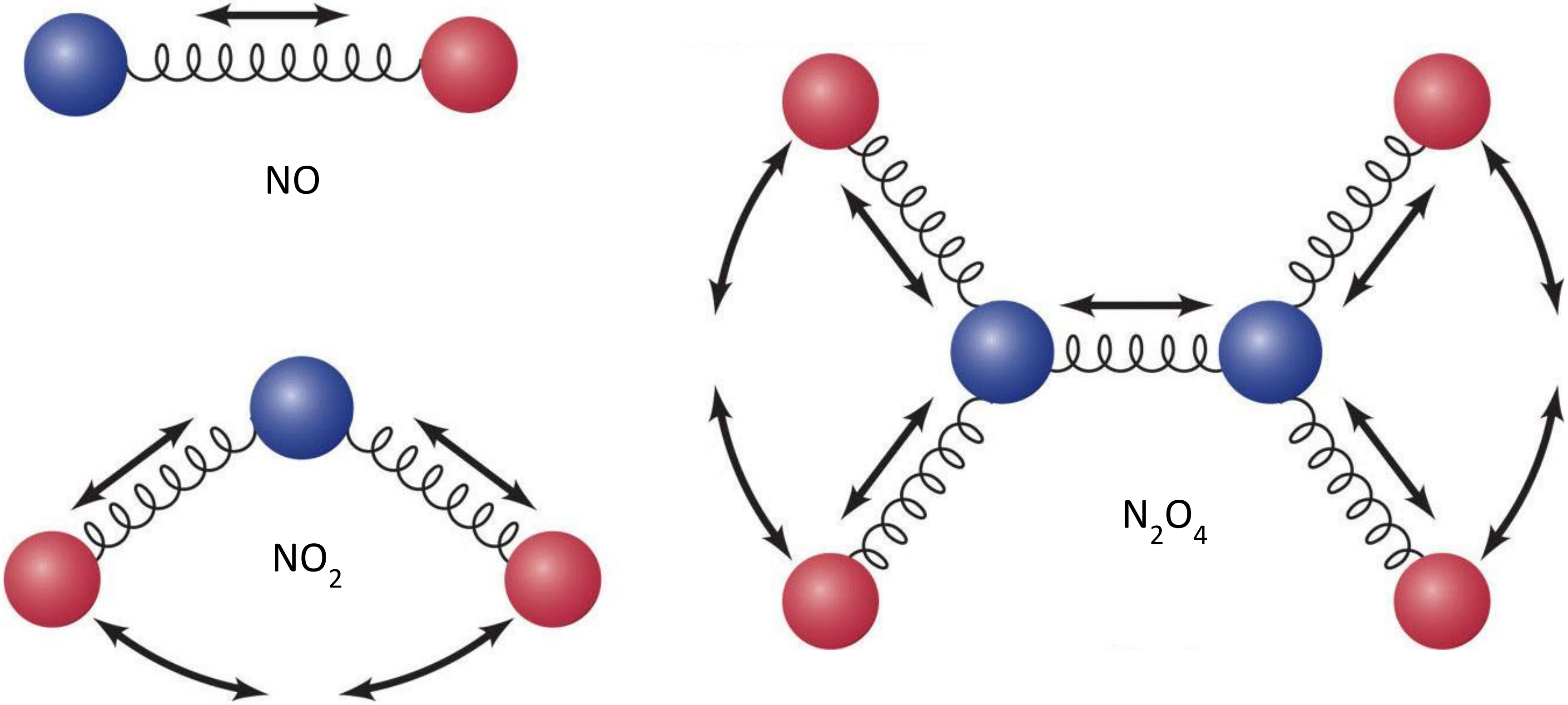
Figure 20.8

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.

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

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

$$\boxed{\Delta S = -374\text{ J/K}}$$

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 25^0C for this reaction.

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

SOLUTION:

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

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

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

20.3 – Entropy, Free Energy, and Work

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

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

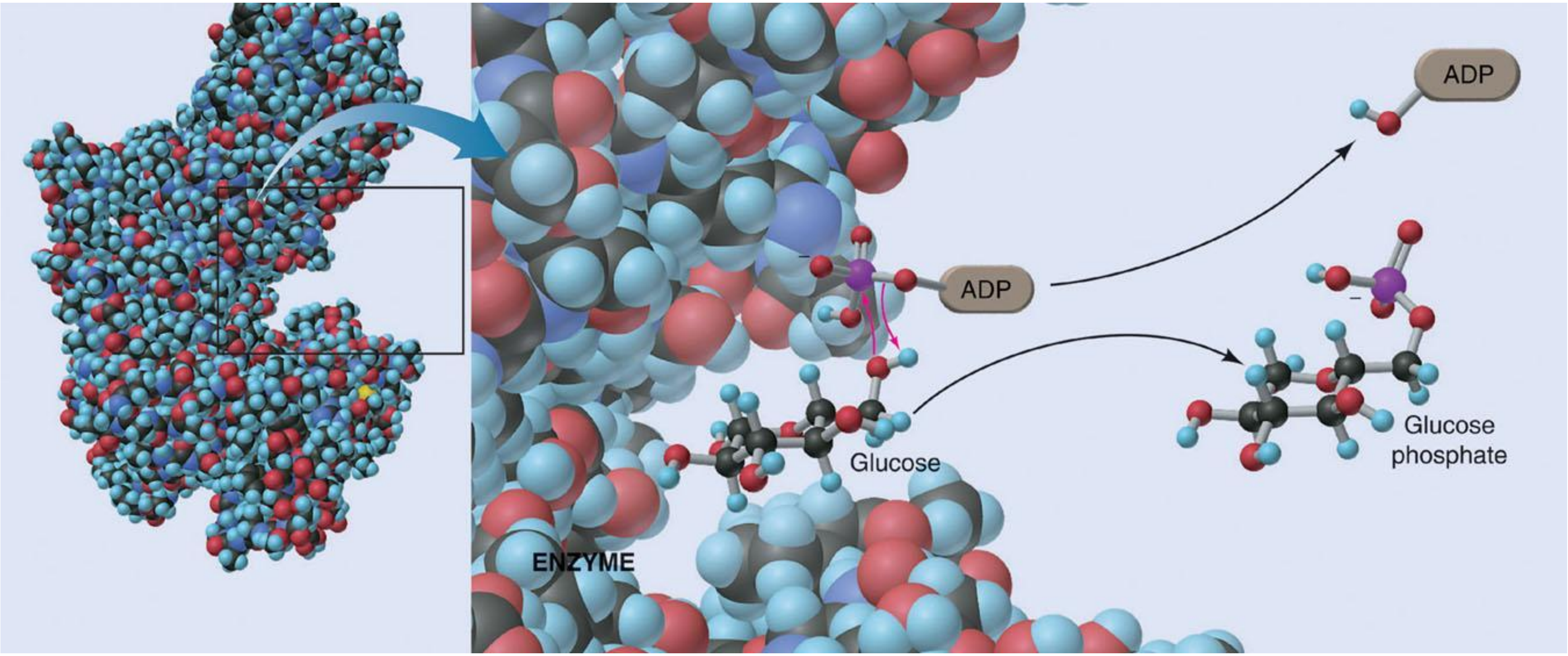
ΔG^0_{rxn} = -198.4kJ - (1173K)(-187.9J/mol*K)(kJ/10^3J)

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

20.3 – Entropy, Free Energy, and Work

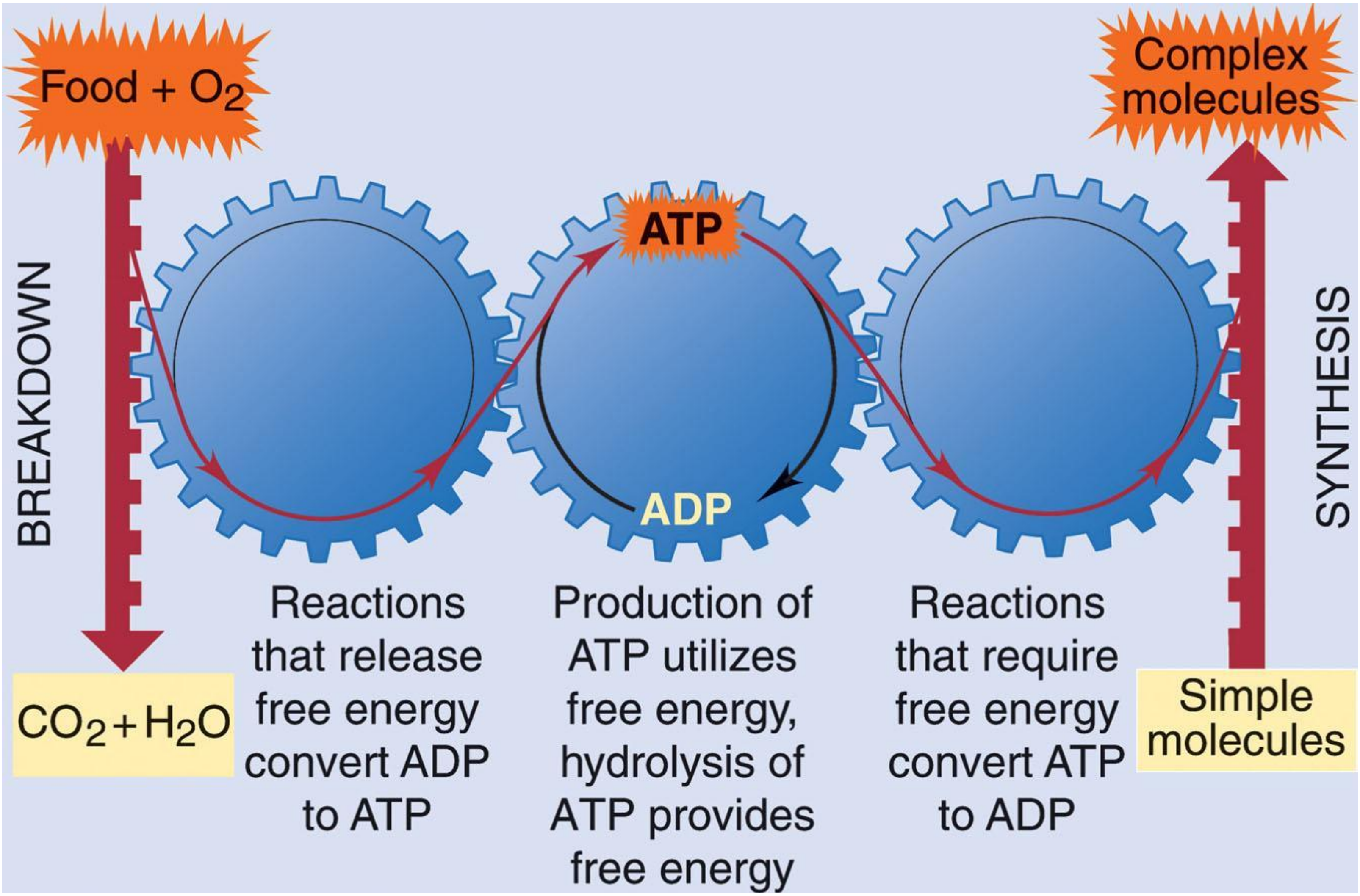
Figure B20.3

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



20.3 – Entropy, Free Energy, and Work

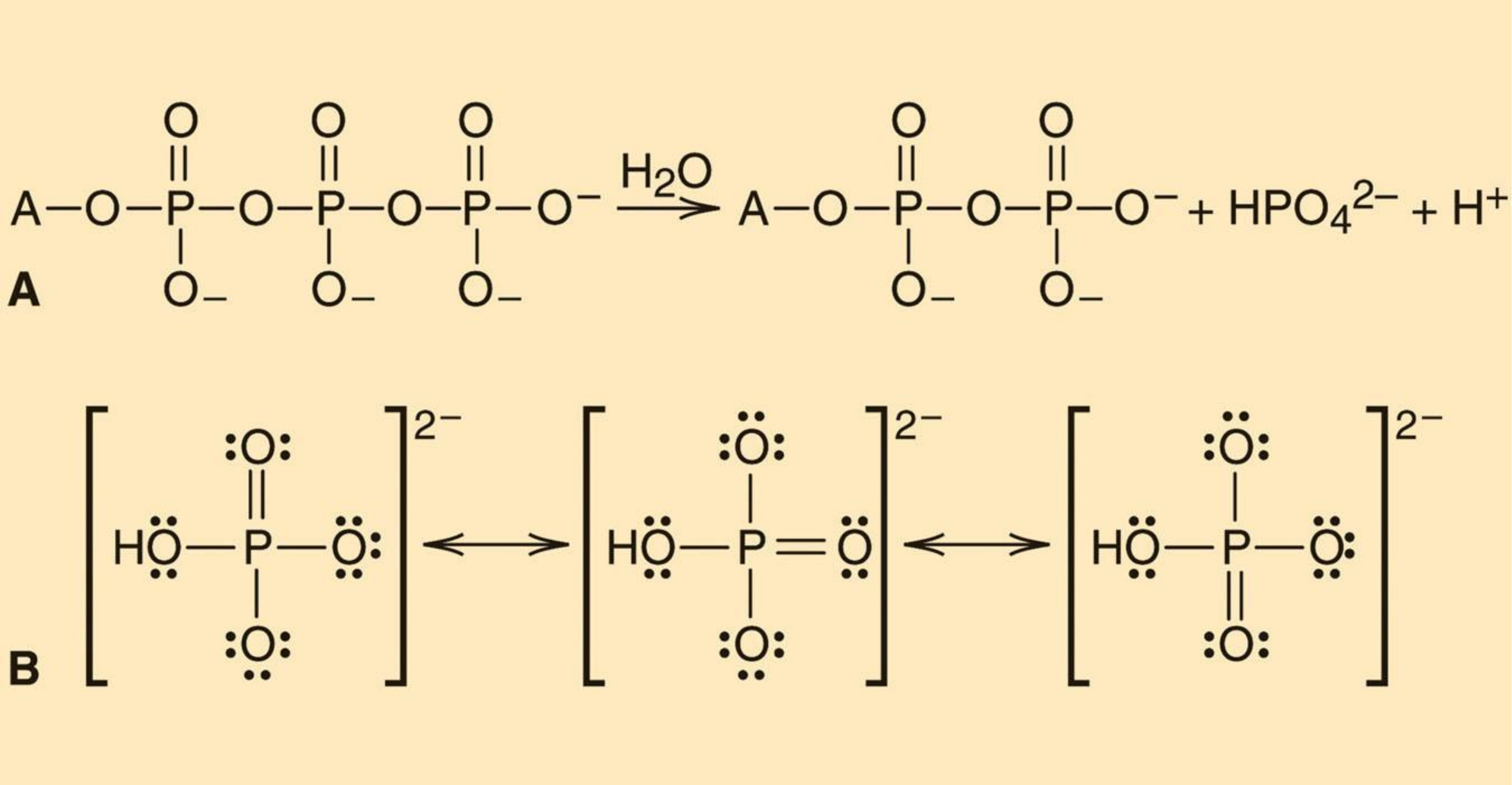
Figure B20.4 **The cycling of metabolic free enery through ATP**



20.3 – Entropy, Free Energy, and Work

Figure B20.5

Why is ATP a high-energy molecule?



20.4 – Free Energy, Equilibrium, and Reaction Direction

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 ($\Delta G = 0$)

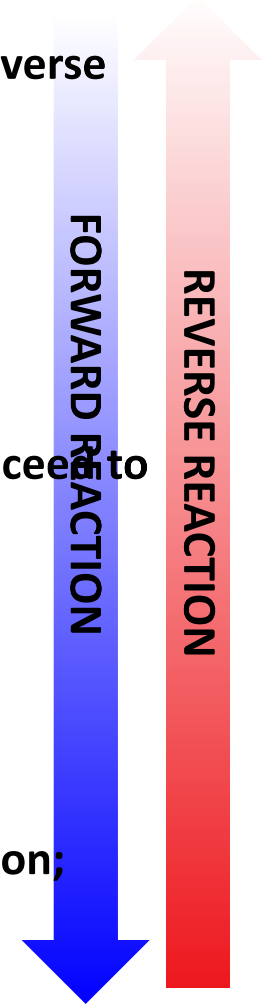
$$\Delta G = RT \ln Q/K = RT \ln Q - RT \ln K$$

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

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

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 $-\Delta G^0/RT$

$$= -\frac{(-141.6\text{kJ/mol})(10^3\text{J/kJ})}{(8.314\text{J/mol*K})(298\text{K})} = 57.2$$

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

At 973, the exponent is $-\Delta G^0/RT$

$$\frac{(-12.12\text{kJ/mol})(10^3\text{J/kJ})}{(8.314\text{J/mol*K})(973\text{K})} = 1.50$$

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

Sample Problem 20.7: Calculating ΔG at Nonstandard Conditions

continued (3 of 3)

(b) The value of Q = $\dfrac{pSO_3{}^2}{(pSO_2)^2(pO_2)} = \dfrac{(0.100)^2}{(0.500)^2(0.0100)} = 4.00$

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 $\Delta G = \Delta G^0 + RT\ln Q$

ΔG_{298} = -141.6kJ/mol + (8.314J/mol*K)(kJ/10^3J)(298K)(ln4.00)

ΔG_{298} = -138.2kJ/mol

ΔG_{973} = -12.12kJ/mol + (8.314J/mol*K)(kJ/10^3J)(973K)(ln4.00)

ΔG_{298} = -0.9kJ/mol