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William L Masterton
Cecile N. Hurley
Edward J. Neth

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Chapter 16
Spontaneity of Reaction

Edward J. Neth • University of Connecticut

Thermodynamics

- Branch of science that deals with heat and energy effects
- Start with thermochemistry (recall Chapter 8)
- Consider other quantities related to the overall favorability (or unfavorability) of reaction
- Arrive at an understanding of the effects that cause a reaction to be spontaneous

Outline

1. Spontaneous processes
2. Entropy, S
3. Free energy, G
4. Standard free energy change, ΔG°
5. Effect of temperature, pressure, and concentration on reaction spontaneity
6. The free energy change and the equilibrium constant
7. Additivity of free energy changes; coupled reactions

Answers

- The answers to the fundamental question of spontaneity are extensions of the concepts in Chapter 8
  - ΔH is the enthalpy change
    - Endothermic reactions
    - Exothermic reactions: these tend to be favorable
  - Another quantity is required to determine spontaneity
    - ΔS is the change in entropy; a positive value helps make a reaction spontaneous
  - ΔG is the change in free energy; a negative value means a reaction will be spontaneous

Fundamental Question

- Will a reaction occur by itself at a given temperature and pressure, without the exertion of any outside force?
  - In other words, is a reaction ***spontaneous***
  - This question must be asked by
    - Synthetic chemists
    - Metallurgists
    - Engineers

Spontaneous Processes

- Everyday processes that are spontaneous (take place on their own, without outside forces)
  - An ice cube will melt when added to a glass of water at room temperature
  - A mixture of hydrogen and oxygen will form water when a spark is applied
  - An iron (or steel) tool will rust if exposed to moist air

The Chemistry of Spontaneous Reactions

- $H_2O\ (s) \rightarrow H_2O\ (l)$
- $2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (l)$
- $2Fe\ (s) + 3/2\ O_2\ (g) \rightarrow Fe_2O_3\ (s)$

- All three reactions are spontaneous

The Energy Factor

- Many spontaneous processes proceed with a decrease in energy
  - Boulders roll downhill
  - Your notebook computer's battery discharges as you use the system if it is unplugged from the wall
- Recall that exothermic reactions proceed with a decrease in energy
  - Spontaneous reactions are typically exothermic
- The reverse is also true
  - Exothermic reactions are typically spontaneous

Spontaneity

- It is important not to confuse spontaneous with fast – rate of reaction and spontaneity are not necessarily connected
- If a reaction is spontaneous in one direction, it will be non-spontaneous in the reverse direction under the same conditions
  - Water does not spontaneously decompose into hydrogen and oxygen at room temperature without sustained outside influence

Exceptions

- The simple rule fails for phase changes
  - $H_2O\ (s) \rightarrow H_2O\ (l)$ is endothermic but spontaneous at room temperature
- Some reactions become spontaneous with a simple increase in temperature
  - $CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g) \quad \Delta H = +178.3\ kJ$
- Clearly, ΔH is not the only criterion for spontaneity

Spontaneity and Equilibrium

- A ***spontaneous*** process moves a reaction system ***toward equilibrium***
- A ***nonspontaneous*** process moves a reaction system ***away from equilibrium***

The Randomness Factor

- Nature tends to move spontaneously from a state of lower probability (order) to one of higher probability (disorder), or
- Each system which is left to its own, will, over time, change toward a condition of maximum probability

Roll of the Dice

- When rolling a pair of dice:
  - There is only one way to roll a 2 or a 12
  - There are six ways to roll a 7
  - The probability of rolling a 7 is six times greater than that of rolling 2 or 12
  - The state 7 is of higher probability than the state 2 or 12

Mixing Gases

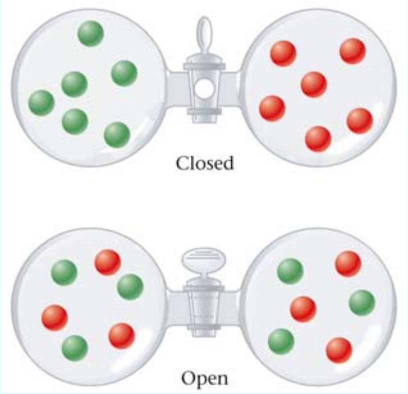
- When an apparatus consisting of flasks of hydrogen and nitrogen is opened to allow the gases to mix, the process proceeds with the result being a random mix of both molecules
  - This process is spontaneous
  - The system will not spontaneously separate itself into hydrogen and nitrogen
  - The mixture is more random than the pure gases

Figure 16.1

Random States

- In general
  - ***Nature tends to move from more ordered to more random states***
  - Randomness is of higher probability than order

Figure 16.2



Entropy, *S*

- Entropy is given the symbol *S*
- Entropy is often described as an increase in disorder or randomness
  - Consider microstates: different ways in which molecules can be distributed
  - An increase in the number of microstates is an increase in entropy
  - The larger the number of possible microstates, the more probable the state, and the greater the entropy

Figure 16.3 – Disorder and Order

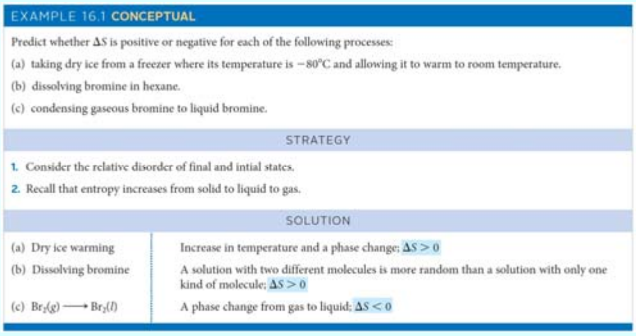
The Third Law of Thermodynamics

- A completely ordered, pure crystalline solid at 0 K has an entropy of zero
  - This is the only time the entropy of a substance is zero
  - Absolute zero has not been reached; it is still a theoretical limit

Factors that Influence Entropy

- A liquid has higher entropy than the solid from which it formed
  - Liquids are more random than solids
- A gas has higher entropy than the liquid or solid from which it formed
  - Gases are more random than either liquids or solids
- Increasing the temperature of a substance increases entropy
  - Molecular kinetic energy increases, and with it, randomness

Example 16.1



EXAMPLE 16.1 **CONCEPTUAL**

Predict whether ΔS is positive or negative for each of the following processes:

(a) taking dry ice from a freezer where its temperature is −80°C and allowing it to warm to room temperature.

(b) dissolving bromine in hexane.

(c) condensing gaseous bromine to liquid bromine.

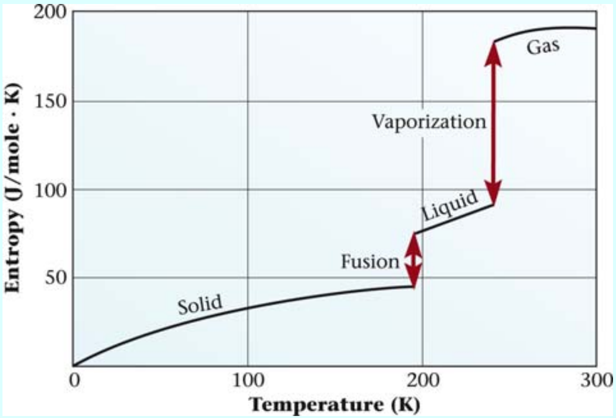
STRATEGY

1. Consider the relative disorder of final and intial states.
2. Recall that entropy increases from solid to liquid to gas.

SOLUTION

(a) Dry ice warming	Increase in temperature and a phase change; $\Delta S > 0$
(b) Dissolving bromine	A solution with two different molecules is more random than a solution with only one kind of molecule; $\Delta S > 0$
(c) $Br_2(g) \longrightarrow Br_2(l)$	A phase change from gas to liquid; $\Delta S < 0$

Figure 16.4



Entropy Change and a Gas-Evolving Reaction

- Decomposition of $NH_4NO_3 \rightarrow N_2O\ (g) + 2H_2O\ (g)$

Entropy and Entropy Changes

- The standard molar entropy of a substance is given the symbol, S°
- The standard molar entropy change for a process is given the symbol, ΔS°

Table 16.1

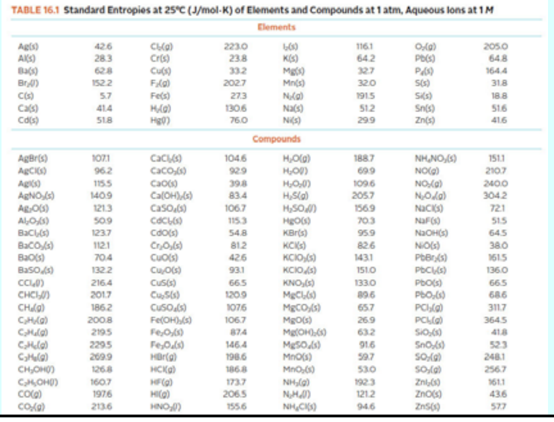


TABLE 16.1 Standard Entropies at 25°C (J/mol·K) of Elements and Compounds at 1 atm, Aqueous Ions at 1 *M*

Elements							
$Ag(s)$	42.6	$Cl_2(g)$	223.0	$I_2(s)$	116.1	$O_2(g)$	205.0
$Al(s)$	28.3	$Cr(s)$	23.8	$K(s)$	64.2	$Pb(s)$	64.8
$Ba(s)$	62.8	$Cu(s)$	33.2	$Mg(s)$	32.7	$P_4(s)$	164.4
$Br_2(l)$	152.2	$F_2(g)$	202.7	$Mn(s)$	32.0	$S(s)$	31.8
$C(s)$	5.7	$Fe(s)$	27.3	$N_2(g)$	191.5	$Si(s)$	18.8
$Ca(s)$	41.4	$H_2(g)$	130.6	$Na(s)$	51.2	$Sn(s)$	51.6
$Cd(s)$	51.8	$Hg(l)$	76.0	$Ni(s)$	29.9	$Zn(s)$	41.6
Compounds							
$AgBr(s)$	107.1	$CaCl_2(s)$	104.6	$H_2O(g)$	188.7	$NH_4NO_3(s)$	151.1
$AgCl(s)$	96.2	$CaCO_3(s)$	92.9	$H_2O(l)$	69.9	$NO(g)$	210.7
$AgI(s)$	115.5	$CaO(s)$	39.8	$H_2O_2(l)$	109.6	$NO_2(g)$	240.0
$AgNO_3(s)$	140.9	$Ca(OH)_2(s)$	83.4	$H_2S(g)$	205.7	$N_2O_4(g)$	304.2
$Ag_2O(s)$	121.3	$CaSO_4(s)$	106.7	$H_2SO_4(l)$	156.9	$NaCl(s)$	72.1
$Al_2O_3(s)$	50.9	$CdCl_2(s)$	115.3	$HgO(s)$	70.3	$NaF(s)$	51.5
$BaCl_2(s)$	123.7	$CdO(s)$	54.8	$KBr(s)$	95.9	$NaOH(s)$	64.5
$BaCO_3(s)$	112.1	$Cr_2O_3(s)$	81.2	$KCl(s)$	82.6	$NiO(s)$	38.0
$BaO(s)$	70.4	$CuO(s)$	42.6	$KClO_3(s)$	143.1	$PbBr_2(s)$	161.5
$BaSO_4(s)$	132.2	$Cu_2O(s)$	93.1	$KClO_4(s)$	151.0	$PbCl_2(s)$	136.0
$CCl_4(l)$	216.4	$CuS(s)$	66.5	$KNO_3(s)$	133.0	$PbO(s)$	66.5
$CHCl_3(l)$	201.7	$Cu_2S(s)$	120.9	$MgCl_2(s)$	89.6	$PbO_2(s)$	68.6
$CH_4(g)$	186.2	$CuSO_4(s)$	107.6	$MgCO_3(s)$	65.7	$PCl_3(g)$	311.7
$C_2H_2(g)$	200.8	$Fe(OH)_3(s)$	106.7	$MgO(s)$	26.9	$PCl_5(g)$	364.5
$C_2H_4(g)$	219.5	$Fe_2O_3(s)$	87.4	$Mg(OH)_2(s)$	63.2	$SiO_2(s)$	41.8
$C_2H_6(g)$	229.5	$Fe_3O_4(s)$	146.4	$MgSO_4(s)$	91.6	$SnO_2(s)$	52.3
$C_3H_8(g)$	269.9	$HBr(g)$	198.6	$MnO(s)$	59.7	$SO_2(g)$	248.1
$CH_3OH(l)$	126.8	$HCl(g)$	186.8	$MnO_2(s)$	53.0	$SO_3(g)$	256.7
$C_2H_5OH(l)$	160.7	$HF(g)$	173.7	$NH_3(g)$	192.3	$ZnI_2(s)$	161.1
$CO(g)$	197.6	$HI(g)$	206.5	$N_2H_4(l)$	121.2	$ZnO(s)$	43.6
$CO_2(g)$	213.6	$HNO_3(l)$	155.6	$NH_4Cl(s)$	94.6	$ZnS(s)$	57.7

Standard Molar Entropies

- Unlike enthalpy, molar entropy cannot be directly measured
- Notes
  - Elements have nonzero molar entropies
    - In calculating the standard molar entropy change, elements must be taken into account
  - Standard molar entropies are always positive numbers, i.e., S° > 0
  - Aqueous ions may have negative S° values, since they are determined relative to S° for H^+, which is defined as 0.0 J/mol-K

Table 16.1, (Cont'd)

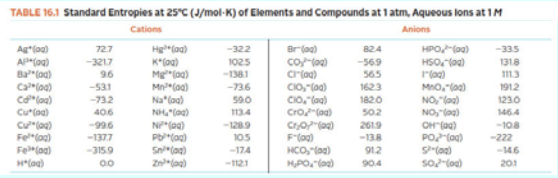


TABLE 16.1 Standard Entropies at 25°C (J/mol·K) of Elements and Compounds at 1 atm, Aqueous Ions at 1 *M*

Cations				Anions			
$Ag^+(aq)$	72.7	$Hg^{2+}(aq)$	−32.2	$Br^-(aq)$	82.4	$HPO_4^{2-}(aq)$	−33.5
$Al^{3+}(aq)$	−321.7	$K^+(aq)$	102.5	$CO_3^{2-}(aq)$	−56.9	$HSO_4^-(aq)$	131.8
$Ba^{2+}(aq)$	9.6	$Mg^{2+}(aq)$	−138.1	$Cl^-(aq)$	56.5	$I^-(aq)$	111.3
$Ca^{2+}(aq)$	−53.1	$Mn^{2+}(aq)$	−73.6	$ClO_3^-(aq)$	162.3	$MnO_4^-(aq)$	191.2
$Cd^{2+}(aq)$	−73.2	$Na^+(aq)$	59.0	$ClO_4^-(aq)$	182.0	$NO_2^-(aq)$	123.0
$Cu^+(aq)$	40.6	$NH_4^+(aq)$	113.4	$CrO_4^{2-}(aq)$	50.2	$NO_3^-(aq)$	146.4
$Cu^{2+}(aq)$	−99.6	$Ni^{2+}(aq)$	−128.9	$Cr_2O_7^{2-}(aq)$	261.9	$OH^-(aq)$	−10.8
$Fe^{2+}(aq)$	−137.7	$Pb^{2+}(aq)$	10.5	$F^-(aq)$	−13.8	$PO_4^{3-}(aq)$	−222
$Fe^{3+}(aq)$	−315.9	$Sn^{2+}(aq)$	−17.4	$HCO_3^-(aq)$	91.2	$S^{2-}(aq)$	−14.6
$H^+(aq)$	0.0	$Zn^{2+}(aq)$	−112.1	$H_2PO_4^-(aq)$	90.4	$SO_4^{2-}(aq)$	20.1

ΔS° for Reactions

- The defining equation for ΔS° is similar to that for ΔH° :

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

- In calculating ΔS° , the coefficients of the balanced equation are taken in exactly the same way as they are for ΔH°

Entropy Units

- Note that standard molar entropies are usually smaller in magnitude than enthalpies
  - Units may be J/mol-K or kJ/mol-K
  - Pay attention to J vs. kJ in calculations!

Example

- $CaCO_3$ (s) → CaO (s) + CO_2 (g)

$$\Delta S^\circ = 1mol(39.8\frac{J}{mol \cdot K}) + 1mol(213.6\frac{J}{mol \cdot K}) - 1mol(92.9\frac{J}{mol \cdot K}) =$$

$$+160.5\frac{J}{mol \cdot K}$$

- Note the positive entropy change and the fact that the reaction evolves a gas
- Gas-forming reactions always have positive entropy changes

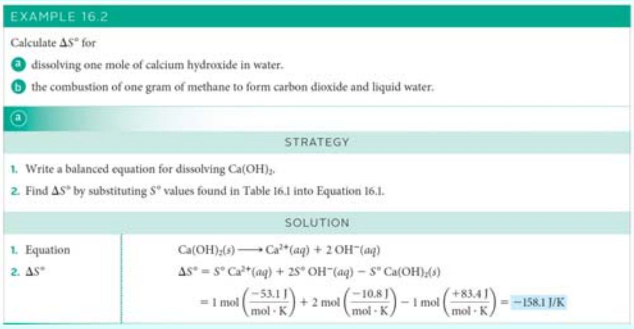
The Second Law of Thermodynamics

- In a spontaneous process, there is a net increase in entropy, taking into consideration both the system and the surroundings
- That is, for a spontaneous process:

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

- In principle, the second law can be used to determine whether a reaction is spontaneous or not; in practice, this is not easy
  - It is difficult to calculate the entropy change of the surroundings
  - There is another quantity that can be used more readily to determine spontaneity

Example 16.2



EXAMPLE 16.2

Calculate ΔS° for

ⓐ dissolving one mole of calcium hydroxide in water.

ⓑ the combustion of one gram of methane to form carbon dioxide and liquid water.

ⓐ

STRATEGY

1. Write a balanced equation for dissolving $Ca(OH)_2$.
2. Find ΔS° by substituting S° values found in Table 16.1 into Equation 16.1.

SOLUTION

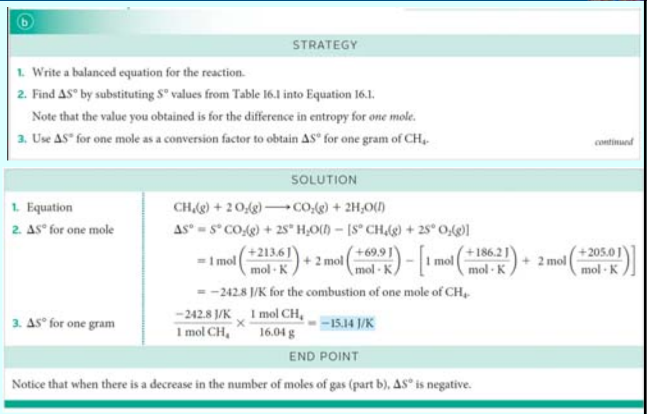
1. Equation $Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$
2. ΔS° $\Delta S^\circ = S^\circ\ Ca^{2+}(aq) + 2S^\circ\ OH^-(aq) - S^\circ\ Ca(OH)_2(s)$

$$= 1\text{ mol}\left(\frac{-53.1\text{ J}}{\text{mol}\cdot\text{K}}\right) + 2\text{ mol}\left(\frac{-10.8\text{ J}}{\text{mol}\cdot\text{K}}\right) - 1\text{ mol}\left(\frac{+83.4\text{ J}}{\text{mol}\cdot\text{K}}\right) = -158.1\text{ J/K}$$

Free Energy, G

- The Gibbs Free Energy
  - Fundamental Relationship
    - G = H-TS
    - ΔG = ΔH-TΔS
- Meaning of ΔG
  - If ΔG < 0, the reaction is spontaneous
  - If ΔG > 0, the reaction is nonspontaneous as written (the reverse reaction is spontaneous)
  - If ΔG = 0, the system is in equilibrium
    - There is no net tendency for the reaction to occur in either direction

Example 16.2, (Cont'd)



ⓑ

STRATEGY

1. Write a balanced equation for the reaction.
2. Find ΔS° by substituting S° values from Table 16.1 into Equation 16.1.

   Note that the value you obtained is for the difference in entropy for *one mole*.
3. Use ΔS° for one mole as a conversion factor to obtain ΔS° for one gram of CH_4.

continued

SOLUTION

1. Equation $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$
2. ΔS° for one mole $\Delta S^\circ = S^\circ\ CO_2(g) + 2S^\circ\ H_2O(l) - [S^\circ\ CH_4(g) + 2S^\circ\ O_2(g)]$

$$= 1\text{ mol}\left(\frac{+213.6\text{ J}}{\text{mol}\cdot\text{K}}\right) + 2\text{ mol}\left(\frac{+69.9\text{ J}}{\text{mol}\cdot\text{K}}\right) - \left[1\text{ mol}\left(\frac{+186.2\text{ J}}{\text{mol}\cdot\text{K}}\right) + 2\text{ mol}\left(\frac{+205.0\text{ J}}{\text{mol}\cdot\text{K}}\right)\right]$$

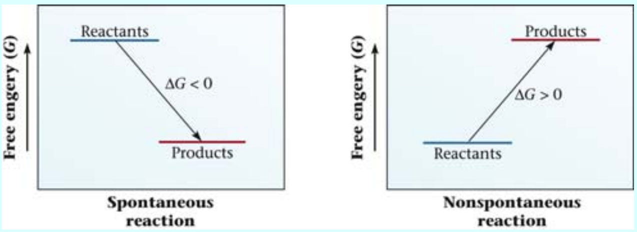
$$= -242.8\text{ J/K for the combustion of one mole of } CH_4.$$

3. ΔS° for one gram $\frac{-242.8\text{ J/K}}{1\text{ mol }CH_4} \times \frac{1\text{ mol }CH_4}{16.04\text{ g}} = -15.14\text{ J/K}$

END POINT

Notice that when there is a decrease in the number of moles of gas (part b), ΔS° is negative.

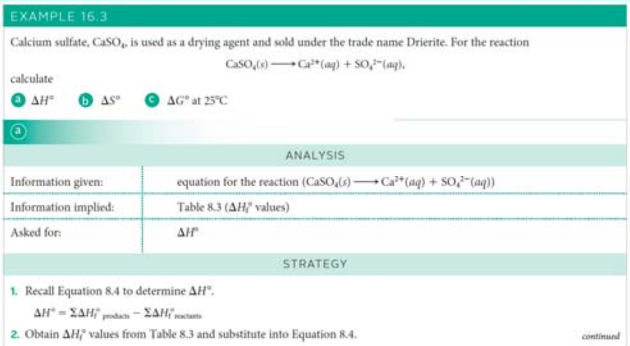
Figure 16.5



Relation Among ΔG, ΔH and ΔS

- The Gibbs-Helmholtz equation
  - $\Delta G = \Delta H - T\Delta S$
- Spontaneous reactions generally have
  - $\Delta H < 0$
  - $\Delta S > 0$
- In specific cases, either term may dominate
  - With phase changes, ΔS is dominant
  - With some reactions, ΔS is nearly zero and ΔH will dominate

Example 16.3



EXAMPLE 16.3

Calcium sulfate, $CaSO_4$, is used as a drying agent and sold under the trade name Drierite. For the reaction

$$CaSO_4(s) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq),$$

calculate

ⓐ ΔH° ⓑ ΔS° ⓒ ΔG° at 25°C

ⓐ

ANALYSIS

Information given:	equation for the reaction ($CaSO_4(s) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$)
Information implied:	Table 8.3 (ΔH_f° values)
Asked for:	ΔH°

STRATEGY

1. Recall Equation 8.4 to determine ΔH°.

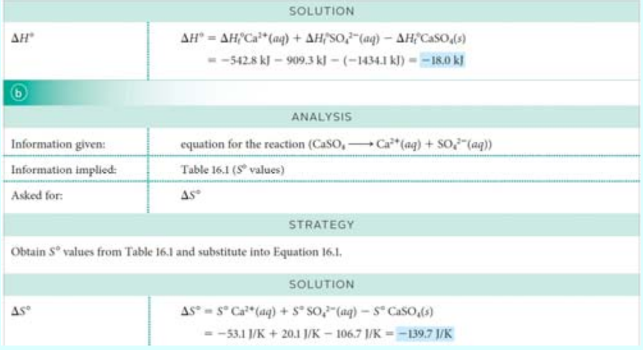
   $\Delta H^\circ = \Sigma \Delta H_f^\circ{}_{\text{products}} - \Sigma \Delta H_f^\circ{}_{\text{reactants}}$
2. Obtain ΔH_f° values from Table 8.3 and substitute into Equation 8.4.

continued

The Standard Free Energy Change, ΔG°

- Standard conditions
  - Gases are at 1 atm partial pressure
  - Solutions are 1M for ions or molecules
- Under standard conditions,
  - $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- Recall that
  - If $\Delta G^\circ < 0$, the reaction is spontaneous
  - If $\Delta G^\circ > 0$, the reaction is nonspontaneous
  - If $\Delta G^\circ = 0$, the reaction is at equilibrium

Example 16.3, (Cont'd)



SOLUTION

ΔH°	$\Delta H^\circ = \Delta H_f^\circ Ca^{2+}(aq) + \Delta H_f^\circ SO_4^{2-}(aq) - \Delta H_f^\circ CaSO_4(s)$ $= -542.8\text{ kJ} - 909.3\text{ kJ} - (-1434.1\text{ kJ}) = -18.0\text{ kJ}$

ⓑ

ANALYSIS

Information given:	equation for the reaction ($CaSO_4 \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$)
Information implied:	Table 16.1 (S° values)
Asked for:	ΔS°

STRATEGY

Obtain S° values from Table 16.1 and substitute into Equation 16.1.

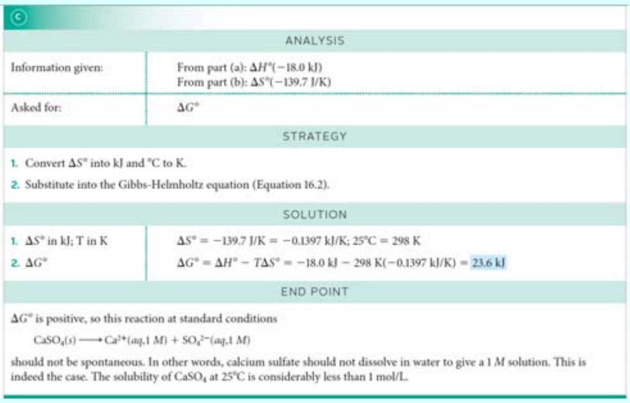
SOLUTION

ΔS°	$\Delta S^\circ = S^\circ Ca^{2+}(aq) + S^\circ SO_4^{2-}(aq) - S^\circ CaSO_4(s)$ $= -53.1\text{ J/K} + 20.1\text{ J/K} - 106.7\text{ J/K} = -139.7\text{ J/K}$

Free Energy of Formation

- We can use the Gibbs-Helmholtz equation to calculate the standard free energy of formation for a compound
  - ΔG_f° for a compound is
    - Analogous to the enthalpy of formation discussed in Chapter 8
    - For the formation of one mole of the compound from elements in their standard (native) states at 25 ° C and 1 atm pressure
  - The sign of ΔG_f°
    - If negative, the formation of the compound is spontaneous
    - If positive, the formation of the compound is nonspontaneous

Example 16.3, (Cont'd)



ⓒ

ANALYSIS

Information given:	From part (a): $\Delta H^\circ(-18.0\text{ kJ})$ From part (b): $\Delta S^\circ(-139.7\text{ J/K})$
Asked for:	ΔG°

STRATEGY

1. Convert ΔS° into kJ and °C to K.
2. Substitute into the Gibbs-Helmholtz equation (Equation 16.2).

SOLUTION

1. ΔS° in kJ; T in K	$\Delta S^\circ = -139.7\text{ J/K} = -0.1397\text{ kJ/K}$; $25^\circ C = 298\text{ K}$
2. ΔG°	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -18.0\text{ kJ} - 298\text{ K}(-0.1397\text{ kJ/K}) = 23.6\text{ kJ}$

END POINT

ΔG° is positive, so this reaction at standard conditions

$$CaSO_4(s) \longrightarrow Ca^{2+}(aq, 1\ M) + SO_4^{2-}(aq, 1\ M)$$

should not be spontaneous. In other words, calcium sulfate should not dissolve in water to give a 1 *M* solution. This is indeed the case. The solubility of $CaSO_4$ at 25°C is considerably less than 1 mol/L.

Examples

- H_2 (g) + ½O_2 (g) → H_2O (l) ΔG_f° = -237.2 kJ/mol
- C (s) + $2H_2$ (g) → CH_4 (g) ΔG_f° = -50.7 kJ/mol
- 2C (s) + H_2 (g) → C_2H_2 (g) ΔG_f° = +209.2 kJ/mol

Calculation of ΔG° at Other Temperatures

- To a good degree of approximation, the temperature variation of ΔH° and ΔS° can be neglected
- To calculate ΔG° at other temperatures, only the value for T needs to be changed

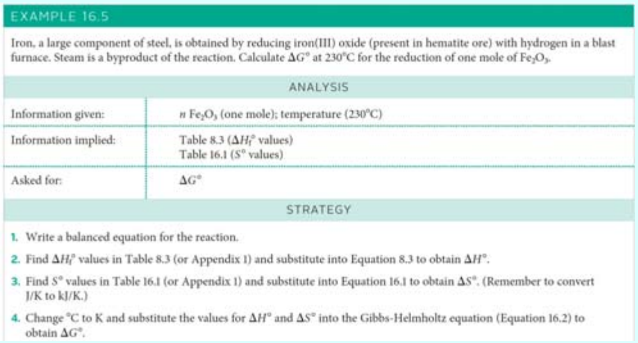
Another Look at the Free Energy of Formation

- Another way to calculate the free energy of formation

$$\Delta G^\circ = \sum \Delta G^\circ,\text{products} - \sum \Delta G^\circ,\text{reactants}$$

- Notice that there is no temperature term in this equation, so it is important to realize that the calculation is valid only at the temperature at which the values of ΔG_f° are tabulated

Example 16.5



EXAMPLE 16.5

Iron, a large component of steel, is obtained by reducing iron(III) oxide (present in hematite ore) with hydrogen in a blast furnace. Steam is a byproduct of the reaction. Calculate ΔG° at 230°C for the reduction of one mole of Fe_2O_3.

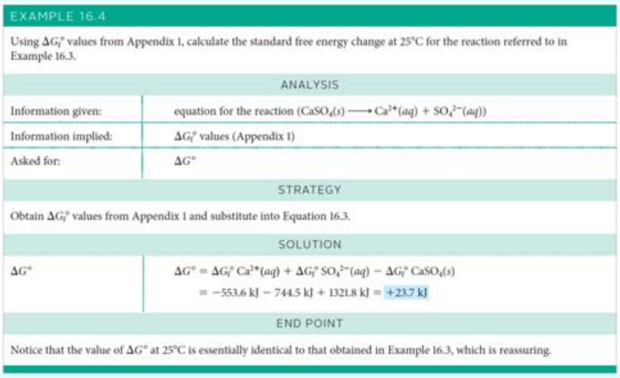
ANALYSIS

Information given:	*n* Fe_2O_3 (one mole); temperature (230°C)
Information implied:	Table 8.3 (ΔH_f° values) Table 16.1 (S° values)
Asked for:	ΔG°

STRATEGY

1. Write a balanced equation for the reaction.
2. Find ΔH_f° values in Table 8.3 (or Appendix 1) and substitute into Equation 8.3 to obtain ΔH°.
3. Find S° values in Table 16.1 (or Appendix 1) and substitute into Equation 16.1 to obtain ΔS°. (Remember to convert J/K to kJ/K.)
4. Change °C to K and substitute the values for ΔH° and ΔS° into the Gibbs-Helmholtz equation (Equation 16.2) to obtain ΔG°.

Example 16.4



EXAMPLE 16.4

Using ΔG_f° values from Appendix 1, calculate the standard free energy change at 25°C for the reaction referred to in Example 16.3.

ANALYSIS

Information given:	equation for the reaction ($CaSO_4(s) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$)
Information implied:	ΔG_f° values (Appendix 1)
Asked for:	ΔG°

STRATEGY

Obtain ΔG_f° values from Appendix 1 and substitute into Equation 16.3.

SOLUTION

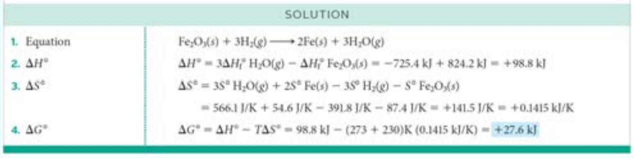
ΔG°

$$\Delta G^\circ = \Delta G_f^\circ\,Ca^{2+}(aq) + \Delta G_f^\circ\,SO_4^{2-}(aq) - \Delta G_f^\circ\,CaSO_4(s)$$
$$= -553.6\text{ kJ} - 744.5\text{ kJ} + 1321.8\text{ kJ} = +23.7\text{ kJ}$$

END POINT

Notice that the value of ΔG° at 25°C is essentially identical to that obtained in Example 16.3, which is reassuring.

Example 16.5, (Cont'd)



SOLUTION

1. Equation	$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(g)$
2. ΔH°	$\Delta H^\circ = 3\Delta H_f^\circ\,H_2O(g) - \Delta H_f^\circ\,Fe_2O_3(s) = -725.4\text{ kJ} + 824.2\text{ kJ} = +98.8\text{ kJ}$
3. ΔS°	$\Delta S^\circ = 3S^\circ\,H_2O(g) + 2S^\circ\,Fe(s) - 3S^\circ\,H_2(g) - S^\circ\,Fe_2O_3(s)$ $= 566.1\text{ J/K} + 54.6\text{ J/K} - 391.8\text{ J/K} - 87.4\text{ J/K} = +141.5\text{ J/K} = +0.1415\text{ kJ/K}$
4. ΔG°	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 98.8\text{ kJ} - (273 + 230)\text{K}\,(0.1415\text{ kJ/K}) = +27.6\text{ kJ}$

Temperature Effects

- Unlike ΔH° and ΔS°, ΔG° is highly temperature dependent
- A plot of ΔG° vs. T will be linear
  - Slope = -ΔS°
  - y-intercept at 0 K is ΔH°

Changes and Spontaneity

- The spontaneity of a reaction will change with
  - Temperature
  - Pressure
  - Concentration

Figure 16.6

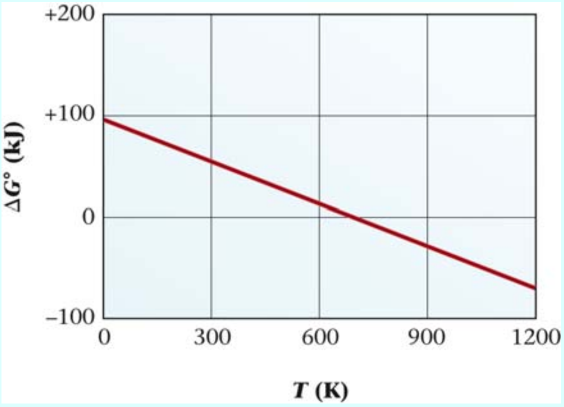


Table 16.2

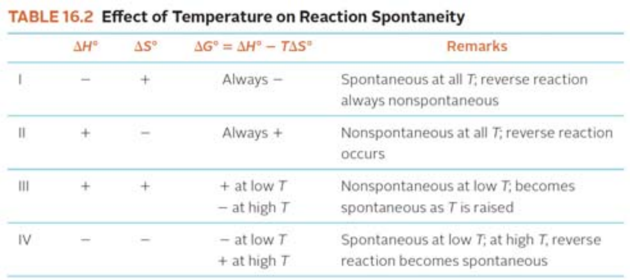


TABLE 16.2 Effect of Temperature on Reaction Spontaneity

	ΔH°	ΔS°	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	Remarks
I	−	+	Always −	Spontaneous at all *T*; reverse reaction always nonspontaneous
II	+	−	Always +	Nonspontaneous at all *T*; reverse reaction occurs
III	+	+	+ at low *T* − at high *T*	Nonspontaneous at low *T*; becomes spontaneous as *T* is raised
IV	−	−	− at low *T* + at high *T*	Spontaneous at low *T*; at high *T*, reverse reaction becomes spontaneous

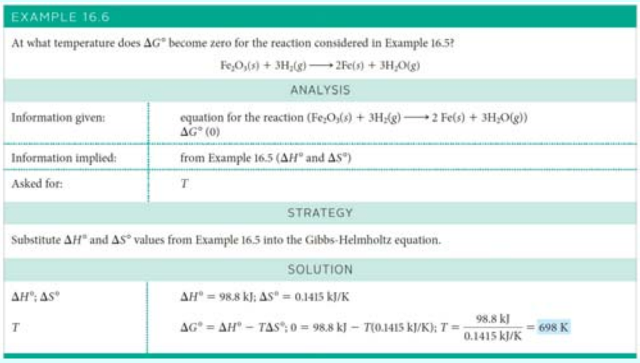
Figure 16.6 – From Example 16.5

- Reduction of Fe_2O_3:
  - $Fe_2O_3\ (s) + 3H_2\ (g) \rightarrow 2Fe\ (s) + 3H_2O\ (l)$
  - Notes
    - ΔG° decreases with increasing temperature
    - The sign of ΔG° changes at 698 K
    - For the plot to appear this way
      - ΔS° must be positive
      - ΔH° must be positive

Temperature

- A reaction for which ΔH° < 0 and ΔS° > 0 is spontaneous at all temperatures
- A reaction for which ΔH° > 0 and ΔS° < 0 is never spontaneous as written
- A reaction for which ΔH° < 0 and ΔS° < 0 is spontaneous at low temperatures
- A reaction for which ΔH° > 0 and ΔS° > 0 is spontaneous at high temperatures

Example 16.6



EXAMPLE 16.6

At what temperature does ΔG° become zero for the reaction considered in Example 16.5?

$$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(g)$$

ANALYSIS

Information given:	equation for the reaction ($Fe_2O_3(s) + 3H_2(g) \longrightarrow 2\,Fe(s) + 3H_2O(g)$) ΔG° (0)
Information implied:	from Example 16.5 (ΔH° and ΔS°)
Asked for:	T

STRATEGY

Substitute ΔH° and ΔS° values from Example 16.5 into the Gibbs-Helmholtz equation.

SOLUTION

ΔH°; ΔS°	$\Delta H^\circ = 98.8$ kJ; $\Delta S^\circ = 0.1415$ kJ/K
T	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; $0 = 98.8\text{ kJ} - T(0.1415\text{ kJ/K})$; $T = \dfrac{98.8\text{ kJ}}{0.1415\text{ kJ/K}} = 698\text{ K}$

Recall the Reaction Quotient

- For the reaction
- Zn (s) + 2H$^+$ (aq) → Zn^{2+} (aq) + H$_2$ (g)

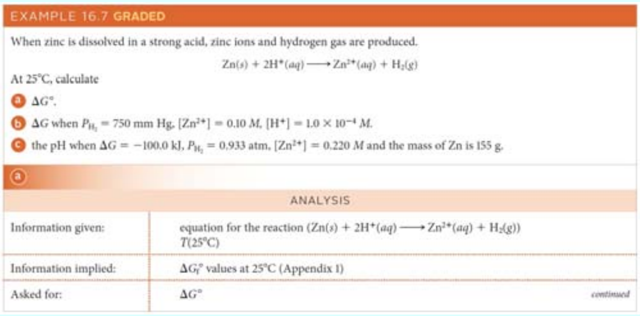
$$Q = \frac{[Zn^{2+}](p_{H_2})}{[H^+]^2}$$

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

Direction of Spontaneity Change

- To calculate the temperature at which the spontaneity changes from …
  - Spontaneous to nonspontaneous
  - Nonspontaneous to spontaneous
- … find the temperature at which $\Delta G^\circ = 0$
  - $T = \Delta H^\circ / \Delta S^\circ$

Example 16.7



EXAMPLE 16.7 GRADED

When zinc is dissolved in a strong acid, zinc ions and hydrogen gas are produced.

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

At 25°C, calculate

ⓐ ΔG°.

ⓑ ΔG when $P_{H_2} = 750$ mm Hg, $[Zn^{2+}] = 0.10\ M$, $[H^+] = 1.0 \times 10^{-4}\ M$.

ⓒ the pH when $\Delta G = -100.0$ kJ, $P_{H_2} = 0.933$ atm, $[Zn^{2+}] = 0.220\ M$ and the mass of Zn is 155 g.

ⓐ

ANALYSIS

Information given:	equation for the reaction ($Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$) T(25°C)
Information implied:	ΔG_f° values at 25°C (Appendix 1)
Asked for:	ΔG°

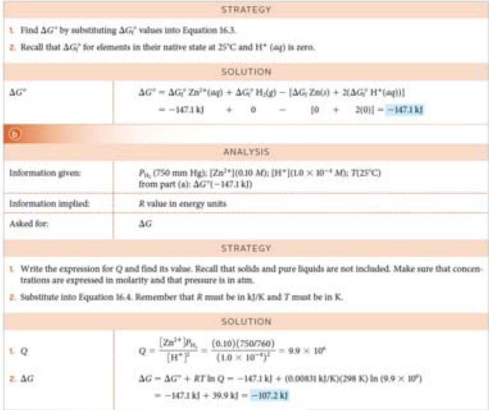
continued

Pressure and Concentration Effects

- There is a connection between the free energy change, the standard free energy change, and the reaction quotient, Q

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

Example 16.7, (Cont'd)



STRATEGY

1. Find ΔG° by substituting ΔG_f° values into Equation 16.3.
2. Recall that ΔG_f° for elements in their native state at 25°C and H$^+$ (aq) is zero.

SOLUTION

ΔG°	$\Delta G^\circ = \Delta G_f^\circ\,Zn^{2+}(aq) + \Delta G_f^\circ\,H_2(g) - [\Delta G_f\,Zn(s) + 2(\Delta G_f^\circ\,H^+(aq))]$ $= -147.1\text{ kJ} + 0 - [0 + 2(0)] = -147.1\text{ kJ}$

ⓑ

ANALYSIS

Information given:	P_{H_2} (750 mm Hg); $[Zn^{2+}]$(0.10 M); $[H^+]$(1.0 × 10^{-4} M); T(25°C) from part (a): ΔG°(−147.1 kJ)
Information implied:	R value in energy units
Asked for:	ΔG

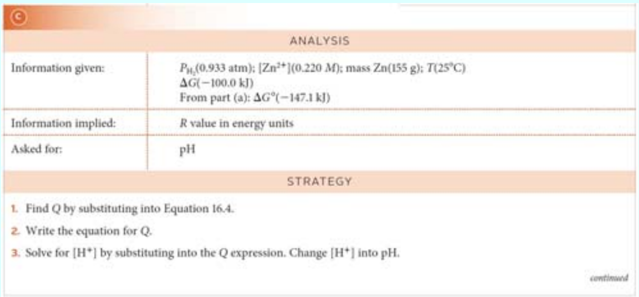
STRATEGY

1. Write the expression for Q and find its value. Recall that solids and pure liquids are not included. Make sure that concentrations are expressed in molarity and that pressure is in atm.
2. Substitute into Equation 16.4. Remember that R must be in kJ/K and T must be in K.

SOLUTION

1. Q	$Q = \dfrac{[Zn^{2+}]P_{H_2}}{[H^+]^2} = \dfrac{(0.10)(750/760)}{(1.0 \times 10^{-4})^2} = 9.9 \times 10^6$
2. ΔG	$\Delta G = \Delta G^\circ + RT\ln Q = -147.1\text{ kJ} + (0.00831\text{ kJ/K})(298\text{ K})\ln(9.9 \times 10^6)$ $= -147.1\text{ kJ} + 39.9\text{ kJ} = -107.2\text{ kJ}$

Example 16.7, (Cont'd)



ANALYSIS

Information given:	P_{H_2}(0.933 atm); [Zn^{2+}](0.220 *M*); mass Zn(155 g); *T*(25°C) $\Delta G(-100.0\text{ kJ})$ From part (a): $\Delta G^\circ(-147.1\text{ kJ})$
Information implied:	*R* value in energy units
Asked for:	pH

STRATEGY

1. Find *Q* by substituting into Equation 16.4.
2. Write the equation for *Q*.
3. Solve for [H^+] by substituting into the *Q* expression. Change [H^+] into pH.

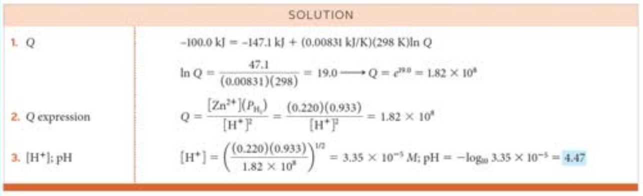
continued

ΔG and the Equilibrium Constant

- There is clearly a relationship between the free energy change and the equilibrium constant
  - It is expressed in the equation involving Q
- Remember that at equilibrium, ΔG = 0 so

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

Example 16.7, (Cont'd)



SOLUTION

1. *Q*	$-100.0\text{ kJ} = -147.1\text{ kJ} + (0.00831\text{ kJ/K})(298\text{ K})\ln Q$ $\ln Q = \dfrac{47.1}{(0.00831)(298)} = 19.0 \longrightarrow Q = e^{19.0} = 1.82\times10^{8}$
2. *Q* expression	$Q = \dfrac{[Zn^{2+}](P_{H_2})}{[H^+]^2} = \dfrac{(0.220)(0.933)}{[H^+]^2} = 1.82\times10^{8}$
3. [H^+]; pH	$[H^+] = \left(\dfrac{(0.220)(0.933)}{1.82\times10^{8}}\right)^{1/2} = 3.35\times10^{-5}\,M$; $\text{pH} = -\log_{10} 3.35\times10^{-5} = 4.47$

Equilibrium Constants

- The relationship between ΔG and K holds for all equilibrium constants we have seen so far
  - K_a ,K_b ,K_w ,K_f ,K_{sp}

Concentration Changes

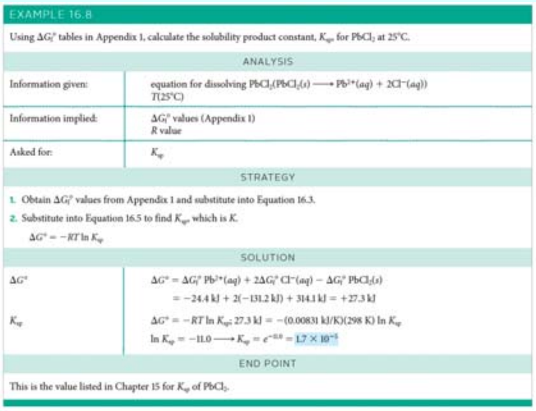
- Changes in concentration will cause Q to change
- For NH_4Cl (s) → NH_3 (g) + HCl (g)   ΔG°   = +13.0 kJ
  - Changing the pressures of NH_3 and HCl from the standard 1.0 atm each to 0.10 atm each and increasing the temperature to 300 ° C:

$$\Delta G = \Delta G^\circ + RT\ln Q$$
$$\Delta G = +13.0kJ + (8.31X10^{-3})(573)\times\ln(0.010)$$
$$\Delta G = -8.9kJ$$

Figure 16.7 – Saturated $SrCrO_4$

- The fact that $SrCrO_4$ does not dissolve readily in water indicates that the reaction is non-spontaneous

Example 16.8



EXAMPLE 16.8

Using ΔG_f° tables in Appendix 1, calculate the solubility product constant, K_{sp}, for $PbCl_2$ at 25°C.

ANALYSIS

Information given:	equation for dissolving $PbCl_2$ ($PbCl_2(s) \longrightarrow Pb^{2+}(aq) + 2Cl^-(aq)$) T(25°C)
Information implied:	ΔG_f° values (Appendix 1) R value
Asked for:	K_{sp}

STRATEGY

1. Obtain ΔG_f° values from Appendix 1 and substitute into Equation 16.3.
2. Substitute into Equation 16.5 to find K_{sp}, which is K.

$\Delta G^\circ = -RT \ln K_{sp}$

SOLUTION

ΔG°	$\Delta G^\circ = \Delta G_f^\circ\ Pb^{2+}(aq) + 2\Delta G_f^\circ\ Cl^-(aq) - \Delta G_f^\circ\ PbCl_2(s)$ $= -24.4\text{ kJ} + 2(-131.2\text{ kJ}) + 314.1\text{ kJ} = +27.3\text{ kJ}$
K_{sp}	$\Delta G^\circ = -RT \ln K_{sp}$; $27.3\text{ kJ} = -(0.00831\text{ kJ/K})(298\text{ K}) \ln K_{sp}$ $\ln K_{sp} = -11.0 \longrightarrow K_{sp} = e^{-11.0} = 1.7 \times 10^{-5}$

END POINT

This is the value listed in Chapter 15 for K_{sp} of $PbCl_2$.

Additivity of ΔG; Coupled Reactions

- As with enthalpy, if
- Reaction 3 = Reaction 1 + Reaction 2, then
  - $\Delta G_3 = \Delta G_1 + \Delta G_2$
  - This is Hess's Law extended to free energy change

Relating Free Energy and Extent of Reaction for A→ B

- If ΔG° is greater than +20 kJ, the equilibrium constant is so small that virtually no reaction takes place; the equilibrium mixture is mostly A
- If ΔG° is less than -20 kJ, the equilibrium constant is so large that the reaction goes virtually to completion; the equilibrium mixture is mostly B
- If ΔG° is between +20 kJ and -20 kJ, the equilibrium mixture will contain appreciable amounts of both A and B

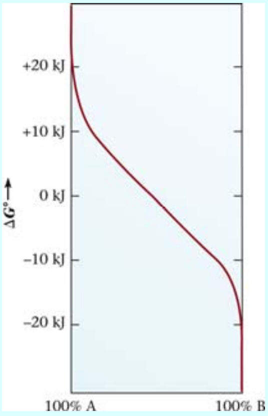
Example

- $Fe_2O_3\ (s) \rightarrow 2Fe\ (s) + 3/2O_2\ (g)$ $\Delta G^\circ = +742.2$ kJ
- $CO\ (g) + ½\ O_2\ (g) \rightarrow CO_2\ (g)$ $\Delta G^\circ = -257.1$ kJ
- For the overall reaction
  - $Fe_2O_3\ (s) + 3CO\ (g) \rightarrow 2Fe\ (s) + 3CO_2\ (g)$

$$\Delta G^\circ = +742.2kJ + 3(-257.1kJ) = -29.1kJ$$

  - ΔG° is negative and the decomposition of Fe_2O_3 into Fe can be made spontaneous by coupling it with the reaction of CO to CO_2

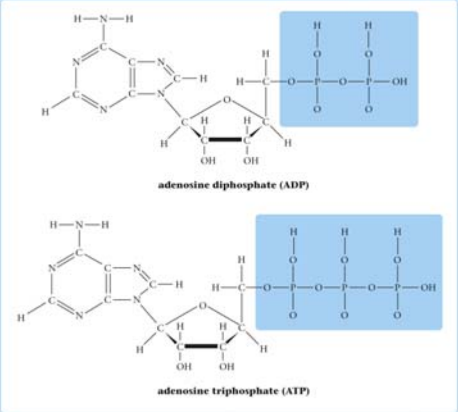
Figure 16.8



Biochemical Reactions

- Consider that the chemical reactions that underlie human physiology must occur at relatively low temperatures
- In order for these reactions to be spontaneous, they are coupled to a highly spontaneous reaction:
  - ATP → ADP $\Delta G^\circ < 0$
- The body stores energy as ATP, which is supplied to otherwise unfavorable reactions in the body

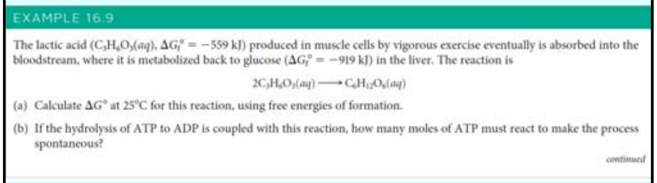
Figure 16.9



Key Concepts

1. Deduce the sign of ΔS° for a process from consideration of randomness
2. Calculate ΔS° for a reaction using thermochemical data
3. Calculate ΔG° at any temperature, knowing ΔH° and ΔS°
4. Calculate ΔG° at 25 °C from free energies of formation
5. Calculate the temperature at which ΔG° = 0
6. Calculate ΔG from ΔG°, knowing pressures and concentrations
7. Relate ΔG° to K

Example 16.9



EXAMPLE 16.9

The lactic acid ($C_3H_6O_3(aq)$, $\Delta G_f^\circ = -559$ kJ) produced in muscle cells by vigorous exercise eventually is absorbed into the bloodstream, where it is metabolized back to glucose ($\Delta G_f^\circ = -919$ kJ) in the liver. The reaction is

$$2C_3H_6O_3(aq) \longrightarrow C_6H_{12}O_6(aq)$$

(a) Calculate ΔG° at 25°C for this reaction, using free energies of formation.

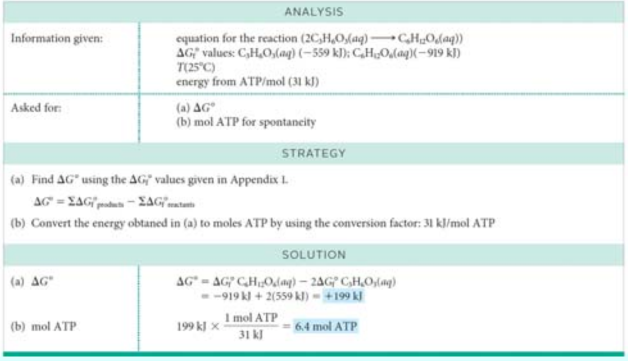
(b) If the hydrolysis of ATP to ADP is coupled with this reaction, how many moles of ATP must react to make the process spontaneous?

continued

Key Concepts, (Cont'd)

8. Calculate ΔG° for a set of coupled reactions

Example 16.9, (Cont'd)



ANALYSIS

Information given:	equation for the reaction ($2C_3H_6O_3(aq) \longrightarrow C_6H_{12}O_6(aq)$) ΔG_f° values: $C_3H_6O_3(aq)$ (−559 kJ); $C_6H_{12}O_6(aq)$(−919 kJ) T(25°C) energy from ATP/mol (31 kJ)
Asked for:	(a) ΔG° (b) mol ATP for spontaneity

STRATEGY

(a) Find ΔG° using the ΔG_f° values given in Appendix 1.

$$\Delta G^\circ = \Sigma\Delta G_f^\circ{}_{\text{products}} - \Sigma\Delta G_f^\circ{}_{\text{reactants}}$$

(b) Convert the energy obtaned in (a) to moles ATP by using the conversion factor: 31 kJ/mol ATP

SOLUTION

(a) ΔG°	$\Delta G^\circ = \Delta G_f^\circ\ C_6H_{12}O_6(aq) - 2\Delta G_f^\circ\ C_3H_6O_3(aq)$ $= -919\text{ kJ} + 2(559\text{ kJ}) = +199\text{ kJ}$
(b) mol ATP	$199\text{ kJ} \times \frac{1\text{ mol ATP}}{31\text{ kJ}} = 6.4\text{ mol ATP}$