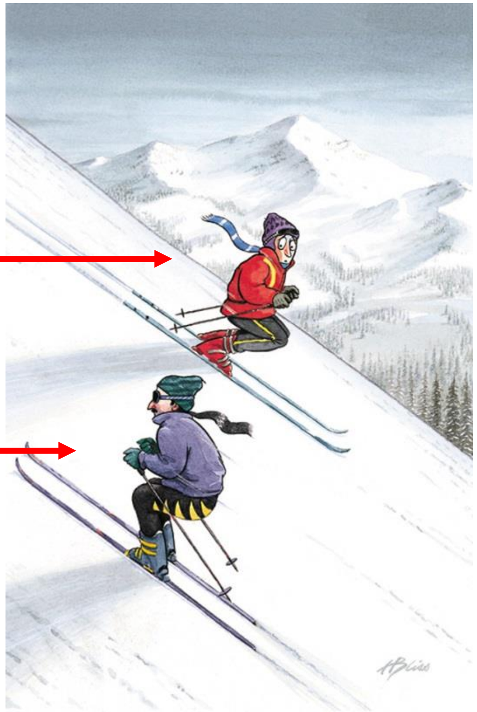
Ch 17 Free Energy and Thermodynamics - Spontaneity of Reaction

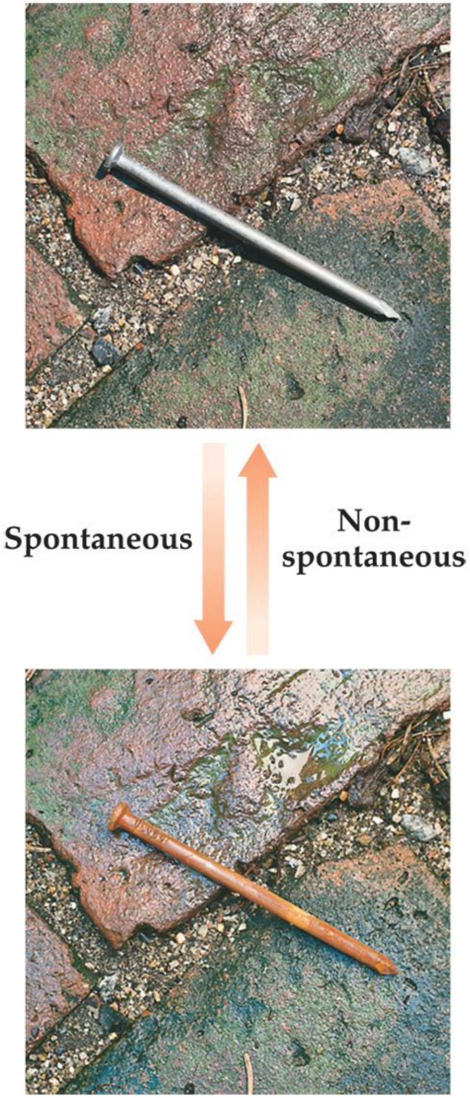
Modified by Dr. Cheng-Yu Lai



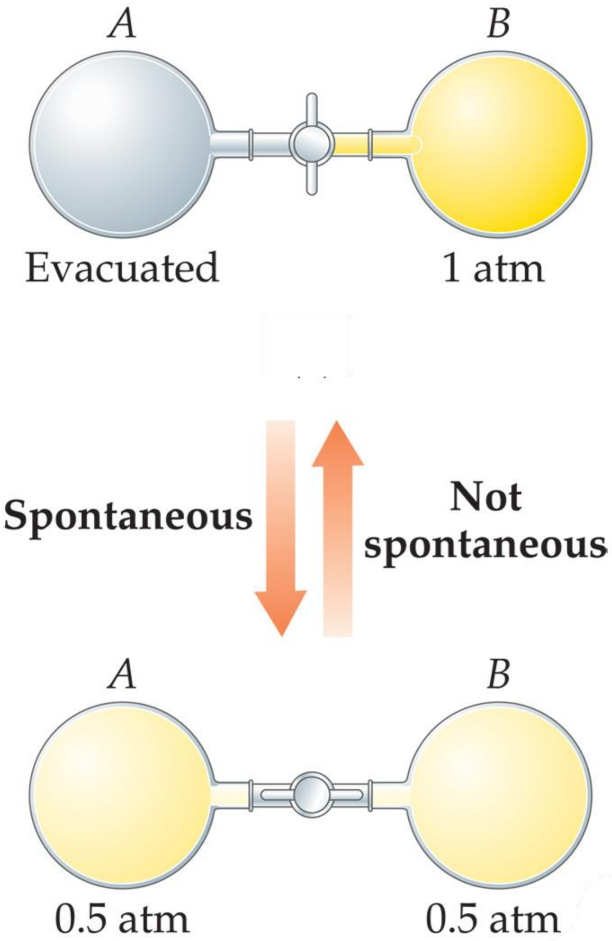
spontaneous

nonspontaneous

Spontaneous Processes



Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.



Spontaneous – 2 Measurements

- A reaction that will occur without outside intervention.
- We can’t determine how fast.
- We need both thermodynamics and kinetics to describe a reaction completely.
- **Thermodynamics compares initial and final states.**
- **Kinetics describes pathway between.**

Thermodynamics

- 1st Law- the energy of the universe is constant. **Energy cannot be created or destroyed.** Energy of (system + surroundings) is constant.

Spontaneous Processes- processes that occur without outside intervention.

May be fast or slow (kinetics not important).

Example: conversion of graphite to diamond is spontaneous, but very slo

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.

Also tend to be spontaneous if the reaction results in an increase in randomness

Review Ch5 - First Law of Thermodynamics

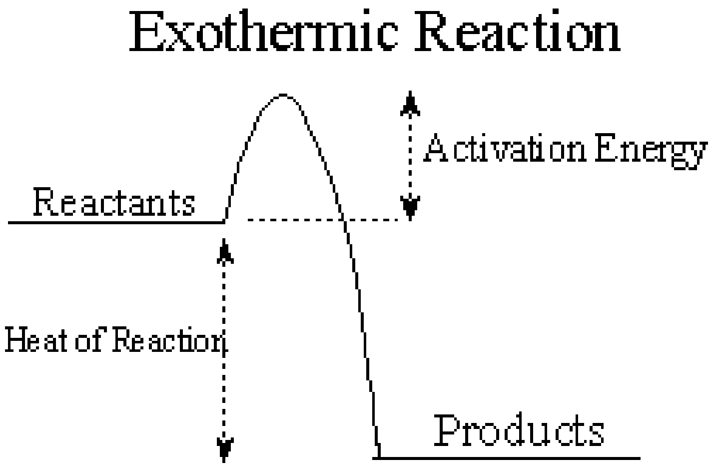
Endothermic and Exothermic Processes

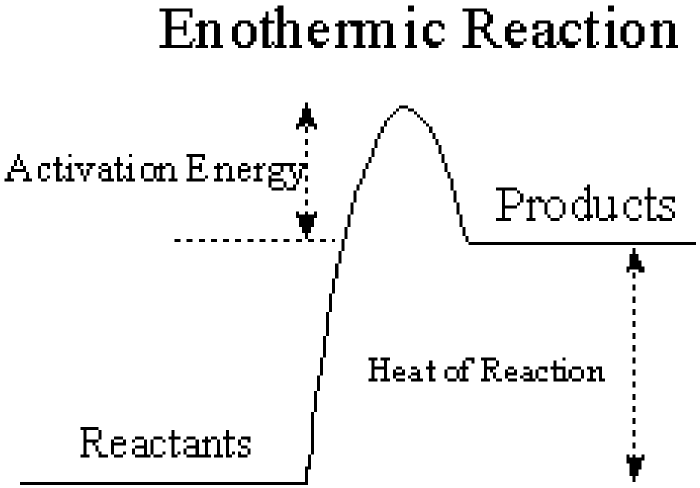
Endothermic: absorbs heat from the surroundings.

Exothermic: transfers heat to the surroundings.

An endothermic reaction feels cold.

An exothermic reaction feels hot.

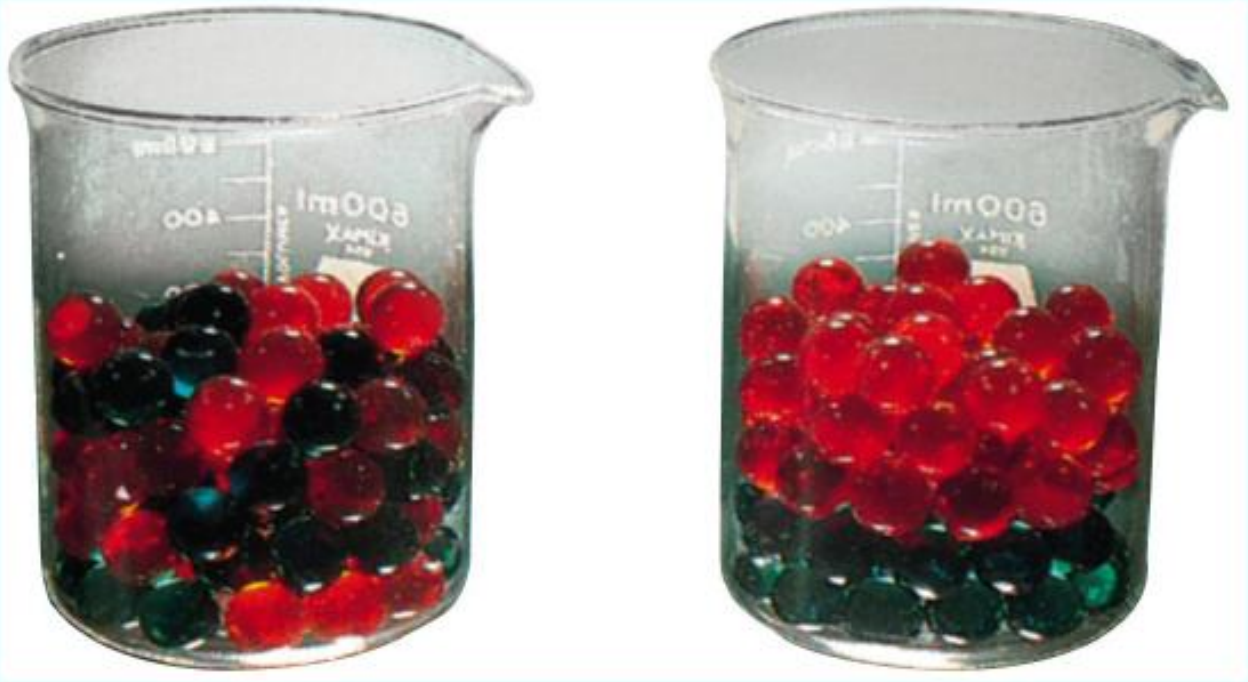




$$\Delta H^o_{rxn} = \Sigma n\Delta H^o_f(\text{products}) - \Sigma n\Delta H^o_f(\text{reactants})$$

Entropy, *S*

- **Entropy** is given the symbol ***S***.
- **Entropy** is often described as a measure of **disorder** or **randomness**.



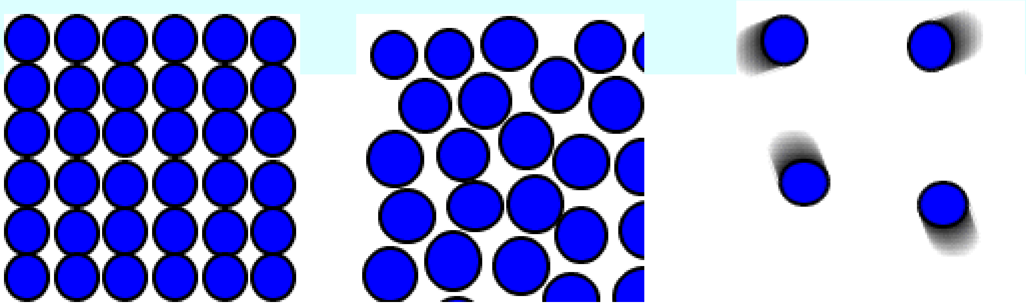
High randomness

Low randomness

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.

$S_{solid} < S_{liquid} \ll S_{gas}$



Entropy

- Entropy (S) is disorder or randomness
- 2nd Law the entropy of the universe increases.
- Defined in terms of probability.
- Nature proceeds toward the states that have the highest probabilities of existing
- The most likely is the most random.
- Calculate the number of arrangements for a system.

Entropy Change and a Gas-Evolving Reaction

For situations increasing entropy

(1) Solids → Pure liquids or liquid solutions;

(2) Liquids or solids → Gases;

(3) Increases of numbers of gaseous molecules in chemical reaction;

(4) Increases of temperature of a substance.

Question:

Entropy, S, increases or decreases?

(1) $2\ NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$

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

(3) Sucrose extraction from juice,
$C_{12}H_{22}O_{11}(aq) \rightarrow C_{12}H_{22}O_{11}(s)$

(4) $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

Which of the following has higher entropy?

Solid CO_2 or gaseous CO_2?

What is the sign of the entropy change for the following?

a) Solid sugar is added to water to form a solution?

ΔS is positive = entropy increases

b) Iodine vapor condenses on a cold surface to form crystals?

ΔS is negative = entropy decreases

Water forms H_2O vapor	$+ \Delta S$
Water freezes	$- \Delta S$
A gas expands	$+ \Delta S$
Student breaks a pyrex beaker	$+ \Delta S$

Entropy Values

We can make generalizations about a reaction's entropy;

$2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$

two solids → two solids + 3 gases

Entropy appears to increase in this reaction.

$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$

one solid + one gas → one solid

Entropy appears to decrease in this reaction.

Need an absolute entropy value ?

Temperature and Entropy

Entropy is directly affected by temperature changes.

Recall that kinetic molecular theory tells us that matter is made up of particles in motion. Temperature is a measurement of the kinetic energy of particles in a system.

Increasing temperature increases particle movement, increasing the disorder in a system, increasing its entropy.

Third Law of Thermodynamics

- The entropy of a pure crystal at 0 K is 0.
- Gives us a starting point.
- All others must be>0.
- Standard Entropies Sº (at 298 K and 1 atm) of substances are listed.
- Products - reactants to find ΔSº (a state function).
- More complex molecules higher Sº.

The entropy of a pure crystalline substance at absolute zero is 0.

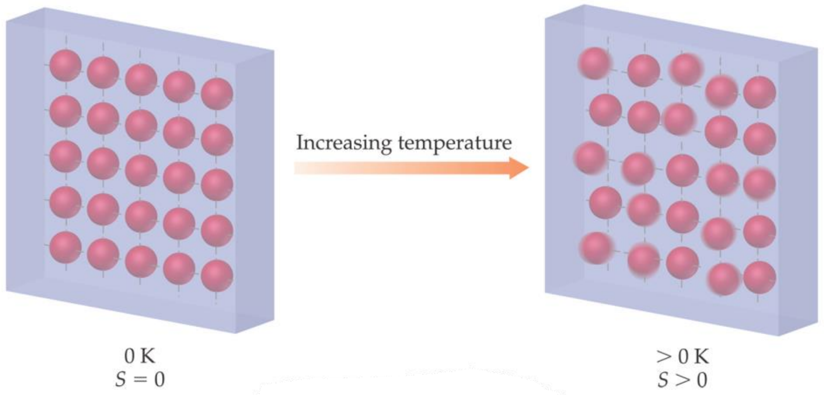
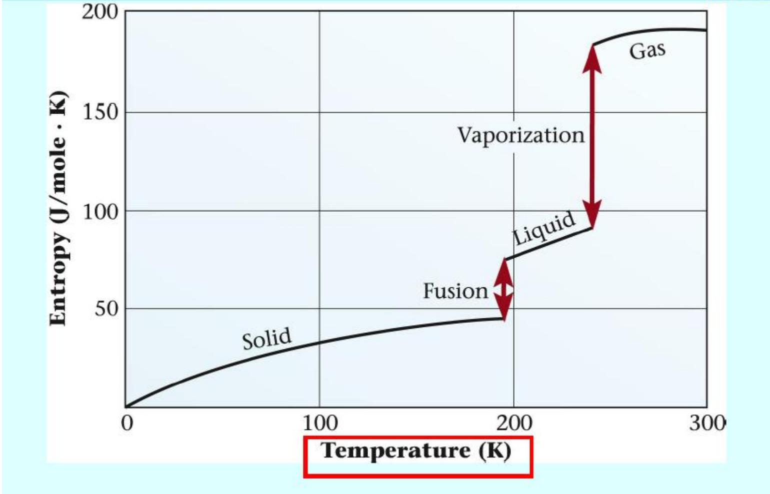


Figure 16.4



Standard Entropies

If we define the entropy of all perfect crystals at 0 K is zero,
we can get the molar absolute entropy of any substances at 1 atm.

This entropy value is called standard molar entropy ($S°$).

- These are molar entropy values of substances in their standard states.
- Standard entropies tend to increase with increasing molar mass.

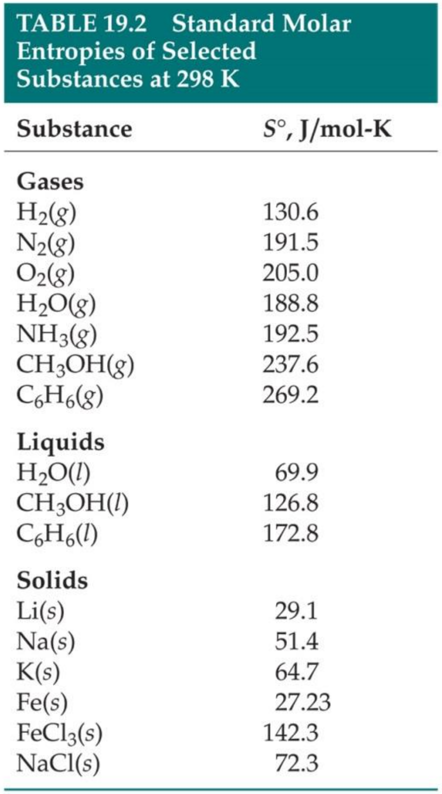


TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	$S°$, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Comparing S^o values

Substances with a greater freedom of motion (or number of possible ways to move) have a greater absolute entropy.

example: $I_{2(g)}$ (S^o = 261 J/K·mol) and
$I_{2(s)}$ (S^o = 117 J/K·mol)
example: $CH_{4(g)}$ (S^o = 186 J/K·mol) and
$C_2H_{6(s)}$ (S^o = 230 J/K·mol)

Entropy Values for a reaction

We can assign values to a species' entropy of formation, called standard entropy, and calculate a reaction's entropy quantitatively. Standard entropy is determined at 25°C and 1 atm (gas partial pressure) or 1 M (sol'n concentration).

Values in Appendix

$$2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$$

$$143.7\ _{J/mol*K} \rightarrow 82.6\ _{J/mol*K} + 205.1\ _{J/mol*K}$$

Using $\Delta S = S_{products} - S_{reactants}$, the reaction has a total entropy change of $+493.1\ _{J/mol*K}$

Entropy Changes

Entropy changes for a reaction can be calculated the same way we used for ΔH:

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

S° for each component is found in a table.

- 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:

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

The second thermodynamic law:
Entropy increasing law.

- Note that standard molar entropies are usually smaller in magnitude than enthalpies
  - Units normally is J/(mol × K), not kJ/(mol × K).
  - Pay attention to **J** vs. **kJ** in calculations!

Practice problems

Calculate the standard entropy changes for the following reactions at 25◌̊C:

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

- $\Delta S^o_{rxn} = [S^o(CaO) + S^o(CO_2)] - S^o(CaCO_3)$
- $\Delta S^o_{rxn} = [39.8\ J/K{\cdot}mol + 213.6\ J/K{\cdot}mol] - (92.9\ J/K{\cdot}mol)$
- $\Delta S^o_{rxn} = 160.5\ J/K{\cdot}mol$

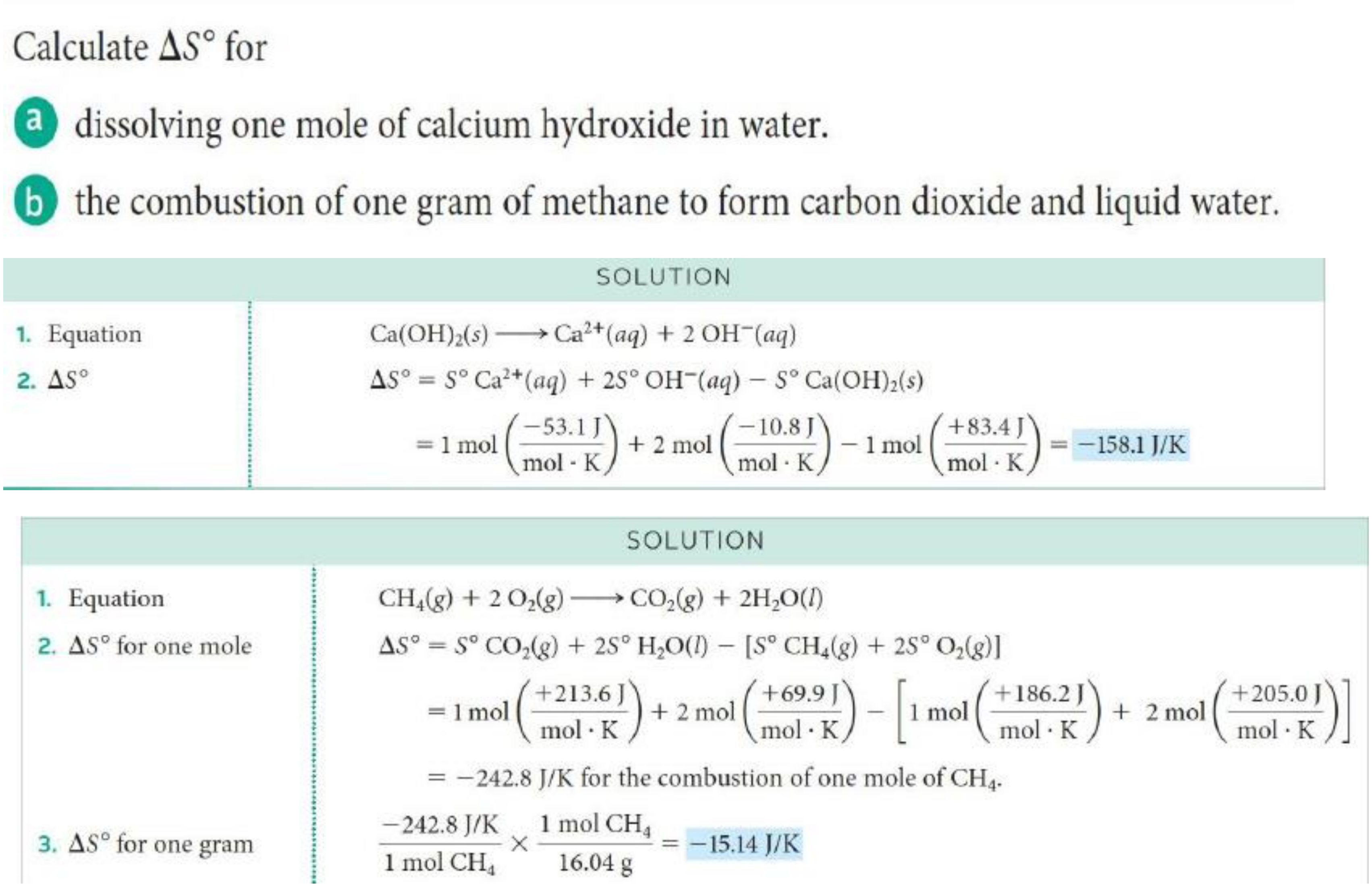
+ΔS= favorable

(b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

- $\Delta S^o_{rxn} = 2S^o(NH_3) - [S^o(N_2) + 3S^o(H_2)]$
- $\Delta S^o_{rxn} = (2)(193)\ J/K{\cdot}mol - [192\ J/K{\cdot}mol] + (3)(131\ J/K{\cdot}mol)]$
- $\Delta S^o_{rxn} = -199\ J/K{\cdot}mol$

-ΔS= unfavorable

More Practice $\Delta S^o_{reaction}$



Calculate $\Delta S°$ for

ⓐ dissolving one mole of calcium hydroxide in water.

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

SOLUTION

1. Equation

$$Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$$

2. $\Delta S°$

$$\Delta S° = S°\,Ca^{2+}(aq) + 2S°\,OH^-(aq) - S°\,Ca(OH)_2(s)$$

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

SOLUTION

1. Equation

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

2. $\Delta S°$ for one mole

$$\Delta S° = S°\,CO_2(g) + 2S°\,H_2O(l) - [S°\,CH_4(g) + 2S°\,O_2(g)]$$

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

$= -242.8$ J/K for the combustion of one mole of CH_4.

3. $\Delta S°$ for one gram

$$\frac{-242.8\text{ J/K}}{1\text{ mol }CH_4} \times \frac{1\text{ mol }CH_4}{16.04\text{ g}} = -15.14\text{ J/K}$$

How can we determine spontaneity using ΔS and ΔH?

Two tendencies exist in nature:

- tendency toward higher entropy -- ΔS
- tendency toward lower energy -- ΔH

If the two processes oppose each other (e.g. melting ice cube), then the direction is decided by the Free Energy, ΔG, and depends upon the temperature.

ΔG -- Free Energy!!!

Free Energy ΔG

A process (at constant *T*, *P*) is spontaneous in the direction in which free energy decreases

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

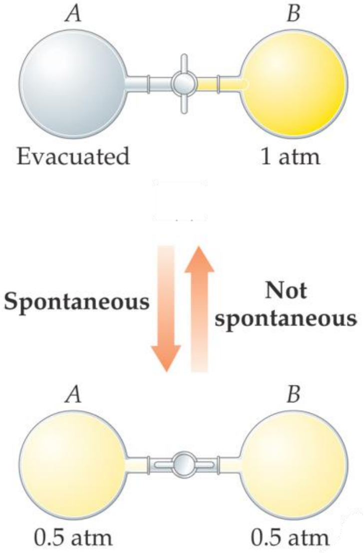
ΔG = negative – spontaneous (RIGHT shift)

ΔG = positive -- spontaneous in opposite direction (SHIFT left)

ΔG = 0 -- at equilibrium, no shift

**so…the MAGNITUDE of ΔG tells us how far the system is from equilibrium*

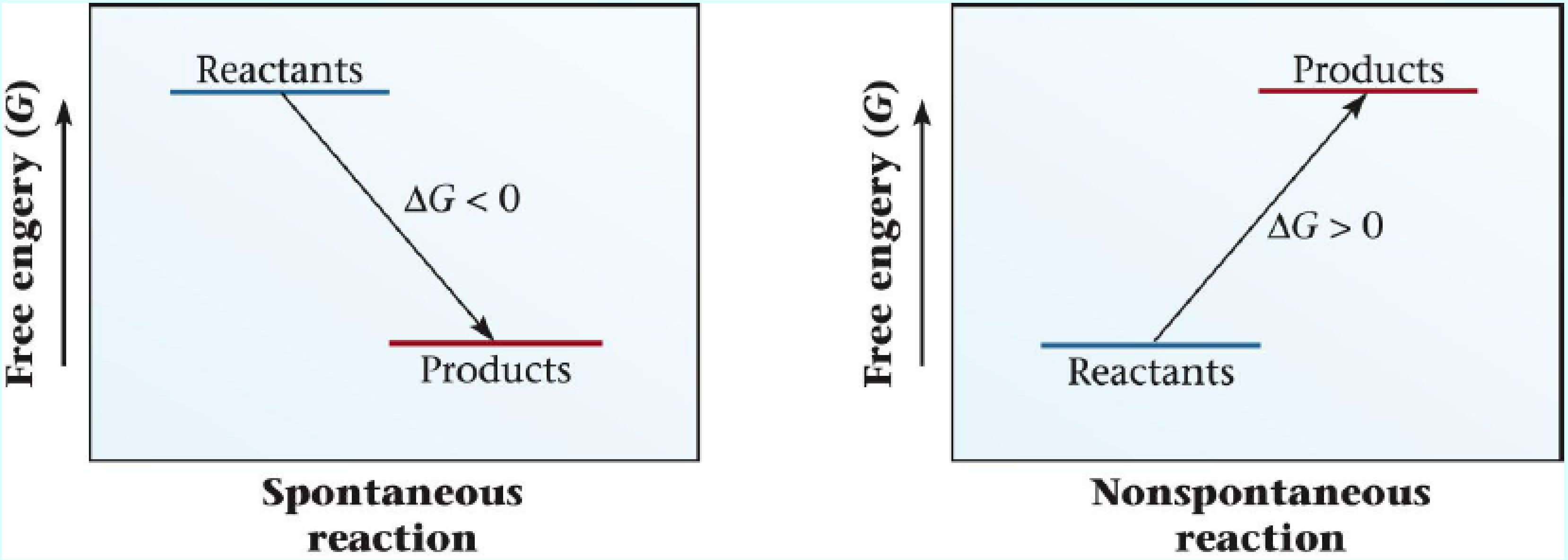
- $\Delta G = \Delta H - T\Delta S$
- To make ΔG negative;
- Negative value for ΔH (exothermic)
- Positive value for ΔS (less ordered= random)



Predicting spontaneity…

ΔH	ΔS	ΔG
-	+	- ALWAYS SPONTANEOUS
+	-	+ NEVER SPONTANEOUS
+	+	- only spontaneous when $T\Delta S$ is greater than ΔH (at high temp.)
-	-	- only spontaneous when $T\Delta S$ is less than ΔH (at low temp.)

Figure 16.5


Free engery (G)
Reactants
ΔG < 0
Products
Spontaneous reaction
Free engery (G)
Products
ΔG > 0
Reactants
Nonspontaneous reaction

The ***standard free-energy of reaction (ΔG_{rxn}^{0})*** is the free-energy change for a reaction when it occurs under standard-state conditions.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G^0_{rxn} = [\ c\Delta G^0_f\,(C) + d\Delta G^0_f\,(D)\,] - [\ a\Delta G^0_f\,(A) + b\Delta G^0_f\,(B)\,]$$

$$\Delta G^0_{rxn} = \Sigma n\Delta G^0_f(\text{products}) - \Sigma m\Delta G^0_f(\text{reactants})$$

Standard free energy of formation (ΔG^0_f) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

ΔG^0_f of any element in its stable form is zero.

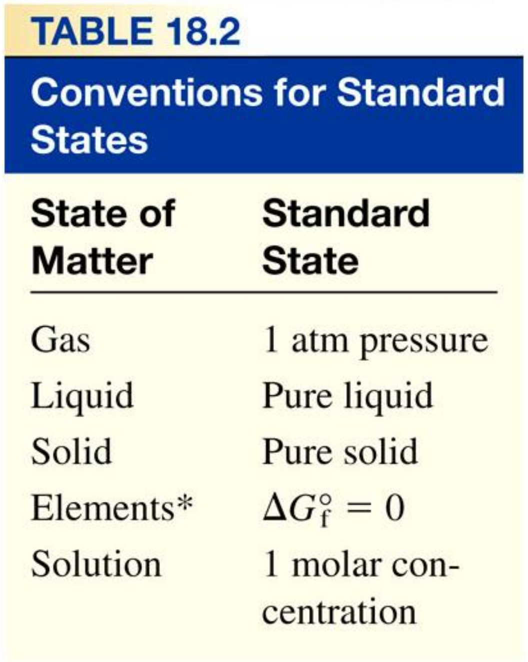


TABLE 18.2

Conventions for Standard States

State of Matter	**Standard State**
Gas	1 atm pressure
Liquid	Pure liquid
Solid	Pure solid
Elements*	$\Delta G^\circ_f = 0$
Solution	1 molar concentration

*The most stable allotropic form at 25°C and 1 atm.

Free Energy Change and Chemical Reactions- $\underline{\Delta H^\circ}$

(a) Calculate ΔH°, ΔS°, & ΔG° for the following reaction at 25°C

$$2\ SO_{2(g)} + O_{2(g)} \text{ ----> } 2\ SO_{3(g)}$$

$\Delta H^\circ = \Sigma n_p \Delta H_f^\circ\text{(products)} - \Sigma n_r \Delta H_f^\circ\text{(reactants)}$

ΔH° = [(2 mol SO_3)(-396 kJ/mol)]-[(2 mol SO_2)(-297 kJ/mol) + (0 kJ/mol)]

ΔH° = - 792 kJ + 594 kJ

ΔH° = $\underline{\text{-198 kJ}}$

$\Delta G°$ Calculations - $\underline{\Delta S°}$

$\Delta S° = \Sigma n_p S°_{(\text{products})} - \Sigma n_r S°_{(\text{reactants})}$

$\Delta S°$ = [(2 mol SO_3)(257 J/Kmol)]-[(2 mol SO_2)(248 J/Kmol) + (1 mol O_2)(205 J/Kmol)]

$\Delta S°$ = 514 J/K - 496 J/K - 205 J/K

$\Delta S°$ = $\underline{\text{-187 J/K}}$

$\underline{\Delta G^\circ}$ Calculations

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

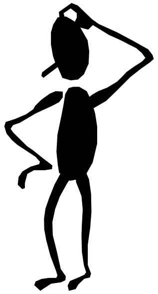
$\Delta G^o = - 198\ \text{kJ} - (298\ \text{K})(-187\ \text{J/K})(1\text{kJ}/1000\text{J})$

$\Delta G^o = - 198\ \text{kJ} + 55.7\ \text{kJ}$

$\Delta G^o = - 142\ \text{kJ}$

The reaction is spontaneous in forward direction at 25 ^{o}C and 1 atm.

Calculating Free Energy



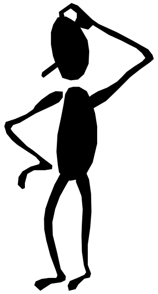
What is the standard free-energy change for the following reaction at 25 ^{0}C?

$$2C_6H_6\ (l) + 15O_2\ (g) \longrightarrow 12CO_2\ (g) + 6H_2O\ (l)$$

$$\Delta G^0_{rxn} = \Sigma n\Delta G^0_f(\text{products}) - \Sigma m\Delta G^0_f(\text{reactants})$$

$$\Delta G^0_{rxn} = [\ 12\Delta G^0_f\ (CO_2) + 6\Delta G^0_f\ (H_2O)] - [\ 2\Delta G^0_f\ (C_6H_6)]$$

$$\Delta G^0_{rxn} = [\ 12\times{-394.4} + 6\times{-237.2}\ ] - [\ 2\times 124.5\ ] = -6405\ \text{kJ}$$



Is the reaction spontaneous at 25 ^{0}C?

$\Delta G^0 = -6405$ kJ < 0 spontaneous

Free Energy, pressure and Temperature

For reactions that occur under partial pressures other than standard, the ΔG at those pressures is calculated as follows:

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

Q = reaction quotient from the law of mass action.

R= 8.314 J/mol K

Gibbs Free Energy and Chemical Equilibrium

From $\Delta G = \Delta H - T\Delta S \Rightarrow \Delta G = \Delta G^0 + RT \ln Q$

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature (K)

Q is the reaction quotient

At Equilibrium

$\Delta G = 0 \qquad Q = K$

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

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

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

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

Equilibrium Calculations

$4Fe_{(s)} + 3O_{2(g)} \longleftrightarrow 2Fe_2O_{3(s)}$
Calculate K for this reaction at 25 °C.

$\Delta G^o = -1.490 \times 10^6$ J from

1. $\Delta H^o = -1.652 \times 10^6$ J and $\Delta S^o = -543$ J/K
2. . $\Delta G^0_{rxn} = \Sigma n \Delta G^0_f(\text{products}) - \Sigma m \Delta G^0_f(\text{reactants})$

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

$K = e^{-\Delta G^\circ/RT}$

$K = e^{601}$ or 10^{261}

K is very large because ΔG° is very negative.

Practice Problem

Calculate ΔG at 25˚C for the following reaction where P_{CO} = 5.0 atm and P_{H_2} = 3.0 atm:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

$\Delta G^o = \Delta G^o_{(CH3OH)} - [\Delta G^o_{(CO)} + \Delta G^o_{(H2)}]$

$\Delta G^o = -166\ kJ/mol - [-137\ kJ/mol + 2(0\ kJ/mol)] = -29\ kJ/mol$

$\Delta G = \Delta G^o + RT\ln(Q) \quad Q = \dfrac{1}{(P_{CO})(P_{H_2})^2} = \dfrac{1}{(5.00)(3.00)^2} = 2.2 \times 10^{-2}$

$\Delta G = -2.9 \times 10^4 + [8.31\ J/K.mol)(298K)\ln(2.2 \times 10^{-2})$

$= -2.9 \times 10^4\ J/mol - 9.4 \times 10^3\ J/mol$

$= -3.8 \times 10^4\ J/mol = -38\ kJ/mol$

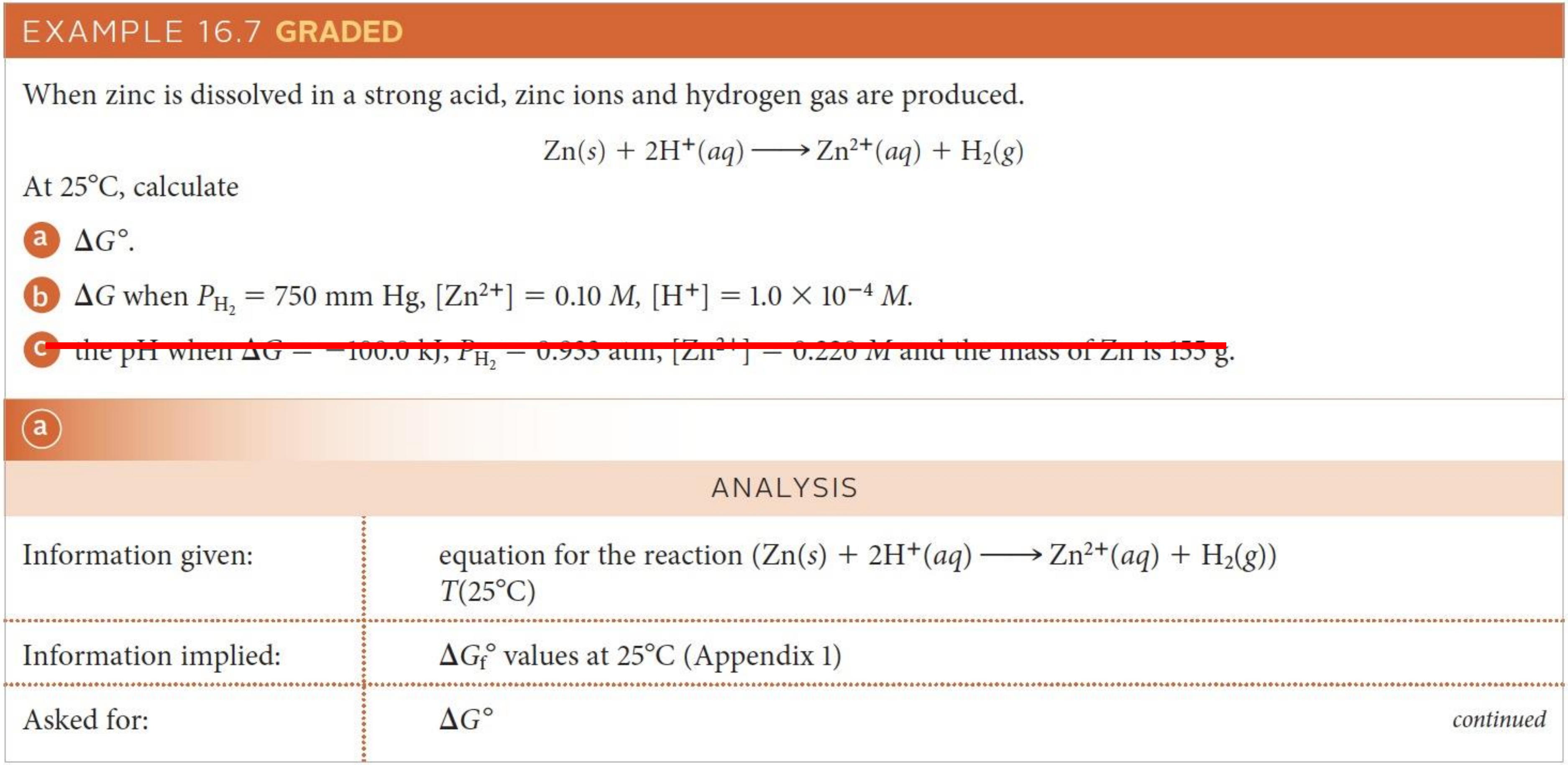
Compare this ΔG to ΔGº: a more negative ΔG means this reaction is more spontaneous (shift to right) than at one atm.

Recall the Reaction Quotient

- For the reaction
- $Zn\ (s) + 2H^+\ (aq) \rightarrow Zn^{2+}\ (aq) + H_2\ (g)$

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

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



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.~~

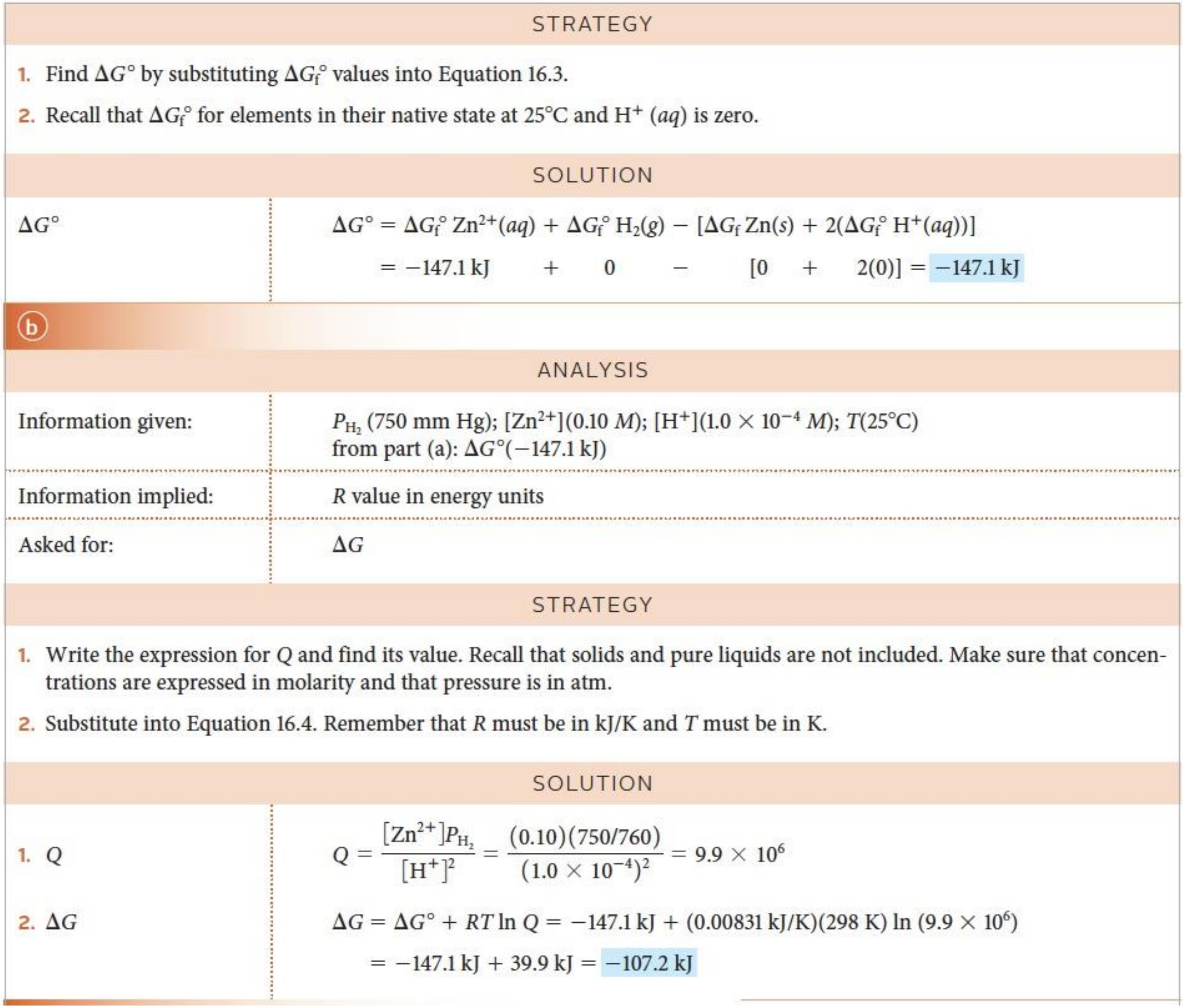
ⓐ

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

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

b

ANALYSIS

Information given:	P_{H_2} (750 mm Hg); $[Zn^{2+}](0.10\ M)$; $[H^+](1.0 \times 10^{-4}\ M)$; $T(25°C)$ from part (a): $\Delta G^\circ(-147.1\text{ kJ})$
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	$Q = \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2} = \frac{(0.10)(750/760)}{(1.0 \times 10^{-4})^2} = 9.9 \times 10^6$
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 17.10 The Equilibrium Constant and ΔG_{rxn}

Use tabulated free energies of formation to calculate the equilibrium constant for the reaction at 298 K:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

Solution

Look up (in Appendix IIB) the standard free energies of formation for each reactant and product.

Reactant or product	**ΔG_f° (in kJ/mol)**
$N_2O_4(g)$	99.8
$NO_2(g)$	51.3

Calculate ΔG_{rxn}° by substituting into Equation 17.13.

$$\begin{aligned}\Delta G_{rxn}^\circ &= \sum n_p \Delta G_f^\circ(\text{products}) - \sum n_r \Delta G_f^\circ(\text{reactants})\\ &= 2[\Delta G_{f,\,NO_2(g)}^\circ] - \Delta G_{f,\,N_2O_4(g)}^\circ\\ &= 2(51.3\ \text{kJ}) - 99.8\ \text{kJ}\\ &= 2.8\ \text{kJ}\end{aligned}$$

$$\Delta G_{rxn}^\circ = -RT\ln K$$

$$\begin{aligned}\ln K &= \frac{-\Delta G_{rxn}^\circ}{RT}\\ &= \frac{-2.8\times 10^3\ \cancel{\text{J}}/\cancel{\text{mol}}}{8.314\dfrac{\cancel{\text{J}}}{\cancel{\text{mol}}\cdot\cancel{\text{K}}}(298\ \cancel{\text{K}})}\\ &= -1.13\end{aligned}$$

$$\begin{aligned}K &= e^{-1.13}\\ &= 0.32\end{aligned}$$

Find the increase in entropy of the phase transition: $H_2O(s) \rightarrow H_2O(l)$

During a phase transition, $\Delta G=0$ since the system is at equilibrium.

This transition occurs when T=273K

- $\Delta G_{rxn} = \Delta H - T\Delta S$
- $0 = \Delta H - T\Delta S$
- $\Delta S_{rxn} = \dfrac{\Delta H_{fusion}}{T}$
- $\Delta S_{rxn} = \dfrac{6010\ J/mol}{273\ K}$
- $\Delta S_{rxn} = 22\ J/K{\cdot}mol$