THERMODYNAMICS: ENTROPY, FREE ENERGY,
AND THE DIRECTION OF CHEMICAL REACTIONS

Chapter 20 Outline

Text Problems: # 14, 16, 21, 28, 40, 46, 48, 51, 56, 64, 74
+ Supplementary Questions (attached)

Text Sample Problems: The text has a number of excellent sample problems (solved in detail) in each section. I would recommend that you study these problems + the "follow up" problems, which have brief solutions at the end of the chapter.

Sect.	Title and Comments	Required?
1.	The Second Law of Thermodynamics: Predicting Spontaneous Change In this section and later, the author uses the relatively advanced (and esoteric) concept that an increase in entropy correlates with an increase in the "number of microstates". We will use the more common notion that an increase entropy corresponds to an increase in "disorder"	YES
2.	Calculating the Change in Entropy of a Reactrion In addition to applying the Second Law of Thermodynamics to predicting entropy, we will show how it can be used to predict the spontaneity of phase transitions (e.g. melting, vaporization,…)	YES
3.	Entropy, Free Energy, and Work We will also show how λG can predict the spontaneity of phase transitions. We will not be covering the subsection on "The Free Energy Change" and the Work a System can do" We will not be covering the subsection on "Coupling of Reactions to Drive a Nonspontaneous Change"	YES
4.	Free Energy, Equilibrium, and Reaction Direction	YES

Note: I have added short discussions of various applications of ΔG in Biological/Biochemical Systems.

Chapter 20

Supplementary Homework Questions

S1. If a reaction is spontaneous at any temperature, then ΔH^o is ____ and ΔS^o is _____ .
  a. positive; positive
  b. positive; negative
  c. zero; positive
  d. negative; positive
  e. negative; negative

S2. At constant *T* and *P*, in which of the following situations will the reaction never be spontaneous?
  a. $\Delta H > 0$ and $\Delta S < 0$
  b. $\Delta H > 0$ and $\Delta S > 0$
  c. $\Delta H < 0$ and $\Delta S < 0$
  d. $\Delta H < 0$ and $\Delta S > 0$
  e. none of the above

S3. A reaction is exothermic and has a negative value of ΔS^o. The value of ΔG^o for this reaction is therefore:
  a. negative at all temperatures.
  b. positive at all temperatures.
  c. positive above 0^oC and negative below 0^oC.
  d. positive above a certain temperature and negative below it.
  e. negative above a certain temperature and positive below it.

S4. The reaction $A \rightarrow B$ is **exergonic** at 25 ^oC and the enthalpy change is +20 kJ. What can be concluded about the entropy change for this reaction?
  a. $\Delta S > +67$ J/K
  b. $\Delta S > +800$ J/K
  c. $\Delta S < -67$ J/K
  d. No conclusion can be made about ΔS

S5. For the **endergonic** reaction $C \rightarrow D$, $\Delta S = +20$ J/K. For this reaction,
  a. $\Delta G<0$ & $\Delta H<0$
  b. $\Delta G>0$ & $\Delta H<0$
  c. $\Delta G<0$ & $\Delta H>0$
  d. $\Delta G>0$ & $\Delta H>0$

S6. Consider a sample containing 322 grams of toluene ($C_6H_5CH_3$, M = 92).

Quantity	T_m	T_b	ΔH_{fus}^o	ΔH_{vap}^o	ΔS_{fus}^o	ΔS_{vap}^o
Value	-95 °C	+111 °C	6.64 kJ/mol	38.1 kJ/mol	37.3 J/mol-K	99.2 J/mol-K

(a) Calculate ΔS_{sys}, ΔS_{surr} and ΔS_{univ} for the vaporization of 322 grams of toluene at:
(1) 130 °C , (2) 111 °C, (3) 90 °C

(b) Calculate ΔG^o for the vaporization of 322 grams of toluene at:
(1) 130 °C , (2) 111 °C, (3) 90 °C

(c) Calculate ΔS_{sys}, ΔS_{surr} and ΔS_{univ} for the freezing (crystallization) of 322 grams of toluene at:
(1) -115 °C , (2) -95 °C, (3) -75 °C

(d) Calculate ΔG^o for the freezing (crystallization) of 322 grams of toluene at:
(1) -115 °C , (2) -95 °C, (3) -75 °C

S7. A certain reaction has $\Delta H° = +177.8$ kJ, and $\Delta S° = +160.5$ J/K. Above or below what temperature (in °C) does it become spontaneous ?

S8. For the reaction shown, $\Delta G° = -32.8$ kJ at 25°C.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

a. Calculate the equilibrium constant for this reaction at 25°C.

b. Is a mixture of the three gases where $p_{N_2} = 3.5$ bar, $p_{H_2} = 1.2$ bar, and $p_{NH_3} = 0.22$ bar at equilibrium? Justify your answer.

c. What is the value of ΔG under the conditions of part b?

S9. For the reaction, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, $\Delta H^o = +178$ kJ/mol and $\Delta S^o = +161$ J/mol-K.
a. What is the value of ΔG^o at 25 °C?
b. What is the value of ΔG^o at 1500 °C?
c. At what temperature, in °C, are the reactants and products in equilibrium? (i.e. $\Delta G^o = 0$)

S10. A hypothetical polypeptide, PP, has two structural forms, PP(α) and PP(β). For the transition, PP(α) → PP(β), the entropy change is -120 J/mol-K and the enthalpy change is -42 kJ/mol. This transition is spontaneous _____ (above or below) _____ °C.

Answers to the Supplementary Homework Questions are posted on the course web site.
Questions about these Problems will be answered in Recitation