Conceptual Questions:

- 1. What is the second law of thermodynamics?
- 2. For any process, what are the four possible combinations of ΔH and ΔS ? Which of these correspond to always spontaneous or always non-spontaneous reactions? Under what conditions would the last two combinations be spontaneous?
- 3. What is the third law of thermodynamics?
- 4. For a gas phase reaction, how do you determine the sign of ΔS° ? How about for a phase change?
- 5. For a liquid, would you expect ΔS_{fusion} or $\Delta S_{\text{evaporation}}$ to be larger? Why?
- 6. True or False: High temperatures are favorable to a reaction both kinetically and thermodynamically? Explain.
- 1. Calculate the standard entropy change for the following reaction at 25 °C:

$$2AI(s) + 3ZnO(s) \rightarrow AI_2O_3(s) + 3Zn(s)$$

- 2. A certain reaction has $\Delta H^{\circ} = -19.5 \text{ kJ}$ and $\Delta S^{\circ} = 42.7 \text{ J K}^{-1}$.
 - a. Calculate ΔG° for the reaction.
 - b. Is the reaction spontaneous under standard conditions?
- 3a. Using the data given below, calculate ΔG° for the reaction: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
 - 3b. Is this reaction spontaneous as written under standard conditions?
 - 3c. What is the equilibrium constant *K* for this reaction?
- 4. Calculate ΔG° for the process: C (diamond) $\leftarrow \rightarrow$ C (graphite)

Is the formation of graphite from diamond favored at 25°C? If so, why is it that diamonds do not become graphite on standing?

- 5. Consider the formation of a dimeric protein: $2P \rightarrow P_2$. At 25°C, we have $\Delta H^\circ = 17$ kJ/mol and $\Delta S^\circ = 65$ J/mol*K. Is the dimerization favored at this temperature? What would be the effect of lowering the temperature?
- 6. The equilibrium constant K_P for the reaction below is 5.62 x 10³⁵ at 25°C. What is $\Delta G^{\circ}f$ for $COCl_2$ at 25°C? Would you predict the ΔS for this reaction to be positive or negative? ($CO(g) + Cl_2(g) \leftarrow COCl_2(g)$)

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7. What is ΔG° for the reaction below at 25°C?

$$3Cl_2(g) + 2CH_4(g) \rightarrow CH_3Cl(g) + CH_2Cl_2(g) + 3HCl(g)$$

8. Consider the following reaction:

$$PCl_5(g) \longleftrightarrow PCl_3(g) + Cl_2(g)$$

$$\Delta G^{\circ}_{rxn}$$
 = 35.4 kJ/mol

Calculate ΔG at 25°C for the reaction if the partial pressures of the initial mixture are

 $P_{PCI5} = 0.0029$ atm, $P_{PCI3} = 0.27$ atm, and $P_{CI2} = 0.40$ atm.

- 9. Which of the following reactions would be spontaneous at 25°C? If either is non-spontaneous, at what temperature would it become spontaneous?
 - a. $\Delta H = 10.5 \text{ kJ/mol}$, $\Delta S = 30 \text{ J/molK}$
 - b $\Delta H = 1.8 \text{ kJ/mol}$, $\Delta S = -113 \text{ J/molK}$
- 10. The equilibrium constant (K_P) for the following reaction is 4.40 at 2000K.

$$H_2(g) + CO_2(g) \longleftrightarrow H_2O(I) + CO(g)$$

- a. Calculate ΔG° for the reaction at 2000K
- b. Calculate ΔG for the reaction when P_{H2} = 0.78 atm, P_{H2O} = 0.66 atm, and P_{CO} = 1.20 atm.

	<u>ΔH_f°</u>	<u>S°</u>	ΔG_f°
Al (s)		28.3 J/K•mol	
$Al_2O_3(s)$		50.99 J/K•mol	
ZnO (s)		43.9 J/K•mol	
Zn (s)		41.6 J/K∙mol	
SO ₂ (g)			-300.4 kJ mol ⁻¹
O ₂ (g)			0 kJ mol ⁻¹
SO ₃ (g)			-370.4 kJ mol ⁻¹
C (diamond)	1.90 kJ mol ⁻¹	2.4 J/K•mol	
C (graphite)	0 kJ mol ⁻¹	5.69 J/K•mol	
Cl ₂ (g)	0 kJ mol ⁻¹	223 J/K•mol	0 kJ mol ⁻¹
CH ₄ (g)	-74.85 kJ mol ⁻¹	186.2 J/K•mol	-50.8 kJ mol ⁻¹
CH₃Cl (g)	-83.68 kJ mol ⁻¹	234.36 J/K•mol	
CH ₂ Cl ₂ (g)	-95.52 kJ mol ⁻¹	270.28 J/K•mol	
HCI (g)	-92.3 kJ mol ⁻¹	187 J/K∙mol	-95.27 kJ mol ⁻¹

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$$3Cl_2(g) + 2CH_4(g) \rightarrow CH_3Cl(g) + CH_2Cl_2(g) + 3HCl(g)$$

8. Consider the following reaction:

$$PCl_5(g) \longleftrightarrow PCl_3(g) + Cl_2(g)$$

$$\Delta G^{\circ}_{rxn} = 35.4 \text{ kJ/mol}$$

Calculate ΔG at 25°C for the reaction if the partial pressures of the initial mixture are

 $P_{PC15} = 0.0029$ atm, $P_{PC13} = 0.27$ atm, and $P_{C12} = 0.40$ atm.

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