Work Session 20: Entropy and Free Energy

1. Explain what is meant by $\Delta S_{\text{sys}}$, $\Delta S_{\text{surr}}$, and $\Delta S_{\text{univ}}$. What relationship among these terms is required for a spontaneous reaction. What law is this? State the law in formal terms.

2. Predict the sign of $\Delta S^\circ$ for the following. Give a brief explanation:
   - $\text{CO}_2(s) \rightarrow \text{CO}_2(g)$
   - $2\text{K}(s) + \text{F}_2(g) \rightarrow 2\text{KF}(s)$
   - $\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$

3. Predict which of each of the following pairs has more entropy. Give a brief explanation.
   - $\text{O}_2(g)$ or $\text{O}_3(g)$
   - $\text{Na}(s)$ or $\text{K}(s)$
   - $\text{C}_3\text{H}_7\text{OH}(l)$ or $\text{C}_2\text{H}_5\text{OH}(l)$

4. Use values in the appendix of the textbook to calculate the $\Delta S^\circ$ for the reaction:
   - $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$

5. Explain why a reaction with $\Delta H^\circ<0$ and $\Delta S^\circ>0$ is spontaneous at all temperatures.

   Explain why a reaction with $\Delta H^\circ>0$ and $\Delta S^\circ<0$ is not spontaneous at any temperature.

   Explain why a reaction with $\Delta H^\circ>0$ and $\Delta S^\circ>0$ becomes spontaneous at high temperatures.

   Explain why a reaction with $\Delta H^\circ<0$ and $\Delta S^\circ<0$ is spontaneous only at low temperatures.

6. For the reaction:
   - $2\text{Fe}_2\text{O}_3(s) + 3 \text{C(graphite)} \rightarrow 4 \text{Fe}(s) + 3 \text{CO}_2(g)$

   Calculate $\Delta H^\circ$ and $\Delta S^\circ$ using appendix B.

   Use these values to calculate $\Delta G^\circ$ at 298K and at 1000K.

   What does the algebraic sign on $\Delta G^\circ$ at each temperature say about the spontaneity of the reaction? What causes the change?
7. For the reaction in question 6, at what T would the $\Delta G^\circ$ become zero?

This temperature is called the crossover temperature. Explain why.

8. For the reaction in question 6, explain what the algebraic sign on the terms $\Delta H^\circ$ and $\Delta S^\circ$ says about the tendency of the reaction to go to the right or to the left as influenced by that term.

9. What is the value for $K_{eq}$ at 298K for the reaction in question 6?

10. $K_{eq}$ for a reaction is $5.6 \times 10^8$ at 25°C. What is $\Delta G^\circ$ at that temperature?

11. For this question, use the equation: $\Delta G = \Delta H^\circ - T\Delta S^\circ + RT \ln Q$, where $R = 8.31 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

   For the reaction in question 6, show the mass action setup for $Q$

   At $T = 800K$, what would the value of $\Delta G$ be if the P of $\text{CO}_2 = 0.1 \text{ atm}$? If the P of $\text{CO}_2 = 10 \text{ atm}$? (Note that $Q = P^3$ of $\text{CO}_2$)

12. If a gas is produced in a reaction, there is a larger entropy change if the pressure is low than if the pressure is high. Why is that?