

## 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:  
 $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$   
 $2\text{K}(\text{s}) + \text{F}_2(\text{g}) \rightarrow 2\text{K}_2\text{F}(\text{s})$   
 $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
3. Predict which of each of the following pairs has more entropy. Give a brief explanation.  
 $\text{O}_2(\text{g})$  or  $\text{O}_3(\text{g})$   
 $\text{Na}(\text{s})$  or  $\text{K}(\text{s})$   
 $\text{C}_3\text{H}_7\text{OH}(\text{l})$  or  $\text{C}_2\text{H}_5\text{OH}(\text{l})$
4. Use values in the appendix of the textbook to calculate the  $\Delta S^\circ$  for the reaction:  
 $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

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:  $2\text{Fe}_2\text{O}_3(\text{s}) + 3\text{C}(\text{graphite}) \rightarrow 4\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$   
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  $T = 800\text{K}$ , 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?