## Thermodynamics.

1. For each reaction, select the correct answer for  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ .

| H2O2 (I) ≓ H2O2 (S) | ΔS > 0                | ∆S < 0 | $C(s) + 4 H(g) \rightleftharpoons CH_4(g)$ | $\Delta S > 0$        | ∆S < 0 |
|---------------------|-----------------------|--------|--|-----------------------|--------|
|                     | ΔH > 0                | ∆H < 0 |  | $\Delta H > 0$        | ∆H < 0 |
|                     | ∆G > 0                | ∆G < 0 |  | $\Delta G > 0$        | ∆G < 0 |
|                     | Temperature Dependent |        |  | Temperature Dependent |        |

2. For each of the following reactions in problem 1, identify which graph most accurately reflects the relationship between  $\Delta G$  and T.

- 3. For melting reaction,  $\Delta G = 0$  at the melting temperature (Tm).
  - a. Write out an equilibrium showing the melting of Li (s).
  - b. Why can't we write an equilibrium constant for this reaction?
  - c. Which of the graphs in problem 2 is most likely to represent the DG vs. T relationship for this melting reaction?
  - d. At the melting temperature, is it more favorable to make solids or liquids? Why?
  - e. With this in mind, rearrange  $\Delta G = \Delta H T\Delta S$  to show the relationship between  $\Delta H$  and  $\Delta S$  at the melting temperature (Tm).
  - f. Use the equation that you developed in 3e to calculate the entropy of melting for lithium and sodium. The melting temperature and melting enthalpy are given below.

| Metal | Tm (K) | ∆H <sub>fus</sub> (kJ mol <sup>-1</sup> ) |
|-------|--------|---|
| Li    | 454    | 2.99                                      |
| Na    | 371    | 2.60                                      |

g. Do the signs of  $\Delta H$  and  $\Delta S$  make sense based on your understanding of the reaction?

4. ATP hydrolysis is a very important reaction in biological systems. Consider the information given below. **This reaction is balanced.** 

ATP (aq) + H<sub>2</sub>O (I)  $\rightleftharpoons$  ADP (aq) + HPO<sub>4</sub><sup>2-</sup> (aq)  $\Delta G^{\circ} = -30.5 \text{ kJ mol}^{-1}$ 

- a. Does this reaction consume or produce energy? How do you know?
- b. Calculate the equilibrium constant for this reaction.
- c. Under the conditions below, will the reaction shift to make reactants or products? What do you predict the sign of  $\Delta G$  to be?

 $[ATP] = 5.0 \text{ mM}, [ADP] = 0.50 \text{ mM}, \text{ and } [HPO_4^{2-}] = 5.0 \text{ mM}$ 

d. For the conditions above, calculate  $\Delta G$  at 37°C.

5. Calculate  $\Delta H^{\circ}$  for CH<sub>3</sub>CH<sub>2</sub>OH (I)  $\rightleftharpoons$  CH<sub>3</sub>OCH<sub>3</sub> (I) noting that:

CH<sub>3</sub>CH<sub>2</sub>OH (I) + 3 O<sub>2</sub> (g)  $\rightleftharpoons$  2 CO<sub>2</sub> (g) + 3 H<sub>2</sub>O (g) △H° = -1234.8 kJ mol<sup>-1</sup> CH<sub>3</sub>OCH<sub>3</sub> (I) + 3 O<sub>2</sub> (g)  $\rightleftharpoons$  2 CO<sub>2</sub> (g) + 3 H<sub>2</sub>O (g) △H° = -1309.1 kJ mol<sup>-1</sup> 6. From the data below, calculate  $\Delta G^{\circ}$  and K for the following reaction at 25°C.

 $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ 

|   | Ag⁺ (ag) | Cl⁻ (aq) | AgCl(s) |
|---|----------|----------|---------|
| $\Delta G_f^0$ (kJ mol <sup>-1</sup> )    | 77.1     | -131.2   | -109.8  |
| S° (J mol <sup>-1</sup> K <sup>-1</sup> ) | 72.7     | 56.5     | 96.3    |

- 7. What do you think the sign of  $\Delta H$  and  $\Delta S$  will be for the reaction in problem 6? Explain your choice.
- 8. For the reaction in problem 6, determine  $\Delta S^{\circ}$  and  $\Delta H^{\circ}$ .

9. Using the information you determined in problems 6 and 7, determine K,  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ , and  $\Delta S^{\circ}$  for the following reactions:

 $3 \text{ Ag}^+(\text{aq}) + 3 \text{ Cl}^-(\text{aq}) \rightleftharpoons 3 \text{ AgCl}(s)$ 

 $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ 

10. From what you learned in problem 6, explain why our solubility rules predict that AgCl is not soluble.

11. Using the values from problems 6 and 8, determine the temperature that would be needed to make dissolving AgCl (s) favorable. Hint: you'll need to calculate K at 25 °C and use ∆H from problem 8. Also, you should figure out what K value is needed when the reaction changes to being nonspontaneous.