Thermodynamics. These problems are mostly from your textbook. More can be found in chapter 14 and 23.

- 1. Define the First and Second Laws of Thermodynamics in words and with an equation. Discuss how they are related to our understanding on ΔH , ΔS , and ΔG .
- 2. Standard molar entropy (S⁰) can be used to calculate reaction entropies (ΔS_{rxn}^0). These values are always positive ($S^0 > 0$). Why?
- 3. (23-6) Predict which molecule will have a higher molar entropy

$$H_2O$$
 (s) vs. H_2O (l)

- 4. Predict whether the following reactions will be spontaneous, non-spontaneous, or temperature dependent.
 - a. $H_2O_2(I) \rightleftharpoons H_2O_2(s)$
 - b. $C(s) 2 H_2(g) \rightleftharpoons CH_4(g)$
- 5. (23.23) Using the information below, calculate the ΔG_{rxn} when [ATP] = 5.0 mM, [ADP] = 0.50 mM, and $[HPO_4^{2-}] = 5.0$ mM. Is the reaction spontaneous under these conditions?

ATP (aq) +
$$H_2O(I) \rightleftharpoons ADP (aq) + HPO_4^{2-}$$

$$\Delta G_{rxn}^o = -30.5 \ kJ \ mol^{-1}$$

6. (14.19) Calculate ΔH_{rxn}^o and for CH₃CH₂OH (I) \rightleftharpoons CH₃OCH₃ (I) noting that:

CH₃CH₂OH (I) + 3 O₂ (g)
$$\rightleftharpoons$$
 2 CO₂ (g) + 3 H₂O (g) $\Delta H_{rxn}^{o} = -1234.8 \, kJ \, mol^{-1}$

$$\Delta H_{rxn}^{o} = -1234.8 \, kJ \, mol^{-1}$$

$$CH_3OCH_3$$
 (I) + 3 O_2 (g) \rightleftharpoons 2 CO_2 (g) + 3 H_2O (g) $\Delta H_{rxn}^o = -1309.1 \, kJ \, mol^{-1}$

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7. (23-67) From the following data, calculate ΔS_{fus} for each metal.

Metal	T _m (K)	$\Delta H_{fus} (kJ mol^{-1})$
Li	454	2.99
Na	371	2.60

8. (23.72) From the data below, calculate ΔG_{rxn}^0 and K for the following reactions at 25°C.

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

$$Pb^{2+}$$
 (aq) + 2 Cl^{-} (aq) $\rightleftharpoons PbCl_2$ (s)

	Pb ²⁺ (aq)	Ag⁺ (aq)	Cl ⁻ (aq)	PbCl ₂ (s)	AgCl (s)
ΔG_f^0 (kJ mol $^{ ext{-}1}$)	-24.4	77.1	-131.2	-314.1	-109.8
S^0 (J mol $^{ ext{-}1}$ K $^{ ext{-}1}$)	10.5	72.7	56.5	136.0	96.3

- 9. For the reactions in problem 8, determine ΔS_{rxn}^0 and ΔH_{rxn}^0 .
- 10. Using your answers from problem 8, determine ΔG_{rxn}^0 , ΔS_{rxn}^0 , ΔH_{rxn}^0 , and K for the following reactions.

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

$$2 \text{ PbCl}_2(s) \rightleftharpoons 2 \text{ Pb}^{2+}(aq) + 4 \text{ Cl}^{-}(aq)$$

11. (23-43) Use the following data to calculate ΔH_{rxn}^{0} the reaction N₂ (g) + O₂ (g) \rightleftharpoons 2 NO (g)

$$Kp = 4.08 \times 10^{-4} \text{ at } 2000 \text{ K}$$

$$Kp = 11.0 \times 10^{-4} \text{ at } 2200 \text{ K}.$$

- 12. For the vaporization of water, $\Delta H_{vap}^0=44.03~kJ~mol^{-1}$ and $\Delta S_{vap}^0=118.89~J~mol^{-1}K^{-1}$.
 - a. Calculate ΔG_{vap}^{0} and K at 25 °C.
 - b. What is the vapor pressure of water at 25 °C? This is the pressure of H_2O (g) at this temperature.
 - c. What is K at 100 °C?
 - d. What is the vapor pressure of water at 100°C?

Thermodynamics Equation Sheet

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G^0 = -RTlnK$$

$$\Delta G = \Delta G^o + RT ln Q$$

$$\Delta U = q + w$$

$$w = -p\Delta V$$

$$\Delta H = q_p$$

$$\Delta G = -T\Delta S_{universe}$$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding}$$

$$\Delta S_{universe} > 0$$

$$\Delta S = \frac{\Delta H}{T}$$

$$C_P = \frac{\Delta H}{\Delta T}$$

$$ln\frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$