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 (S°) can be used to calculate reaction entropies. These values are always positive (S° > 0). Why?
3. (23-6) For each pair, predict which molecule will have a higher molar entropy:

CO vs. CO_2 $\quad$ H_2O (s) vs. H_2O (l) $\quad$ CH_4 (g) at 25 °C vs. CH_4 (g) at 250 °C

4. For each reaction, select the correct answer for ΔH, ΔS, and ΔG.

H_2O_2 (l) ⇌ H_2O_2 (s)	ΔS > 0	ΔS < 0	C (s) + 4 H (g) ⇌ CH_4 (g)	ΔS > 0	ΔS < 0
	ΔH > 0	ΔH < 0		ΔH > 0	ΔH < 0
	ΔG > 0	ΔG < 0		ΔG > 0	ΔG < 0
	Temperature Dependent			Temperature Dependent	

5. (23.23) Using the information below, calculate the ΔG at 37°C when [ATP] = 5.0 mM, [ADP] = 0.50 mM, and $[HPO_4^{2-}]$ = 5.0 mM. Is the reaction spontaneous under these conditions?

$$ATP\ (aq) + H_2O\ (l) \rightleftharpoons ADP\ (aq) + HPO_4^{2-} \qquad \Delta G° = -30.5\ kJ\ mol^{-1}$$

6. (14.19) Calculate ΔH° for CH_3CH_2OH (l) ⇌ CH_3OCH_3 (l) noting that:

$$CH_3CH_2OH\ (l) + 3\ O_2\ (g) \rightleftharpoons 2\ CO_2\ (g) + 3\ H_2O\ (g) \qquad \Delta H° = -1234.8\ kJ\ mol^{-1}$$

$$CH_3OCH_3\ (l) + 3\ O_2\ (g) \rightleftharpoons 2\ CO_2\ (g) + 3\ H_2O\ (g) \qquad \Delta H° = -1309.1\ kJ\ mol^{-1}$$

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

Metal	Tm (K)	ΔH_{fus} (kJ mol^{-1})
Li	454	2.99
Na	371	2.60

8. (23.72) From the data below, calculate **ΔG° and K** for the following reaction at 25°C.

Ag^+ (aq) + Cl^- (aq) ⇌ $AgCl(s)$

	Ag^+ (aq)	Cl^- (aq)	AgCl(s)
ΔG_f^0 (kJ mol^{-1})	77.1	-131.2	-109.8
S° (J mol^{-1}K^{-1})	72.7	56.5	96.3

9. For the reaction in problem 8, determine ΔS° and ΔH°.

10. Using the information you determined in problems 8 and 9, determine **K, ΔG°, ΔH°, and ΔS°** for the following reactions:

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

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

⑤ $\Delta G = \Delta G^\circ + RT \ln Q$

$\Delta G^\circ = -30.5 \frac{kJ}{mol} = -30500 \frac{J}{mol}$

$R = 8.314 \frac{J}{mol \cdot K}$

$T = 37 + 273.15 = 310.15 K$

$Q = \frac{[ATP][HPO_4^{2-}]}{[ATP]}$

$Q = \frac{(5 \times 10^{-4} M)(5 \times 10^{-3} M)}{5 \times 10^{-3} M} = 5 \times 10^{-4}$

$\Delta G = -30500 \frac{J}{mol} + 8.314 \frac{J}{mol K} \cdot 310.15 K \cdot \ln 5 \times 10^{-4}$

$\Delta G = -50,097.6 \frac{J}{mol} = -50.1 \frac{kJ}{mol}$

⑥

$CH_3CH_2OH(l) + 3O_2(g) \rightleftharpoons 2CO_2(g) + 3H_2O(g) \quad \Delta H = -1234.8 \frac{kJ}{mol}$

$CH_3OCH_3(l) + 3O_2(g) \rightleftharpoons 2CO_2(g) + 3H_2O(g) \quad \Delta H = -1309.1 \frac{kJ}{mol}$

reverse ↳ $2CO_2(g) + 3H_2O(g) \rightleftharpoons CH_3OCH_3(l) + 3O_2(g) \quad \Delta H = 1309.1 \frac{kJ}{mol}$

$CH_3CH_2OH(l) + 3O_2(g) \rightleftharpoons 2CO_2(g) + 3H_2O(g) \quad \Delta H = -1234.8 \frac{kJ}{mol}$

$CH_3CH_2OH(l) \rightleftharpoons CH_3OCH_3(l) \quad \Delta H = 74.3 kJ/mol$

⑦ @ phase change temps, $\Delta G = 0$

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

$0 = \Delta H - T\Delta S$

$T\Delta S = \Delta H$

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

$\Delta S^\circ_{fus} = \frac{\Delta H^\circ_{fus}}{T_m}$

Li: $\Delta S^\circ_{fus} = \frac{2.99 \frac{kJ}{mol}}{454 K} = 0.00659 \frac{kJ}{mol \cdot K} = 6.59 \frac{J}{mol \cdot K}$

Na: $\Delta S^\circ_{fus} = \frac{2.60 kJ/mol}{371 K} = 0.007 \frac{kJ}{mol \cdot K} = 7 \frac{J}{mol \cdot K}$

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

($\frac{kJ}{mol}$) ΔG_f° 77.1 −131.2 −109.8

$$\Delta G^\circ = -109.8 \frac{kJ}{mol} - \left[77.1 \frac{kJ}{mol} + -131.2 \frac{kJ}{mol}\right]$$

$$\Delta G^\circ = -55.7 \frac{kJ}{mol} = -55700 \frac{J}{mol}$$

$\Delta G^\circ = -RT \ln K$

$-55700 \frac{J}{mol \cdot K} = -8.314 \frac{J}{mol \cdot K} \cdot 298.15\ K \ln K$ $\quad \ln K = -22.47$

$K = 1.74 \times 10^{-10}$

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

S° ($\frac{J}{mol \cdot K}$) 72.7 56.5 96.3

$$\Delta S^\circ = 96.3 - [72.7 + 56.5] = -32.9 \frac{J}{mol \cdot K}$$

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

$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$

$$\Delta H^\circ = -55700 \frac{J}{mol} + 298.15\ K \left(-32.9 \frac{J}{mol \cdot K}\right) = -65{,}509 \frac{J}{mol} = -65.5 \frac{kJ}{mol}$$

(10)

$Ag^+ + Cl^- \rightleftharpoons AgCl(s)$ $\quad \Delta G = -55.7$ $\quad \Delta H$ $\quad \Delta S$

×3 ↳ $3Ag^+ + 3Cl^- \rightleftharpoons 3AgCl(s)$ $\quad$ ×3 $\quad$ ×3 $\quad$ ×3

$\Delta G = -152.1 \frac{kJ}{mol}$ $\quad \Delta H = -196.5 \frac{kJ}{mol}$ $\quad \Delta S = -98.7 \frac{J}{mol \cdot K}$

$K = [1.74 \times 10^{-10}]^3 = 5.27 \times 10^{-30}$

$Ag^+ + Cl^- \rightleftharpoons AgCl(s)$ $\quad \Delta G$ $\quad \Delta H$ $\quad \Delta S$

reverse $(\times -1)$ $\quad \downarrow \times -1$ $\quad \downarrow \times -1$ $\quad \downarrow \times -1$

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$ $\quad \Delta G = 55.7 \frac{kJ}{mol}$ $\quad \Delta H = 65.5 \frac{kJ}{mol}$ $\quad \Delta S = 32.9 \frac{J}{mol \cdot K}$

$$K = [1.74 \times 10^{-10}]^{-1} = 5.74 \times 10^{9}$$