

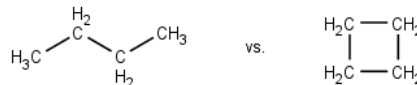
Thermodynamics. These problems are mostly from your textbook. More can be found in chapter 14 and 23.

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^0) 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

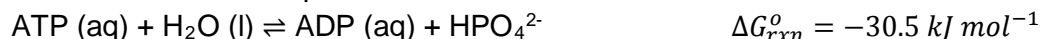
CO vs. CO₂

H₂O (s) vs. H₂O (l)

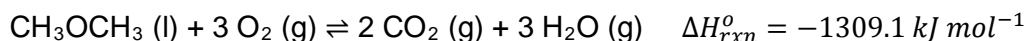
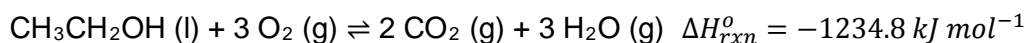


4. Predict whether the following reactions will be spontaneous, non-spontaneous, or temperature dependent.
 - a. H₂O₂ (l) \rightleftharpoons H₂O₂ (s)
 - b. C (s) + 2 H₂ (g) \rightleftharpoons CH₄ (g)

5. (23.23) Using the information below, calculate the ΔG_{rxn} when [ATP] = 5.0 mM, [ADP] = 0.50 mM, and [HPO₄²⁻] = 5.0 mM. Is the reaction spontaneous under these conditions?



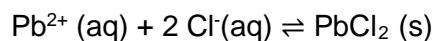
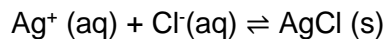
6. (14.19) Calculate ΔH_{rxn}^0 and for CH₃CH₂OH (l) \rightleftharpoons CH₃OCH₃ (l) noting that:



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

Metal	T _m (K)	ΔH_{fus} (kJ mol ⁻¹)
Li	454	2.99
Na	371	2.60

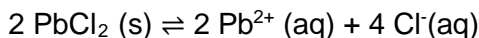
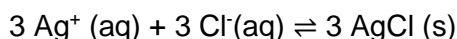
8. (23.72) From the data below, calculate ΔG_{rxn}^0 and K for the following reactions at 25°C.



	Pb ²⁺ (aq)	Ag ⁺ (aq)	Cl ⁻ (aq)	PbCl ₂ (s)	AgCl (s)
ΔG_f^0 (kJ mol ⁻¹)	-24.4	77.1	-131.2	-314.1	-109.8
S^0 (J mol ⁻¹ K ⁻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.



11. (23-43) Use the following data to calculate ΔH_{rxn}^0 the reaction $N_2 (g) + O_2 (g) \rightleftharpoons 2 NO (g)$

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

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

12. For the vaporization of water, $\Delta H_{vap}^0 = 44.03 \text{ kJ mol}^{-1}$ and $\Delta S_{vap}^0 = 118.89 \text{ J mol}^{-1} \text{K}^{-1}$.

- Calculate ΔG_{vap}^0 and K at 25°C .
- What is the vapor pressure of water at 25°C ? This is the pressure of $\text{H}_2\text{O} (g)$ at this temperature.
- What is K at 100°C ?
- What is the vapor pressure of water at 100°C ?

① 1st Law → Energy must be conserved $\Delta U = q + w$ we were able to show that $\Delta H = q_p$ using the 1st Law

2nd Law → Everything tends toward disorder

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

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

- the definition of entropy is built into the second law. We also used this to derive $\Delta G = \Delta H - T\Delta S$

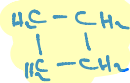
② Thermal energy is distributed throughout a molecule - this is a form of entropy.

Because of this, the only way that entropy reaches 0 is for the Temp to be 0 Kelvin → the 3rd Law prevents this!

③ CO vs CO₂ larger molecules have higher S°

H₂O (s) vs. H₂O (l) liquid always has more disorder than solids

CH₃CH₂CH₂CH₃ vs



more rigid structure

④ H₂O (l) ⇌ H₂O (s) $\Delta H < 0$ ($-\Delta H_{\text{fusion}}$)

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

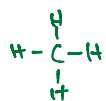
spontaneous at low

$$\Delta S < 0$$

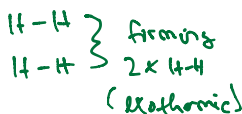
becoming more ordered

$$\leftarrow \quad \leftarrow$$

temperatures, non-spontaneous at high temperatures



breaking 4 C-H
(endothermic)



$\Delta S > 0$ 1 molecule → 3 molecules
1 gas → 2 gas

$\Delta H > 0$ breaking more bonds than creating

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

(+) (+)

- spontaneous at high temp, non-spontaneous at low temp

$$\textcircled{5} \Delta G_{\text{rxn}} = \Delta G^{\circ}_{\text{rxn}} + RT \ln Q$$

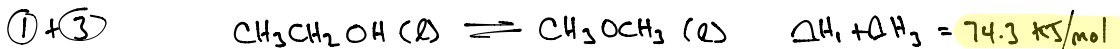
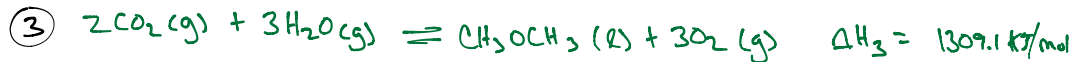
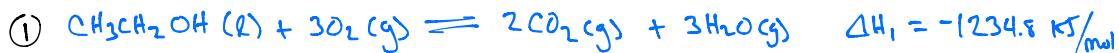
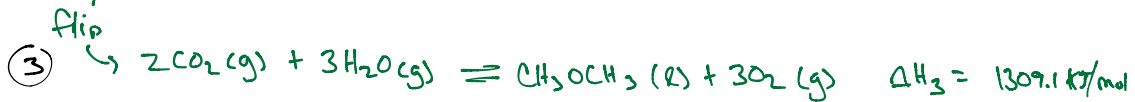
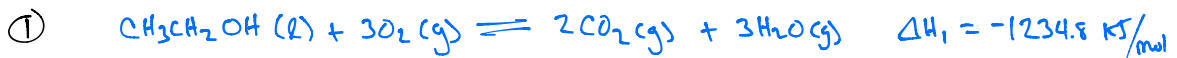


$$Q = \frac{[\text{ADP}][\text{HPO}_4]}{[\text{ATP}]} = \frac{(0.0005)(0.005)}{(0.005)} = 0.0005$$

$$\Delta G_{\text{rxn}} = -30500 \frac{\text{J}}{\text{mol}} + 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} (310.15\text{K}) \ln 0.0005 = -50,100 \frac{\text{J}}{\text{mol}}$$

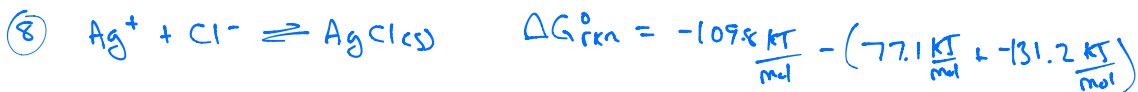
yes, it is spontaneous

⑥ Hess' Law



$$\textcircled{7} \Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_m} \quad \text{Li} \quad \Delta S_{\text{fus}} = \frac{2.99 \text{ kJ/mol}}{454 \text{ K}} = 6.58 \times 10^{-3} \frac{\text{kJ}}{\text{mol}\cdot\text{K}} = 6.58 \text{ J/mol}\cdot\text{K}$$

$$\text{Na} \quad \Delta S_{\text{fus}} = \frac{2.60 \text{ kJ/mol}}{371 \text{ K}} = 7.00 \times 10^{-3} \frac{\text{kJ}}{\text{mol}\cdot\text{K}} = 7.00 \text{ J/mol}\cdot\text{K}$$



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

$$-55700 \frac{\text{J}}{\text{mol}} = -8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} (298.15\text{K}) \ln K$$

$$K = 5.74 \times 10^9$$

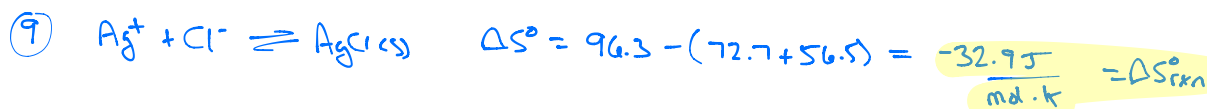
$$\Delta G^{\circ}_{\text{rxn}} = -55.7 \frac{\text{kJ}}{\text{mol}}$$



$$\Delta G_{\text{rxn}}^{\circ} = -27.3 \text{ kJ/mol}$$

$$-27300 = 8.314 (298.15) \ln K$$

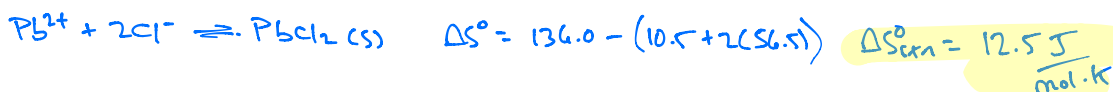
$$K = 6.07 \times 10^4$$



$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$$

$$-55.7 \frac{\text{kJ}}{\text{mol}} = \Delta H_{\text{rxn}}^{\circ} - 298.15 \text{ K} \left(-0.0329 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \right)$$

$$\Delta H_{\text{rxn}}^{\circ} = -65.5 \frac{\text{kJ}}{\text{mol}}$$



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

$$-27.3 \frac{\text{kJ}}{\text{mol}} = \Delta H^{\circ} - 298.15 (0.0125)$$

$$\Delta H_{\text{rxn}}^{\circ} = -23.6 \text{ kJ/mol}$$



$\Delta H, \Delta S \downarrow \Delta G$ ALL $\times 3$

K gets cubed

$$\Delta H = 3(-65.5) = -196.5 \frac{\text{kJ}}{\text{mol}}$$

$$K = (5.74 \times 10^9)^3 = 1.89 \times 10^{29}$$

$$\Delta S = 3(-32.7) = -98.1 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\Delta G = 3(-55.7) = -167.1 \frac{\text{kJ}}{\text{mol}}$$



This is reversal and $\times 2$

$\Delta H, \Delta G \uparrow \Delta S$ $\times -2$

$(K)^{-2}$

$$\Delta G = -2(-27.3) = -54.6 \frac{\text{kJ}}{\text{mol}} \quad \Delta H = -2(-23.6) = -47.2 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S = -2(12.5) = -25 \frac{\text{J}}{\text{mol} \cdot \text{K}} \quad K = (6.07 \times 10^4)^{-2} = 2.71 \times 10^{-10}$$

$$11. \ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad K_2 = 4.08 \times 10^{-4} \quad K_1 = 11.0 \times 10^{-4}$$

$$T_2 = 2000 \text{ K}$$

$$T_1 = 2200 \text{ K}$$

$$\ln \frac{4.08 \times 10^{-4}}{11.0 \times 10^{-4}} = \frac{\Delta H}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{2200} - \frac{1}{2000} \right)$$

$$-0.992 = -5.47 \times 10^{-6} \Delta H$$

$$\Delta H = 181315.9 \frac{\text{J}}{\text{mol}} = 181.3 \frac{\text{kJ}}{\text{mol}}$$

$$12. \Delta H_{\text{vap}}^{\circ} = 44.03 \frac{\text{kJ}}{\text{mol}} \quad \Delta S_{\text{vap}}^{\circ} = 115.89 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$a. \Delta G_{\text{vap}}^{\circ} = 44.03 \frac{\text{kJ}}{\text{mol}} - 298.15 \text{ K} \left(0.11589 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \right) = 8.58 \frac{\text{kJ}}{\text{mol}}$$

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

$$8580 \frac{\text{J}}{\text{mol}} = -8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298.15 \text{ K}) \ln K \quad K = 0.0314$$

$$b. \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g) \quad K = P_{\text{H}_2\text{O}} = 0.0314 \text{ atm}$$

$$c. \ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \ln \frac{K_2}{0.0314} = \frac{44030}{8.314} \left(\frac{1}{298.15} - \frac{1}{373.15} \right)$$

$$\ln \frac{K_2}{0.0314} = 3.57$$

$$\frac{K_2}{0.0314} = 35.5 \quad K_2 = 1.12$$

$$d. K = P_{\text{H}_2\text{O}} = 1.12 \text{ atm}$$