

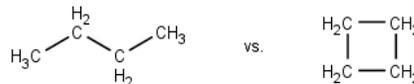
**Thermodynamics.** These problems are mostly from your textbook. More can be found in chapter 14 and 23.

1. Define the First and Second Laws of Thermodynamics in words and with an equation. Discuss how they are related to our understanding on  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ .
2. Standard molar entropy ( $S^0$ ) can be used to calculate reaction entropies ( $\Delta S_{rxn}^0$ ). These values are always positive ( $S^0 > 0$ ). Why?

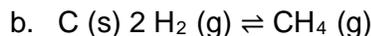
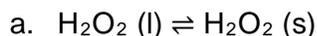
3. (23-6) Predict which molecule will have a higher molar entropy

CO vs. CO<sub>2</sub>

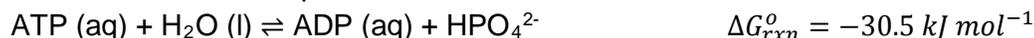
H<sub>2</sub>O (s) vs. H<sub>2</sub>O (l)



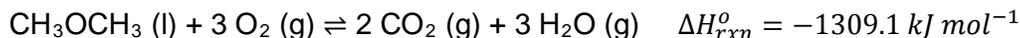
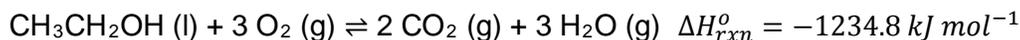
4. Predict whether the following reactions will be spontaneous, non-spontaneous, or temperature dependent.



5. (23.23) Using the information below, calculate the  $\Delta G_{rxn}$  when  $[\text{ATP}] = 5.0 \text{ mM}$ ,  $[\text{ADP}] = 0.50 \text{ mM}$ , and  $[\text{HPO}_4^{2-}] = 5.0 \text{ mM}$ . Is the reaction spontaneous under these conditions?



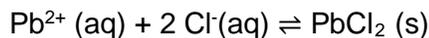
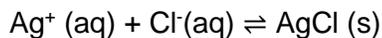
6. (14.19) Calculate  $\Delta H_{rxn}^0$  and for  $\text{CH}_3\text{CH}_2\text{OH} (\text{l}) \rightleftharpoons \text{CH}_3\text{OCH}_3 (\text{l})$  noting that:



7. (23-67) From the following data, calculate  $\Delta S_{fus}$  for each metal.

Metal	T <sub>m</sub> (K)	$\Delta H_{fus}$ (kJ mol <sup>-1</sup> )
Li	454	2.99
Na	371	2.60

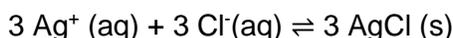
8. (23.72) From the data below, calculate  $\Delta G_{rxn}^0$  and K for the following reactions at 25°C.



	Pb <sup>2+</sup> (aq)	Ag <sup>+</sup> (aq)	Cl <sup>-</sup> (aq)	PbCl <sub>2</sub> (s)	AgCl (s)
$\Delta G_f^0$ (kJ mol <sup>-1</sup> )	-24.4	77.1	-131.2	-314.1	-109.8
$S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )	10.5	72.7	56.5	136.0	96.3

9. For the reactions in problem 8, determine  $\Delta S_{rxn}^0$  and  $\Delta H_{rxn}^0$ .

10. Using your answers from problem 8, determine  $\Delta G_{rxn}^0$ ,  $\Delta S_{rxn}^0$ ,  $\Delta H_{rxn}^0$ , and K for the following reactions.



11. (23-43) Use the following data to calculate  $\Delta H_{rxn}^0$  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  $\Delta S_{vap}^0 = 118.89 \text{ J mol}^{-1} K^{-1}$ .

- Calculate  $\Delta G_{vap}^0$  and  $K$  at  $25^\circ\text{C}$ .
- What is the vapor pressure of water at  $25^\circ\text{C}$ ? This is the pressure of  $H_2O(g)$  at this temperature.
- What is  $K$  at  $100^\circ\text{C}$ ?
- What is the vapor pressure of water at  $100^\circ\text{C}$ ?

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

2<sup>nd</sup> 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  $\Delta G = \Delta H - T\Delta S$

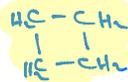
② Thermal energy is distributed throughout a molecule - this is a form of entropy.

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

③ CO vs CO<sub>2</sub> larger molecules have higher S°

H<sub>2</sub>O (s) vs. H<sub>2</sub>O (l) liquid always has more disorder than solids

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> vs



more rigid structure

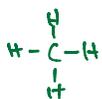
④ H<sub>2</sub>O (l) ⇌ H<sub>2</sub>O (s)  $\Delta H < 0$  ( $-\Delta H_{\text{fusion}}$ )

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

spontaneous at low temperatures, non-spontaneous at high temperatures

$\Delta S < 0$  becoming more ordered

(-) (-)



breaking 4 C-H  
(endothermic)

H-H } forming  
H-H } 2x H-H  
(exothermic)

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

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

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

(+) (+)

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

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

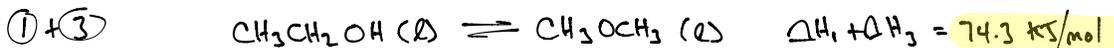
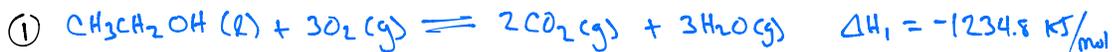
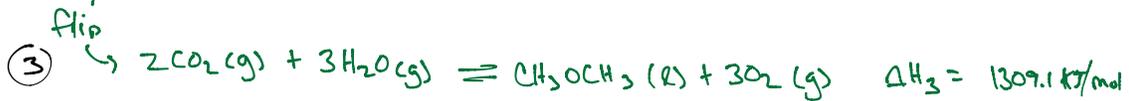
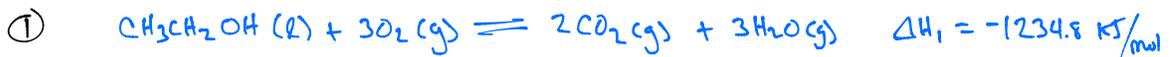


$$Q = \frac{[\text{ADP}][\text{HPO}_4]}{[\text{ATP}]} = \frac{(0.0005)(0.005)}{(0.005)} = 0.0005$$

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

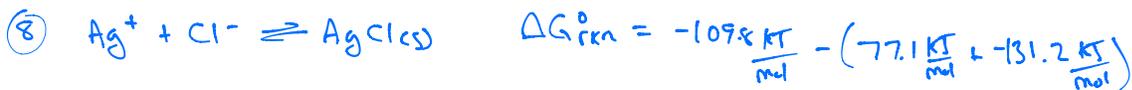
yes, it is spontaneous

### ⑥ Hess' Law



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

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



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

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

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

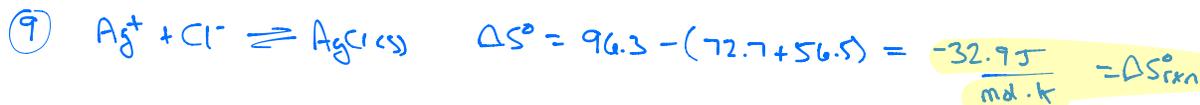
$$\Delta G^{\circ}_{\text{rxn}} = -55.7 \frac{\text{kJ}}{\text{mol}}$$



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

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

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



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

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

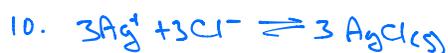
$$\Delta H_{\text{rxn}}^\circ = -65.5 \frac{\text{kJ}}{\text{mol}}$$



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

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

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



$\Delta H, \Delta S \downarrow \Delta G$  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  $\times 2$

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

$(K)^{-2}$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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