

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

- energy is conserved $\Delta U_{sys} = -\Delta U_{surr}$ → ΔH comes from concepts of 1st Law
- 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 . $\Delta G = -T\Delta S_{univ}$
 - Standard molar entropy (S°) can be used to calculate reaction entropies. These values are always positive ($S^\circ > 0$). Why? $T > \emptyset$, so there is heat. heat "distribution" is a form of Entropy
 - (23-6) For each pair, predict which molecule will have a higher molar entropy:

CO vs. CO_2 bigger $\text{H}_2\text{O (s)}$ vs. $\text{H}_2\text{O (l)}$ $s < l < g$ $\text{CH}_4 \text{ (g) at } 25^\circ\text{C}$ vs. $\text{CH}_4 \text{ (g) at } 250^\circ\text{C}$

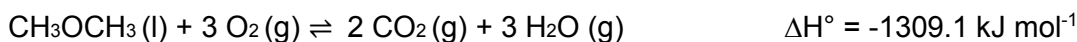
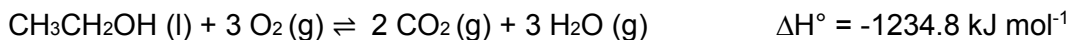
- For each reaction, select the correct answer for ΔH , ΔS , and ΔG . S increases with T

$\text{H}_2\text{O}_2 \text{ (l)} \rightleftharpoons \text{H}_2\text{O}_2 \text{ (s)}$ $l \rightarrow g \Delta S < 0$ Freezing = making bonds $\Delta H < 0$	$\Delta S > 0$ $\Delta S < 0$	$\text{C (s)} + 4 \text{ H (g)} \rightleftharpoons \text{CH}_4 \text{ (g)}$ $\#:$ $5 \rightarrow 1$ $\Delta S < 0$ $\text{gas: } 4 \rightarrow 1$ $\Delta S < 0$ making bonds = exothermic	$\Delta S > 0$ $\Delta S < 0$
	$\Delta H > 0$ $\Delta H < 0$		$\Delta H > 0$ $\Delta H < 0$
	$\Delta G > 0$ $\Delta G < 0$		$\Delta G > 0$ $\Delta G < 0$
	Temperature Dependent		Temperature Dependent

- (23.23) Using the information below, calculate the ΔG at 37°C 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?



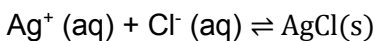
- (14.19) Calculate ΔH° for $\text{CH}_3\text{CH}_2\text{OH (l)} \rightleftharpoons \text{CH}_3\text{OCH}_3 \text{ (l)}$ noting that:



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

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

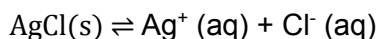
- (23.72) From the data below, calculate ΔG° and K for the following reaction at 25°C .



	$\text{Ag}^+ \text{ (aq)}$	$\text{Cl}^- \text{ (aq)}$	AgCl (s)
$\Delta G_f^\circ \text{ (kJ mol}^{-1}\text{)}$	77.1	-131.2	-109.8
$S^\circ \text{ (J mol}^{-1}\text{K}^{-1}\text{)}$	72.7	56.5	96.3

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

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



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

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

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

$$T = 37 + 273.15 = 310.15 \text{ K}$$

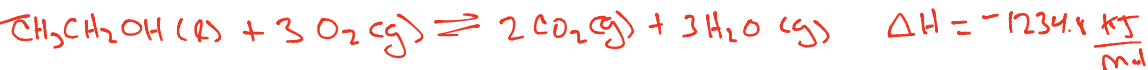
$$Q = \frac{[\text{ATP}][\text{HPO}_4^{2-}]}{[\text{ATP}]}$$

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

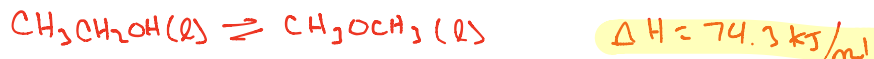
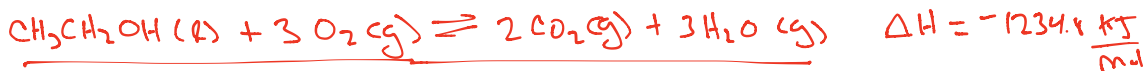
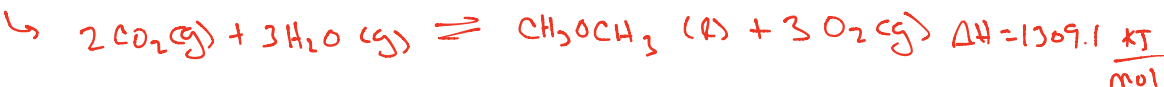
$$\Delta G = -30500 \frac{\text{J}}{\text{mol}} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 310.15 \text{ K} \cdot \ln 5 \times 10^{-4}$$

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

⑥



reverse



⑦ @ phase change temp, $\Delta G = 0$

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

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

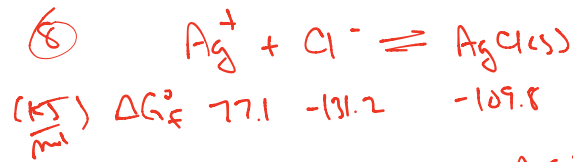
$$T\Delta S = \Delta H$$

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

$$\Delta S_{\text{fus}}^\circ = \frac{\Delta H_{\text{fus}}^\circ}{T_m}$$

$$\text{Li: } \Delta S_{\text{fus}}^\circ = \frac{2.97 \frac{\text{kJ}}{\text{mol}}}{454 \text{ K}} = 0.00659 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} = \frac{6.59 \text{ J}}{\text{mol} \cdot \text{K}}$$

$$\text{Na: } \Delta S_{\text{fus}}^\circ = \frac{2.60 \frac{\text{kJ}}{\text{mol}}}{371 \text{ K}} = 0.007 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} = \frac{7 \text{ J}}{\text{mol} \cdot \text{K}}$$



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

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

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

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

$$\ln K = -22.47$$

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



$$S^\circ \left(\frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$$
 72.7 56.5 96.3

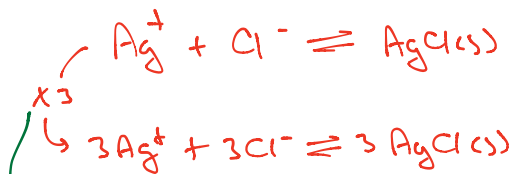
$$\Delta S^\circ = 96.3 - [72.7 + 56.5] = -32.9 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

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

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

$$\Delta H^\circ = -55700 \frac{\text{J}}{\text{mol}} + 298.15 \text{ K} \left(-32.9 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) = -65509 \frac{\text{J}}{\text{mol}} = -65.5 \frac{\text{kJ}}{\text{mol}}$$

10)



$$\Delta G = -55.7$$

$\downarrow \times 3$

$$\Delta H$$

$\downarrow \times 3$

$$\Delta S$$

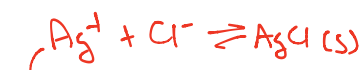
$\downarrow \times 3$

$$\Delta G = -152.1 \frac{\text{kJ}}{\text{mol}}$$

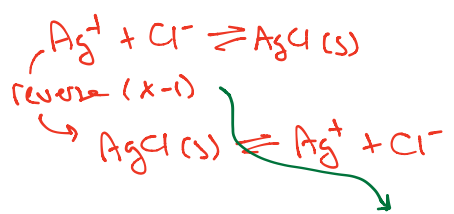
$$\Delta H = -196.5 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S = -98.7 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

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



reverse (x-1)



$$\Delta G$$

↓ x-1

$$\Delta G = 55.7 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H$$

↓ x-1

$$\Delta H = 65.5 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S$$

↓ x-1

$$\Delta S = 32.9 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

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