

# Free Energy Homework - Answers

15. Free energy is a convenient way to determine the spontaneity of a chemical reaction. It is derived from the second law of thermodynamics and relates the entropy, temperature, and enthalpy of a reaction. It generally has units of kJ/mol.

$$\begin{aligned} 7. a) \Delta G_{\text{rxn}}^{\circ} &= \sum \Delta G_f^{\circ}(\text{products}) - \sum \Delta G_f^{\circ}(\text{reactants}) \\ &= [2 \Delta G_f^{\circ}(\text{NO})] - [\Delta G_f^{\circ}(\text{N}_2) + \Delta G_f^{\circ}(\text{O}_2)] \\ &= [2(86.7 \text{ kJ/mol})] - [(0) + (0)] \\ \Delta G_{\text{rxn}}^{\circ} &= 173.4 \text{ kJ/mol} \end{aligned}$$

can calculate each using two different formulas; try both to make sure you get the same answer

$$\begin{aligned} b) \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} \\ &= \left[ \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants}) \right] - T \left[ \sum S^{\circ}(\text{products}) - \sum S^{\circ}(\text{reactants}) \right] \\ &= \left[ \Delta H_f^{\circ}(\text{H}_2\text{O}_{(g)}) - \Delta H_f^{\circ}(\text{H}_2\text{O}_{(l)}) \right] - (25^{\circ} + 273.15) \left[ S^{\circ}(\text{H}_2\text{O}_{(g)}) - S^{\circ}(\text{H}_2\text{O}_{(l)}) \right] \\ &= \left[ (-241.8 \frac{\text{kJ}}{\text{mol}}) - (-285.8 \frac{\text{kJ}}{\text{mol}}) \right] - [298.15 \text{ K}] \left[ 188.7 \times 10^{-3} \frac{\text{kJ}}{\text{mol K}} - 69.9 \times 10^{-3} \frac{\text{kJ}}{\text{mol K}} \right] \\ &= \left( 44 \frac{\text{kJ}}{\text{mol}} \right) - 298.15 \text{ K} \left( 118.8 \times 10^{-3} \frac{\text{kJ}}{\text{mol K}} \right) \\ \Delta G_{\text{rxn}}^{\circ} &= 8.58 \text{ kJ/mol} \end{aligned}$$

$$c) \Delta G_{\text{rxn}}^{\circ} = [4(-394.4) + 2(-237.2)] - [2(209.2) + 5(0)] = -2470.4 \text{ kJ/mol}$$

19. Reaction A:  $\Delta H > 0$ ,  $\Delta S > 0$ ; only spontaneous at high  $T$ , probably not at  $25^{\circ}\text{C}$

Reaction B:  $\Delta H > 0$ ,  $\Delta S < 0$ ; never spontaneous

Reaction A will be spontaneous at  $T = 350 \text{ K}$

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T \Delta S_{\text{rxn}} < 0$$

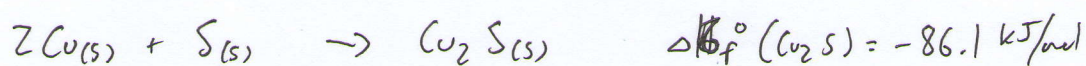
$$T > \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} = \frac{10.5 \times 10^3}{30} = 350$$

20. a)  $T > \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} = \frac{-126 \times 10^3}{84} = -1,500 \text{ K} \Rightarrow$  in other words, at any  $T$ , since it is impossible to have  $T < 0 \text{ K}$ .

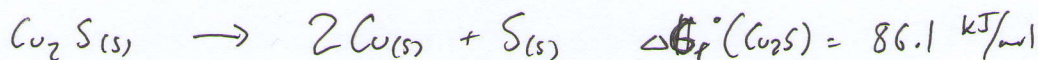
b)  $T > \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} = \frac{-11.7 \times 10^3}{-105} = 111.4 \text{ K} \Rightarrow$  the reaction <sup>becomes</sup> spontaneous at  $111.4 \text{ K}$



78. The formation reaction for  $\text{Cu}_2\text{S}$ , for which we are given the heat of formation is

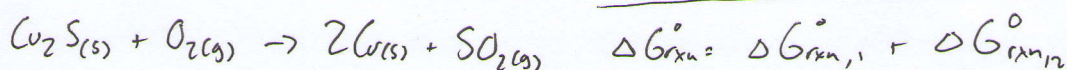
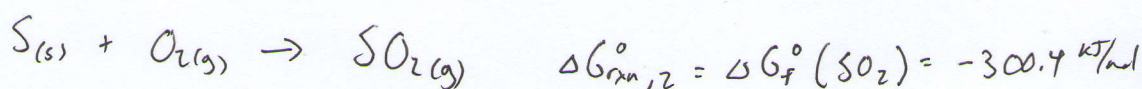
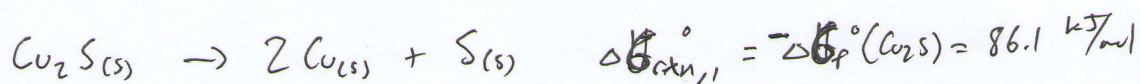


Since the formation of  $\text{Cu}_2\text{S}$  is spontaneous ( $\Delta G_f^\circ < 0$ ), its decomposition into  $\text{Cu}(s)$  and  $\text{S}(s)$  is non-spontaneous:



Thus, the extraction of Cu from  $\text{Cu}_2\text{S}$  is infeasible by the above reaction.

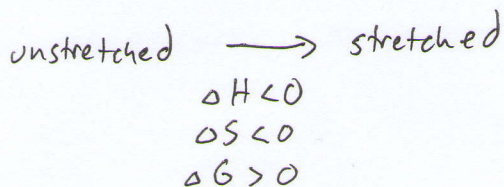
However, if coupled to the conversion of sulfur to sulfur dioxide:



$$\Delta G_{\text{rxn}}^\circ = -214.3 \text{ kJ/mol}$$

then the overall reaction is spontaneous ( $\Delta G_{\text{rxn}}^\circ < 0$ ), making copper extraction much more feasible.

83. From the "Chemistry in Action" essay, we saw that stretching a rubber band is exothermic, non-spontaneous, and leads to a decrease in entropy:



We were ~~led~~ led to this conclusion by analyzing the following rearranged formula for  $\Delta G$ :

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

By heating a stretched rubber band, you are making  $\Delta H$  "less negative" and "more positive", which means that  $(\Delta H - \Delta G)$  is overall a ~~more~~ negative number with a smaller magnitude than before the rubber band was heated. This results in a smaller magnitude of  $\Delta S$ , which means a smaller change in entropy compared to the initial state. ~~Since~~ Since the initial state was the unstretched rubber band, the heated rubber band will shrink back towards its initial unstretched state to accommodate the heat added. We will learn about an "easier" way to explain the same process during our discussion of equilibrium and L'Chatelier's Principle.