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.

7. a) $\Delta G^\circ_{rxn} = \sum \Delta G^\circ_f(\text{products}) - \sum \Delta G^\circ_f(\text{reactants})$

$= [2\Delta G^\circ_f(NO)] - [\Delta G^\circ_f(N_2) + \Delta G^\circ_f(O_2)]$

$= [2(86.7 \text{ kJ/mol})] - [(0) + (0)]$

$\Delta G^\circ_{rxn} = 173.4 \text{ kJ/mol}$

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

b) $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$

$= \left[\sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})\right] - T\left[\sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})\right]$

$= \left[\Delta H^\circ_f(H_2O_{(g)}) - \Delta H^\circ_f(H_2O_{(l)})\right] - (25^\circ + 273.15)\left[S^\circ(H_2O_{(g)}) - S^\circ(H_2O_{(l)})\right]$

$= \left[\left(-241.8 \frac{kJ}{mol}\right) - \left(-285.8 \frac{kJ}{mol}\right)\right] - (298.15\text{ K})\left[188.7\times10^{-3}\frac{kJ}{mol\,K} - 69.9\times10^{-3}\frac{kJ}{mol\,K}\right]$

$= \left(44 \frac{kJ}{mol}\right) - 298.15\text{ K}\left(118.8\times10^{-3}\frac{kJ}{mol\,K}\right)$

$\Delta G^\circ_{rxn} = 8.58 \text{ kJ/mol}$

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

19. Reaction A: $\Delta H > 0$, $\Delta S > 0$; only spontaneous at high T, probably not at 25°C

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

Reaction A will be spontaneous at $T = 350K$

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

$T > \frac{\Delta H_{rxn}}{\Delta S_{rxn}} = \frac{10.5\times10^3}{30} = 350$

20. a) $T > \frac{\Delta H_{rxn}}{\Delta S_{rxn}} = \frac{-126\times10^3}{84} = -1{,}500\text{ K}$ ⇒ in other words, at any T, since it is impossible to have $T < 0\text{ K}$.

b) $T > \frac{\Delta H_{rxn}}{\Delta S_{rxn}} = \frac{-11.7\times10^3}{-105} = 111.4\text{ K}$ ⇒ the reaction ~~is~~ becomes spontaneous at 111.4K

42. The reaction is the melting of ammonia: $NH_{3(s)} \rightarrow NH_{3(l)}$

$S_{liquid} > S_{solid}$ (not always true, but assume so for this problem); $\Delta S > 0$

$\Delta H_{melt} > 0$ (must put in heat – absorb heat – to convert solid to liquid)

(a) $\Delta S > 0$, $\Delta H > 0$, $\Delta G < 0$, since melting is spontaneous at T greater than melting point

(b) $\Delta S > 0$, $\Delta H > 0$, $\Delta G < 0$ as solid coverts to liquid, $\Delta G = 0$ at equilibrium between two phases

(c) $\Delta S > 0$, $\Delta H > 0$, $\Delta G > 0$, since melting is non-spontaneous at T less than melting point

43. With a decrease in entropy, $\Delta S_{rxn} < 0$. For a spontaneous process $\Delta G_{rxn} < 0$. From the formula $\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$, we see that a spontaneous process can lead to a decrease in entropy only if the reaction is exothermic (i.e. $\Delta H_{rxn} < 0$).

44. Since the dissolution is endothermic, $\Delta H_{rxn} > 0$. Since it is spontaneous, $\Delta G_{rxn} < 0$. By $\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$, we see that $\boxed{\Delta S_{rxn} > 0}$.

56. The minimum value of ΔS_{rxn} is that which will make $\Delta G_{rxn} < 0$.

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

$$0 > \Delta H_{rxn} - T\Delta S_{rxn}$$

$$0 > 19\,\frac{kJ}{mol} - (72 + 273.15)\,\Delta S_{rxn}$$

$$\Delta S_{rxn} > 55.05\ J/mol\ K$$

The minimum ΔS_{rxn} is $55.05\ J/mol\ K$

57. a) $\underset{solid}{Zn_{(s)}} \underset{+}{+} \underset{aqueous}{2HCl_{(aq)}} \rightarrow \underset{aqueous}{ZnCl_{2\,(aq)}} + \underset{gas}{H_{2\,(g)}}$ $\quad S_{gas} > S_{solid} \Rightarrow \boxed{\Delta S > 0}$

b) $\underset{2\,mol\ gas}{O_{(g)} + O_{(g)}} \rightarrow \underset{1\,mol\ gas}{O_{2(g)}}$ $\quad \Delta n(gas) < 0 \Rightarrow \boxed{\Delta S < 0}$

c) $\underset{solid}{NH_4NO_{3(s)}} \rightarrow \underset{gas}{N_2O_{(g)}} + \underset{gas}{2H_2O_{(g)}}$ $\quad S_{gas} > S_{solid} \Rightarrow \boxed{\Delta S > 0}$

d) $\underset{liquid}{2H_2O_{2(l)}} \rightarrow \underset{liquid}{2H_2O_{(l)}} + \underset{gas}{O_{2(g)}}$ $\quad S_{gas} > S_{liquid} \Rightarrow \boxed{\Delta S > 0}$

78. The formation reaction for Cu_2S, for which we are given the heat of formation is,

$$2\,Cu_{(s)} + S_{(s)} \rightarrow Cu_2S_{(s)} \qquad \Delta G_f^\circ(Cu_2S) = -86.1\ kJ/mol$$

Since the formation of $Cu_2S_{(s)}$ is spontaneous ($\Delta G_f^\circ < 0$), its decomposition into $Cu_{(s)}$ and $S_{(s)}$ is non-spontaneous:

$$Cu_2S_{(s)} \rightarrow 2\,Cu_{(s)} + S_{(s)} \qquad \Delta G_f^\circ(Cu_2S) = 86.1\ kJ/mol$$

Thus, the extraction of Cu from Cu_2S is infeasible by the above reaction.

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

$$Cu_2S_{(s)} \rightarrow 2\,Cu_{(s)} + S_{(s)} \qquad \Delta G^\circ_{rxn,1} = -\Delta G_f^\circ(Cu_2S) = 86.1\ kJ/mol$$

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \qquad \Delta G^\circ_{rxn,2} = \Delta G_f^\circ(SO_2) = -300.4\ kJ/mol$$

$$Cu_2S_{(s)} + O_{2(g)} \rightarrow 2\,Cu_{(s)} + SO_{2(g)} \qquad \Delta G^\circ_{rxn} = \Delta G^\circ_{rxn,1} + \Delta G^\circ_{rxn,2}$$

$$\Delta G^\circ_{rxn} = -214.3\ kJ/mol$$

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

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

$$\text{unstretched} \longrightarrow \text{stretched}$$

$$\Delta H < 0$$
$$\Delta S < 0$$
$$\Delta G > 0$$

We were led to this conclusion by analyzing the following rearranged formula for ΔG:

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

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