

CHEM 1422 - Homework # 2

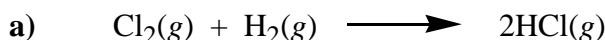
ANSWER KEY

Thermodynamics

Due January 29, 2009

Check the box to the right if you want your graded homework to be placed out in the public rack outside Prof. Stanley's office. Otherwise you will have to pick up your homework from Prof. Stanley in person:

1. (12 pts) From the thermodynamic data given at the end of your lecture notes calculate ΔH°_{rxn} , ΔS°_{rxn} and ΔG°_{rxn} for the following reactions. For ΔG°_{rxn} please use the $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$ formula with $T = 298\text{K}$. Indicate whether the reactions are spontaneous or non-spontaneous. Show your work.



$$\Delta H_{rxn} = \sum \Delta H_{prod} - \sum \Delta H_{react} = [(2)(-92.3 \text{ kJ/mol})] - [(0 \text{ kJ/mol}) + (0 \text{ kJ/mol})]$$

$$\Delta H_{rxn} = (-184.6 \text{ kJ/mol}) - (0 \text{ kJ/mol}) = \mathbf{-184.6 \text{ kJ/mol}}$$

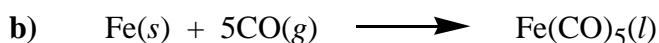
$$\Delta S_{rxn} = \sum \Delta S_{prod} - \sum \Delta S_{react} = [(2)(186.8 \text{ J/molK})] - [223.0 \text{ J/molK} + 130.6 \text{ J/molK}]$$

$$\Delta S_{rxn} = 373.6 \text{ J/molK} - 353.6 \text{ J/molK} = \mathbf{20 \text{ J/molK}}$$

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} = -184.6 \text{ kJ/mol} - (298\text{K})(0.02 \text{ kJ/molK})$$

$$\Delta G_{rxn} = -184.6 \text{ kJ/mol} - 6.0 \text{ kJ/mol} = \mathbf{-190.6 \text{ kJ/mol}}$$

spontaneous



$$\Delta H_{rxn} = \sum \Delta H_{prod} - \sum \Delta H_{react} = [(-774 \text{ kJ/mol})] - [(0 \text{ kJ/mol}) + (5)(-110.5 \text{ kJ/mol})]$$

$$\Delta H_{rxn} = (-774 \text{ kJ/mol}) + (552.5 \text{ kJ/mol}) = \mathbf{-221.5 \text{ kJ/mol}}$$

$$\Delta S_{rxn} = \sum \Delta S_{prod} - \sum \Delta S_{react} = [(338 \text{ J/molK})] - [27.3 \text{ J/molK} + (5)(197.6 \text{ J/molK})]$$

$$\Delta S_{rxn} = 338 \text{ J/molK} - 1015 \text{ J/molK} = \mathbf{-677 \text{ J/molK}}$$

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} = -221.5 \text{ kJ/mol} - (298\text{K})(-0.677 \text{ kJ/molK})$$

$$\Delta G_{rxn} = -221.5 \text{ kJ/mol} + 202 \text{ kJ/mol} = \mathbf{-19.5 \text{ kJ/mol}}$$

spontaneous



$$\Delta H_{rxn} = \sum \Delta H_{prod} - \sum \Delta H_{react} = [(-2331 \text{ kJ/mol}) + (2)(-286 \text{ kJ/mol})] - [(-911 \text{ kJ/mol}) + (6)(-271 \text{ kJ/mol})]$$

$$\Delta H_{rxn} = (-2903 \text{ kJ/mol}) + (2537 \text{ kJ/mol}) = \mathbf{-366 \text{ kJ/mol}}$$

$$\Delta S_{rxn} = \sum \Delta S_{prod} - \sum \Delta S_{react} = [(190 \text{ J/molK}) + (2)(70 \text{ J/molK})] - [42 \text{ J/molK} + (6)(174 \text{ J/molK})]$$

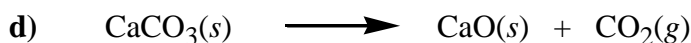
$$\Delta S_{rxn} = 330 \text{ J/molK} - 1086 \text{ J/molK} = \mathbf{-756 \text{ J/molK}}$$

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} = -366 \text{ kJ/mol} - (298\text{K})(-0.756 \text{ kJ/molK})$$

$$\Delta G_{rxn} = -366 \text{ kJ/mol} + 225 \text{ kJ/mol} = \mathbf{-141 \text{ kJ/mol}}$$

spontaneous

I provided the S° value for H_2SiF_6 in class (190 J/mol·K)



$$\Delta H_{rxn} = \sum \Delta H_{prod} - \sum \Delta H_{react} = [(-635 \text{ kJ/mol}) + (-393 \text{ kJ/mol})] - [(-1207 \text{ kJ/mol})]$$

$$\Delta H_{rxn} = (-1028 \text{ kJ/mol}) + (1207 \text{ kJ/mol}) = \mathbf{179 \text{ kJ/mol}}$$

$$\Delta S_{rxn} = \sum \Delta S_{prod} - \sum \Delta S_{react} = [(40 \text{ J/molK}) + (214 \text{ J/molK})] - [93 \text{ J/molK}]$$

$$\Delta S_{rxn} = 254 \text{ J/molK} - 93 \text{ J/molK} = \mathbf{161 \text{ J/molK}}$$

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} = 179 \text{ kJ/mol} - (298\text{K})(0.161 \text{ kJ/molK})$$

$$\Delta G_{rxn} = 179 \text{ kJ/mol} - 48 \text{ kJ/mol} = \mathbf{131 \text{ kJ/mol}}$$

non-spontaneous

2. (8 pts) Is the entropy *increasing*, *decreasing* or staying *about the same*? Use the qualitative entropy rules discussed in lecture to determine the answer. Write the answer to the right of each process.

- a) $\text{Fe}_2\text{O}_3(s) + \text{Al}(s) \longrightarrow \text{Fe}(s) + \text{Al}_2\text{O}_3(s)$ **about the same**
- b) raw egg \longrightarrow hard boiled egg **decreasing** (liquid egg going to solid egg)
- c) $\text{CaCl}_2(s) + 6\text{H}_2\text{O}(l) \longrightarrow [\text{Ca}(\text{H}_2\text{O})_6]\text{Cl}_2(s)$ **decreasing** (7 particles combining into 1 particle)
- d) $\text{C}_6\text{H}_{12}(l) + 9\text{O}_2(g) \longrightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(g)$ **increasing** (9 gas & 1 liquid making 12 gases)
- e) $\text{H}_2\text{CO}(aq) + \text{H}_2\text{O}(l) \longrightarrow 2\text{H}_2(g) + \text{CO}_2(g)$ **increasing** (2 liquids going to 3 gases)
- f) mowing the lawn **increasing** (cutting up longer grass blades into many short pieces)
- g) $\text{AgCl}(s) + \text{I}^-(aq) \longrightarrow \text{AgI}(s) + \text{Cl}^-(aq)$ **about the same**
- h) $\text{Sr}(s) + 2\text{H}_2\text{O}(l) \longrightarrow \text{Sr}^{2+}(aq) + 2\text{OH}^-(aq) + \text{H}_2(g)$ **increasing**

3. (2 pts) Circle the compound that has the highest entropy. Give a brief reason explaining your answer.

- a) Hg(l) b) H₂O(l) c) Pb(s) d) C₂H₅OH(l) e) CCl₄(l)

If you look up the entropies, $S^\circ[\text{CCl}_4(l)] = 216 \text{ J/molK}$, while $S^\circ[\text{C}_2\text{H}_5\text{OH}(l)] = 161 \text{ J/molK}$. Although C₂H₅OH (ethanol) has more atoms and has a somewhat more complex structure, the heavier Cl atoms in CCl₄ end up contributing more to the entropy. It was not easy, therefore, to qualitatively order these two choices so I'll give full credit for either one, but you also have to have some qualitative reasoning and not just that you looked up the entropies and CCl₄ had the largest value.

4. (4 pts) Why does Al₂O₃(s) have a lower entropy than Fe₂O₃(s)? There are two primary qualitative reasons for this. You may have to use the chemistry library to get more information (i.e., properties) on these two common compounds to answer the question.

Al₂O₃(s), alumina, has a lower entropy ($S^\circ = 51 \text{ J/molK}$) vs. Fe₂O₃(s), rust, ($S^\circ = 87 \text{ J/molK}$) because it has stronger bonding. This is indicated by the higher melting point of alumina (2015°C) vs. rust (1565°C). Alumina is one of the harder common materials and the main component in rubies and sandpaper, while rust is a relatively soft, flaky solid. Hardness and melting point of a material is usually related to the strength of the bonds that connect the solid together. The Al-O-Al bonding network is very strong relative to iron. We discussed this in class with the difference in entropy between graphite and diamond. The second main reason is that Al₂O₃ has a lower MW, but the same relative complexity as Fe₂O₃, which usually indicates a lower entropy. Each of these factors counts for about 50% of the entropy difference.

5. (4 pts) a) Small amounts of Fe(CO)₅(l) usually form in steel tanks containing pressurized CO(g). You worked out the thermodynamics of this in question 1b. At what temperature (°C) will the formation of Fe(CO)₅ become non-spontaneous? Show your work. b) A similar reaction occurs to make Ni(CO)₄(l) with $\Delta G^\circ_{\text{rxn}} = -38 \text{ kJ/mol}$, $\Delta H^\circ_{\text{rxn}} = -230 \text{ kJ/mol}$, and $\Delta S^\circ_{\text{rxn}} = -480 \text{ J/Kmol}$. High pressure reactors use a thin disk of metal as a safety mechanism that will rupture and release gasses if the pressure in the reactor gets too high. If one was using CO gas, which disk (Fe or Ni) would be more likely to prematurely fail due to the metal being dissolved away by CO? Briefly explain why.

a) We can find this temperature by using the $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$ formula, setting $\Delta G^\circ_{\text{rxn}} = 0$ (the point at which the reaction shifts from negative ΔG to positive ΔG), and solving for the temperature:

$$T = \frac{\Delta H^\circ_{\text{rxn}}}{\Delta S^\circ_{\text{rxn}}} = \frac{-221 \text{ kJ/mol}}{-0.677 \text{ kJ/molK}} = 327 \text{ K} \quad \text{or} \quad \boxed{54^\circ\text{C}}$$

b) $\Delta G^\circ_{\text{rxn}}$ for the nickel reaction is more spontaneous (-38 kJ/mol for Ni vs. -19 kJ/mol for Fe) meaning that it will be more likely to occur and release more "free" energy in doing so. That means from a thermodynamic viewpoint that it is more favorable for the Ni disk to be dissolved away by CO gas. Although that does NOT mean that the Ni reaction will be any faster (reaction rates are governed by kinetics and not thermodynamics), this does turn out to be the case and this actually happened repeatedly for one of our high pressure reactors a number of years ago.