1. (***Su11***) For each of the following chemical processes, state whether ΔS and ΔG are positive, negative, essentially zero, or undeterminable (based on the information provided).

A. $F_2(g) \rightarrow 2F(g)$

ΔS is ______________________________; ΔG is ______________________________

B. $H_2O(s) \rightarrow H_2O(l)$ at 0°C

ΔS is ______________________________; ΔG is ______________________________

C. $H_2O(s) \rightarrow H_2O(l)$ at 25°C

ΔS is ______________________________; ΔG is ______________________________

D. $O_2(g) + F_2(g) \rightarrow FOOF(g)$

ΔS is ______________________________; ΔG is ______________________________

2. (***Sp16***) Methane is cheap and abundant (sort of redundant, everything cheap is abundant; Econ 101). A low-temperature (200°C) synthesis of methanol from methane and molecular oxygen was recently reported (*Angew. Chem. Int. Ed.*. doi: 10.1002/anie.201511065), generating a great deal of excitement in the chemical industry community. The balanced chemical equation for this reaction is given below.

$$CH_4(g) + \tfrac{1}{2}O_2(g) \rightarrow H_3C\text{–}O\text{–}H(\ell)$$

A. First predict the sign of $\Delta S°$ and give your reasoning.

B. Now, using the thermodynamic data provided, calculate...

	$\Delta H_f°$ (kJ/mol)	$S°$ (J/K·mol)
$CH_4(g)$	–74.85	186.2
$H_3COH(\ell)$	–238.7	126.8
$O_2(g)$	0	205.0

1. $\Delta H°_{rxn}$

2. $\Delta S°_{rxn}$

3. $\Delta G°_{rxn}$

C. Is the reaction driven by enthalpy, entropy, both, or neither?

Based on your answer above, should the reaction be more favored or less favored at higher temperature? Explain your reasoning.

Now calculate ΔG_{rxn} at 200°C.

Does your calculated value agree with your prediction?

D. Calculate K_{eq} at 25°C (not 200°C).

3. (***Sp14***) Everyone else in this room knows more biology than I do, but even I know that the process by which plants convert CO_2 and H_2O into $C_6H_{12}O_6$ and O_2 is called photosynthesis. This process is nonspontaneous, so energy must be provided to make the reaction occur, and that energy is provided by sunlight. "Chemosynthesis" refers to the biological conversion of simple carbon-containing molecules (e.g. CO_2 or methane, CH_4) into more complex energy-rich molecules using non-biological (inorganic) molecules as the energy source, rather than sunlight, as in photosynthesis. For example, giant tube worms found near deep-ocean sulfur vents contain bacteria that convert carbon dioxide to simple sugars using hydrogen sulfide as the energy source according to the chemical equation

$$12H_2S + 6CO_2 \rightarrow C_6H_{12}O_6 + 6H_2O + 12S$$

A. Using the data provided on this page, calculate the following thermodynamic parameters for the above reaction.

	$\Delta H_f°$ (kJ/mol)	$\Delta S°$(J/K·mol)
$CO_2(aq)$	–412.9	121.3
$C_6H_{12}O_6(s)$	–1274.5	212.1
$H_2O(l)$	–285.8	69.9
$H_2S(aq)$	–39.7	121
$S(s)$	0	31.88

1. $\Delta H°$

2. $\Delta S°$

3. $\Delta G°$

B. You may have been surprised by the value you calculated for $\Delta G°$. I know I was surprised because I expected the reaction to be spontaneous, but my calculations indicate that the reaction is nonspontaneous at 25°C.

At what temperature will the reaction become spontaneous?

When the reaction becomes spontaneous, will it be driven by enthalpy or entropy?

4. (***Sp12***) One of the major sources of NOx compounds in our atmosphere is the reaction between nitrogen and oxygen, for example

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$$

This reaction is not favored at normal surface temperatures, but it does occur within internal combustion engines when air is mixed with the fuel to provide oxygen for the combustion reaction.

A. Before doing any calculations, predict the sign of $\Delta S°$. ______________________

Explain your reasoning.

B. Now calculate $\Delta H°$ and $\Delta S°$ for the above reaction. Some thermodynamic data is provided on the right.

	$\Delta H_f°$ (kJ/mol)	$S°$ (J/K · mol)
$N_2(g)$	0	191.5
$O_2(g)$	0	205.0
$NO_2(g)$	33.85	240.46

C. Is there a temperature range at which the above reaction would be spontaneous? If so, give the temperature range. If not, speculate on why the reaction occurs at higher temperatures.

5. (***Sp11***) We spent a fair of time this semester on acid-base chemistry, but going back to last semester (or perhaps before then), we knew that HF(*aq*) is the only weak acid in the family HX(*aq*), where X is a halogin (F, Cl, Br, I). Let's see if we can use thermodynamics to understand the special nature of HF(*aq*) a little better.

   A. The acidity of HF(aq) is represented by the chemical equation

   $$HF(aq) \rightleftharpoons H^{+}(aq) + F^{-}(aq)$$

   Using the thermodynamic data provided, determine the following parameters at 25°C:

	$\Delta H_f°$ (kJ mol^{-1})	$\Delta G_f°$ (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
HF(*aq*)	–320.08	–296.82	88.7
H^{+}(*aq*)	0	0	0
F^{-}(*aq*)	–333.63	–278.79	–13.8

   1. ΔH°

   2. ΔS°

   3. ΔG° (Yes, I realize there are two ways to calculate this value. Do it one way, and if you have time, you can do it the other way as a check.)

   B. Which thermodynamic parameter is responsible for HF(aq) being a weak acid: enthalpy, ΔH°; entropy, ΔS°; or both? ______________________

   C. Is the value you calculated for ΔG° consistent with HF(*aq*) being a weak acid? Explain.

   D. Will HF(*aq*) be more acidic or less acidic at 50°C? Explain.

6. (***Su09***) As concerns grow about the increasing concentration of CO_2 in the atmosphere due to burning fossil fuels, an expansion of use of nuclear power seems likely. One of the major concerns about nuclear power is the safe management of nuclear wastes, given the potential consequences if this waste were to mix with ground water, so chemists are studying the interaction of heavy-metal ions with the components of ground water (*Inorg. Chem.* **2009**, *48*, 6748-6754). One of the reactions being investigated is shown below.

   $$UO_2^{2+}(aq) + 2F^{-}(aq) \rightleftharpoons UO_2F_2(aq) \qquad \Delta H° = 5.2 \text{ kJ/mol} \qquad \Delta S° = 171 \text{ J/(K} \cdot \text{mol)}$$

   A. Determine ΔG° for the reaction at 25°C.

   B. Is the reaction driven by enthalpy, entropy, both, or neither?

   C. The sign of ΔS° for this reaction might surprise you initially.

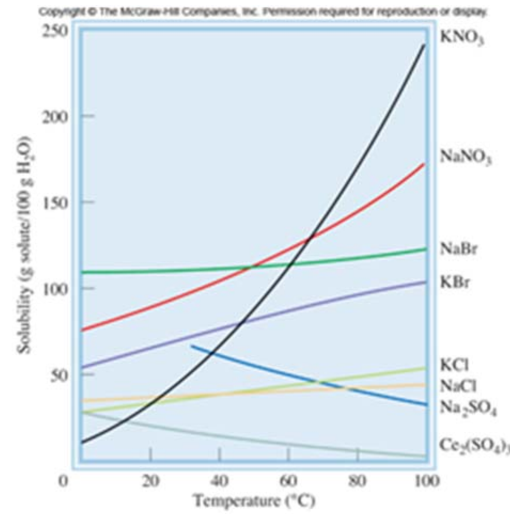
   1. Why might it be surprising?

   2. Provide an explanation for the sign of ΔS°.

   D. Calculate K_{eq} for the reaction at 25°C.

   E. At what temperature would the reaction change from being spontaneous to nonspontaneous?

7. (***Su11***) Earlier in the term we considered the temperature dependence of the solubility of ionic compounds in water. We noted that solubility generally increases with temperature, but there are some exceptions, for example sodium sulfate as shown in the figure on the right.



We are now equipped to understand what makes the exceptions exceptional.

A. Using the thermodynamic data provided for dissolving $Na_2SO_4(s)$ in water, that is, for the chemical process

$$Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$$

calculate ΔH°.

B. When I calculated ΔS°, I got −11.84 J/K·mol. Using this value and your answer to part A, calculate ΔG° at 25°C.

	$\Delta H_f°$ (kJ/mol)	S° (J/K·mol)
$Na^+(aq)$	– 239.66	60.25
$Na_2SO_4(s)$	– 1384.49	149.49
$SO_4^{2-}(aq)$	– 907.51	17.15

C. Which term is responsible for the temperature dependence of ΔG: enthalpy (ΔH°), entropy (ΔS°), both, or neither (ΔG is not temperature dependent)?

Will increasing the temperature make ΔG larger (more positive), smaller (more negative), or have no effect?

D. So based on your answer to part C, will the solubility of Na_2SO_4 increase or decrease with increasing temperature?

E. Does your answer to part D agree with or contradict the behavior shown in the figure above?

8. (***Sp08***) Consider the conversion of $H_2O(\ell)$ to $H_2O(g)$.

A. Calculate ΔH° and ΔS° for

$$H_2O(\ell) \rightarrow H_2O(g)$$

from the data provided in the table.

	$\Delta H_f°$ (kJ/mol)	S° (J/mol·K)
$H_2O(g)$	– 241.826	188.72
$H_2O(\ell)$	– 285.840	69.940

B. At what temperature does the conversion of $H_2O(\ell)$ to $H_2O(g)$ become spontaneous?

At the temperatures where it is spontaneous, the conversion of $H_2O(\ell)$ to $H_2O(g)$ is (circle one) ….

enthalpy driven   entropy driven   enthalpy and entropy driven   neither enthalpy nor entropy driven

C. You could have predicted the answer to part B before you did the calculation. Explain. In other words, what else do we call the answer to part B? (If you have not done so already, it might help if you converted the temperature you calculated in part B to °C.)

But the answer you calculated in part B will not exactly match the temperature you expected. Speculate on the source of the error.