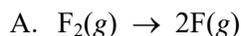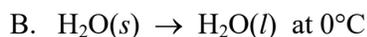1. (**Su11**) For each of the following chemical processes, state whether ΔS and ΔG are positive, negative, essentially zero, or undeterminable (based on the information provided).
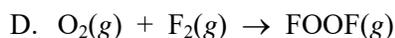
A. $F_2(g) \rightarrow 2F(g)$

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.

$$CH_4(g) + \tfrac{1}{2}O_2(g) \rightarrow H_3C-O-H(l)$$
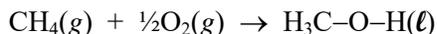
A. First predict the sign of $\Delta S°$ and give your reasoning.

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

	$\Delta H_f°$ (kJ/mol)	$S°$ (J/K·mol)
$CH_4(g)$	−74.85	186.2
$H_3COH(l)$	−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. (**Sp15**) The Department of Health and Human Services recently recommended the concentration of fluoride in drinking water be limited to 0.7 mg/L (the current policy allows for a range of 0.7 to 1.2 mg/L): http://www.npr.org/blogs/health/2015/04/27/402579949/feds-say-its-time-to-cut-back-on-fluoride-in-drinking-water. The concentration of fluoride in natural water depends on the presence of fluoride-containing minerals. For example, the mineral fluorite (also called fluorspar) is essentially $CaF_2(s)$.

Note: Parts A-C were included in the homework for Unit III.

A. Convert the concentration of fluoride from 0.7 mg/L to M, using 18.998 g/mol for F^- (in other words, do not the mass of the Ca^{2+} ion).

B. Calculate the concentration (in M) of fluoride in water in contact with an excess of fluorite. The K_{sp} of CaF_2 is 4.0×10^{-11}.

C. Based on your answers to parts A and B, will the concentration of fluoride in water over fluorite be less than or greater than the limit in the new federal guidelines?

Now let's consider the thermodynamics of dissolving CaF_2 in water: $CaF_2(s) \rightarrow Ca^{2+}(aq) + 2F^-(aq)$

D. Calculate the following parameters for the above reaction, and write your answer in the box provided.

1. $\Delta H°$

$\Delta H° =$	kJ/mol

2. $\Delta S°$

$\Delta S° =$	J/K·mol

3. $\Delta G°$

$\Delta G° =$	kJ/mol

4. K_{eq}

$K_{eq} =$

Does your answer to D.4 agree with the K_{sp} from Question II?
If not, you might want to check your work.

E. Is there a temperature at which $CaF_2(s)$ will become soluble in water?

If so, calculate that temperature. If not, explain why not.

4. (*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?

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

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$$
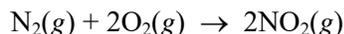
This reaction is not favored at normal surface temperatures, but it does occur within internal combustion engines when air is mixed with the fuel to provide oxygen for the combustion reaction.

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.

6. (*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:

	ΔH_f° (kJ mol^{-1})	ΔG_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.

7. (*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$_2$F$_2$(aq) ΔH° = 5.2 kJ/mol ΔS° = 171 J/(K · 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?

8. (**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.

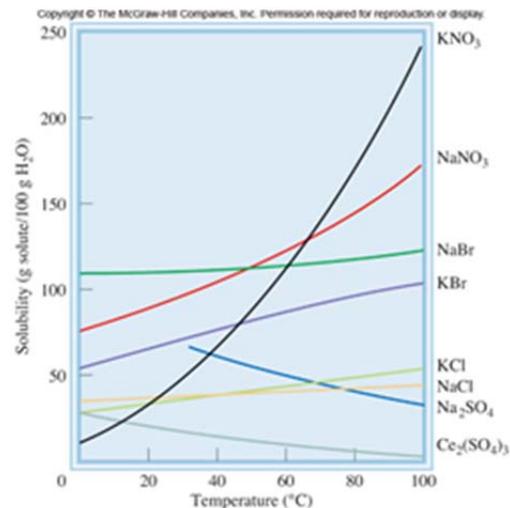A. Using the thermodynamic data provided for dissolving $Na_2SO_4(s)$ in water, that is, for the chemical process

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

calculate $\Delta H°$.

B. When I calculated $\Delta S°$, I got -11.84 J/K·mol. Using this value and your answer to part A, calculate $\Delta G°$ at 25°C.

C. Which term is responsible for the temperature dependence of ΔG: enthalpy ($\Delta H°$), entropy ($\Delta S°$), both, or neither (ΔG is not temperature dependent)?

	$\Delta H_f°$ (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

Will increasing the temperature make ΔG larger (more positive), smaller (more negative), or have no effect?
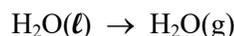
D. So based on your answer to part C, will the solubility of Na_2SO_4 increase or decrease with increasing temperature?

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

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

A. Calculate $\Delta H°$ and $\Delta S°$ for

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

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

from the data provided in the table.

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.

10. (*Sp08*) Throughout this semester I have asked you to think about whether or not the answers you calculate actually make sense. (Part C in the above question would be another example.) Yet when I calculated the K_{sp} of barium sulfate ($BaSO_4$) in Homework Assignment Twelve and found that it decreased at higher temperature (and hence the solubility decreased at higher temperature), I did not go back and check my math as I should have. Instead I assumed that barium sulfate is one of those unusual salts that become less soluble at higher temperatures.

Calculate $\Delta H°$ for ….

A. $BaSO_4(s) \rightarrow Ba^{2+}(aq) + SO_4{}^{2-}(aq)$

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

C. Based on the $\Delta H°$ values you calculated above, do you expect either $BaSO_4(s)$ or $Na_2SO_4(s)$ to become less soluble at higher temperature? Explain you reasoning.

	$\Delta H_f°$ (kJ/mol)
$Ba^{2+}(aq)$	-538.36
$BaSO_4(s)$	-1465
$Na^+(aq)$	-239.66
$Na_2SO_4(s)$	-1375.653
$SO_4{}^{2-}(aq)$	-907.51

11. (*Sp08*) We have worked a variety of equilibrium problems in this class, but we were always provided the necessary equilibrium constants. Now that we have covered thermodynamics and electrochemistry, we can actually calculate equilibrium constants. This problem and the next one give you an opportunity to demonstrate your ability to calculate equilibrium constants from thermodynamic data and electrochemical data, respectively.

$HCN(aq)$ is a weak acid, as illustrated in the reaction below.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

	$\Delta G_f°$ (kJ/mol)
$CN^-(aq)$	166
$H^+(aq)$	0
$HCN(aq)$	112

Calculate K_{eq} for the above reaction at 25°C from the thermodynamic data provided.

Is your answer consistent with $HCN(aq)$ being a weak acid? Explain.

12. (***Chang, 12e***) Heating copper(II) oxide at 400°C does not produce appreciable amounts of copper metal by the reaction shown below.
$$CuO(s) \rightleftharpoons Cu(s) + \tfrac{1}{2}O_2(g)$$

A. Determine $\Delta G°$ at 400°C, and comment on the value of $\Delta G°$ with respect to the insignificant yield for the above reaction.

B If this reaction is coupled to the reaction graphite with oxygen to carbon monoxide, then the yield of copper is great enough to make copper(II) oxide a viable source of copper metal. Write a chemical equation for the coupled process and calculate the equilibrium constant for the coupled reaction.

13. We all learned in David Duchovny's pioneering documentary, *Evolution*, that the selenium disulfide in dandruff shampoo can be used to destroy alien life forms from other parts of the galaxy. Determine the oxidation number of selenium in the following compounds:

A. SeO_2 _____

B. H_2Se _____

C. H_2SeO_4 _____

D. Na_2SeO_3 _____

E. Se_8 _____

14. Dioxygen difluoride, affectionately known as *foof*, is formed from oxygen and fluorine under low pressure in the presence of an electric discharge:

$$O_2(g) + F_2(g) \rightarrow F\text{–}O\text{–}O\text{–}F(g)$$
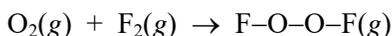
FOOF is a very powerful oxidizing agent, and it can be used to process nuclear fuels by forming hexafluoride compounds such as UF_6.

Assign the oxidation numbers of oxygen and fluorine in FOOF. (Lone pairs are not shown, but you know where they are.)

    the oxidation number of oxygen is _____   the oxidation number of fluorine is _____

15. (*Sp12*) Nitric acid, $HNO_3(aq)$, is one of our six strong acids, but nitrous acid, $HNO_2(aq)$, is a weak acid.

  A. Assign the oxidation number of nitrogen in these two acids.

     1. HNO_3 ON(N) = _____   2. HNO_2 ON(N) = _____

  B. We mentioned in class that we can use oxidation numbers to predict which oxides form certain oxyacids when reacted with water. Oxides of nitrogen (often written as NOx and pronounced "nox") are important because of the role they play in atmospheric chemistry. Assign the oxidation number of nitrogen in the following NOx compounds. If the dot structure is provided, then assign oxidation numbers for each nitrogen.

     1. NO_2 ON(N) = _____   2. N_2O_2 ON(N) = _____

     3. $\overset{..}{N}$ ON(N) = _____

        $\vert\vert\vert$

        N   ON(N) = _____

        $\vert$

      :$\overset{..}{\underset{..}{O}}$:

  C. You may have already noticed that predicting the nitrogen oxide the forms certain HNO_x oxyacids is not straight forward. Indeed, the reaction of $NO_2(g)$ with water forms both nitric acid and nitrous acid

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

and $NO_2(g)$ is both oxidized and reduced in the reaction. Balance the half-reactions under acidic conditions.

     $NO_2 \rightarrow HNO_2$ $NO_2 \rightarrow HNO_3$
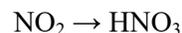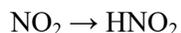
   Now show that these half-reactions combine to give the overall reaction shown above.

16. Aquaponics a food production method that combines growing crops and fish in a system that recirculates the water. The fish release ammonia into the water, and two types of bacteria convert the ammonia into, first nitrite, and then nitrate. The plants use the nitrate as fertilizer.

   A. *Nitrosomonas sp.* converts ammonia (NH_3) to nitrite (NO_2^-).

   What is the oxidation number of nitrogen in NH_3? _____

   What is the oxidation number of nitrogen in NO_2^-? _____

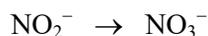   Because ammonia is a base, balance this half-reaction under basic conditions.

   $$NH_3 \rightarrow NO_2^-$$
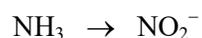
   Is this half-reaction an oxidation or a reduction? _____

   B. *Nitrobacter sp.* converts nitrite (NO_2^-) to nitrate (NO_3^-).

   What is the oxidation number of nitrogen in NO_3^-? _____

   Balance this half-reaction under acidic conditions.

   $$NO_2^- \rightarrow NO_3^-$$

   Is this half-reaction an oxidation or a reduction? _____

   C. The plants, of course, convert CO_2 and H_2O into $C_6H_{12}O_6$ and O_2.

   Is this a redox reaction? _____

   Explain your reasoning?

17. The chemosynthesis reaction on the previous page as a redox reaction,

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

   so we can break the reaction into two half-reactions as shown below.

   A. $H_2S \rightarrow S$

   What is the oxidation number of sulfur in H_2S? _____

   What is the oxidation number of sulfur in S? _____

   Write the balanced half-reaction under acidic conditions.

   B. $CO_2 \rightarrow C_6H_{12}O_6$ (assume that the oxidation number of H is +1)

   What is the oxidation number of carbon in CO_2? _____

   What is the oxidation number of carbon in $C_6H_{12}O_6$? _____

   Write the balanced half-reaction under acidic conditions.

   C. Show that when you combine the two half-reactions you get the chemical equation at the top of the page.

   Which gas is being oxidized in the above reaction?

18. (*Sp16*) Balance the following half-reactions under acidic conditions. The half-reactions are not necessarily reductions; in other words, the electrons might be on the left or right side of the chemical equation.

   A. $Mo^{3+} \rightarrow MoO_4^{2-}$

   B. $2BrO_3^- \rightarrow Br_2$

   C. $H_3AsO_4 \rightarrow AsH_3$
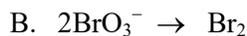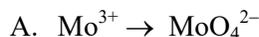
19. (*Su09*) Most of the commercial lithium batteries involve manganese dioxide or thionyl chloride (back in Spring 2009), but we could envision a very simple electrochemical cell based on the following two half-reactions:

$$\underline{E^\circ \text{ (V)}}$$

$$I_2(s) + 2e^- \rightarrow 2I^-(aq) \qquad 0.535$$
$$Li^+(aq) + e^- \rightarrow Li(s) \qquad -3.045$$
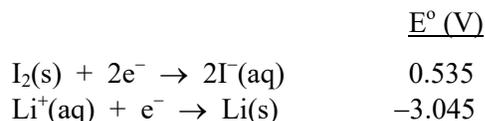
   A. Write a balanced chemical equation for the spontaneous redox reaction that would occur in this cell.

   B. Which half-reaction corresponds to the cathode?

   C. Do electrons move from $Li(s)$ to $I_2(s)$ or $I^-(aq)$ to $Li^+(aq)$?

   D. Do cations move towards the lithium electrode or away from the lithium electrode?

   E. Determine the standard cell potential.

   F. What would be the potential of the cell if $[I^-] = 0.23$ M and $[Li^+] = 2.6 \times 10^{-4}$ M?

20. (*Su09*) The titration reactions we discussed this semester were based on acid-base reactions, but you can also use redox reactions to carry out titrations. Two examples are given here. Balance the redox reactions under acidic conditions. Circle the balanced half-reactions that you generate along the way, and write your final balanced redox reaction in the box provided.

   A. Iron(II) ion (Fe^{2+}) is reacted with the species being analyzed, and then dichromate ion ($C_2O_7^{2-}$) is used to oxidize the unreacted Fe^{2+}. The overall redox reaction (unbalanced) is given below
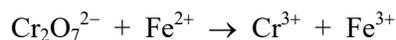
$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

   Balance the half reactions and then write the overall balanced redox reaction.

 $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ $\qquad\qquad\qquad\qquad$ $Fe^{2+} \rightarrow Fe^{3+}$
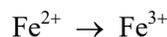
   Write the balanced redox reaction in this box.

B. A common technique in analytical chemistry is to carry out a redox reaction with iodide to form triiodide (I_3^-), and then titrate the I_3^- to determine the amount of the original species. For example, this technique can be used to analyze for nitrous acid by carrying out the following (unbalanced) redox reaction.

$$HNO_2 + I^- \rightarrow NO + I_3^-$$

Balance the half reactions and then write the overall balanced redox reaction.

$HNO_2 \rightarrow NO$ $\qquad\qquad\qquad\qquad\qquad$ $I^- \rightarrow I_3^-$
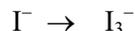
> Write the balanced redox reaction in this box.

What is the oxidizing agent in this reaction? _____

21. You construct a very environmentally unfriendly voltaic cell using the half-reactions shown on the right.

	E° (V)
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74

   A. Write a balanced chemical equation for the redox reaction that drives cell.

   B. What is E° for this reaction?

   C. Calculate the cell potential when $[Cr^{3+}] = 0.20\ M$ and $[Pb^{2+}] = 0.30\ M$.

22. A recent article in the New York Times stated the flow cells might be the best way to store energy from solar and wind powered generators (www.nytimes.com/2015/04/23/business/energy-environment/liquid-batteries-for-solar-and-wind-power.html). One fuel cell uses vanadium half reactions for both the cathode and anode:

> *Both electrolytes are vanadium based, the electrolyte in the positive half-cells contains VO_2^+ and VO^{2+} ions, the electrolyte in the negative half-cells, V^{3+} and V^{2+} ions. The solution remains strongly acidic in use.*
>
> from http://en.wikipedia.org/wiki/Vanadium_redox_battery

   A. Calculate $E°$ for the vanadium cell described above. Several half-reactions are given in the information packet, but you have to pick the correct half-reactions based on the description above.

   B. Write a balanced chemical equation for the redox reaction that is powering the cell.

   C. According to Wikipedia, the solution is "strongly acidic." Will increasing the concentration of H^+ increase of decrease the potential of the cell?

      Explain your reasoning.

23. Balance the following half reactions under the conditions given:

   A. $Mo^{3+} \rightarrow MoO_4^{2-}$ (in acid)

   B. $BrO_3^- \rightarrow Br^-$ (in acid)

24. (**Sp10**) The standard reduction potentials for Ag^+ and Cd^{2+} in water at 25°C are given below.

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad 0.80 \text{ V}$$
$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \qquad -0.40 \text{ V}$$
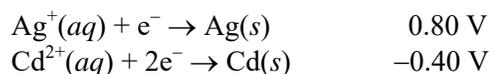
A. A simple voltaic cell could be constructed based on these two half-cell reactions.

1. What would be the standard potential for the cell (i.e. the cell potential if the concentration of $Ag^+(aq)$ and $Cd^{2+}(aq)$ were both 1 M)?

2. Write a balanced chemical equation for the spontaneous redox reaction that powers this cell.

3. Label one of the electrodes as Ag and the other electrode as Cd. Now annotate the diagram to show

    a. which solution contains $Ag^+(aq)$ and which contains $Cd^{2+}(aq)$

    b. which side is the anode and which side is the cathode

    c. which way the electrons move

   d. which way the cations move and which way the anions move
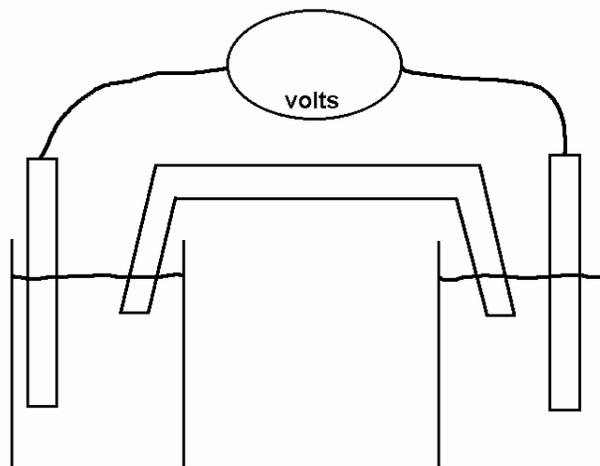
B. As we discussed in class, you can use voltaic cells to determine the concentration of ions involved in the overall redox reaction. Suppose the beaker containing $Cd^{2+}(aq)$ was removed and replaced with a beaker containing an unknown concentration of $Cd^{2+}(aq)$, and the cell potential changed to 1.37 V.

   Determine the concentration of $Cd^{2+}(aq)$ in the beaker.

25. (**Sp10**) Balance the following half reactions under the conditions given:

A. $Mo^{3+} \rightarrow MoO_4^{2-}$ (in acid)

B. $BrO_3^- \rightarrow Br^-$ (in acid)

C. $SO_3^{2-} \rightarrow SO_4^{2-}$ (in base)
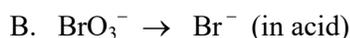
D. Write an overall balanced redox reaction using the half reactions you wrote for parts A and B.

E. Consider the redox reaction: $O_2(g) + 2F_2(g) \rightarrow 2OF_2(g)$
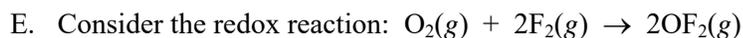
1. Write a dot structure for OF_2 and sketch its molecular shape.

2. Assign the oxidation numbers of oxygen and fluorine in OF_2.

    the oxidation number of oxygen is _____   the oxidation number of fluorine is _____

3. Which gas is being oxidized in the above reaction? _____

4. What is the reducing agent in the above reaction? _____

26. (**Sp11**) An electrochemical cell is constructed using the half-reactions given in the table.

	$E°$ (V)
$Ni^{2+} + 2e^- \rightarrow Ni(s)$	−0.250
$Cu^+ + e^- \rightarrow Cu(s)$	0.521

A. What is the overall chemical equation for the <u>spontaneous</u> redox reaction that would occur under standard conditions?

B. Which half-reaction is acting as the anode under standard conditions?

C. What is $E°$ for this reaction?

D. What is n for this reaction? _____

E. Write the expression for Q for the reaction.

F. The cell was constructed with $[Ni^{2+}] = 0.139$ M and an unknown concentration of $Cu^+(aq)$. A potential of 0.604 V was measured for the cell under those conditions. What is the concentration of $Cu^+(aq)$?

27. (**Sp11**) Write balance equations for the following half-reactions:

A. $ClO_3^- \rightarrow Cl^-$ (in acid)

B. $IO_3^- \rightarrow I_2$ (in acid)

C. $SO_3^{2-} \rightarrow SO_4^{2-}$ (in base)

28. (**Su11**) It has been suggested that the exposed lead in older plumbing systems can be coated with a layer of copper by running a solution of copper(II) through the pipes, allowing the following reaction to occur:

$$Pb(s) + Cu^{2+}(aq) \rightleftharpoons Pb^{2+}(aq) + Cu(s)$$
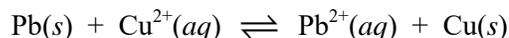
The standard cell potential for this redox reaction is 0.47 V.

A. Is this reaction spontaneous? _____

B. Calculate $\Delta G°$ for the above reaction.

Based on the $\Delta G°$ you calculated, do you expect K_{eq} to be less than 1 or greater than 1?

(Check: Are your answers to part B consistent with your answer to part A?)

C. Suppose the two half reactions were separated and used to construct a voltaic cell.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ +0.34 V
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ −0.13 V

1. Which half-reaction would correspond to the cathode?

2. Which way would the electrons move in the cell: from the copper electrode to the lead electrode, or from the lead electrode to the copper electrode?

Which way would the ions move in the cell: from the copper cell to the lead cell, or from the lead cell to the copper cell?

3. Calculate E_{cell} for the cell based on this redox reaction where $[Cu^{2+}] = 0.80$ M and $[Pb^{2+}] = 0.20$ M.

29. (*Sp12*) Best known as the fuel of choice for the flux capacitor, plutonium also exhibits very interesting redox chemistry.

A. Balance the following half-reaction under acidic conditions.

$$PuO_2^{2+} \rightarrow Pu^{4+}$$
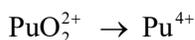
B. In perhaps the worst product development decision of all time, your boss asks you to develop a voltaic cell based on the following half-reactions:

$$Pu^{3+} + 3e^- \rightarrow Pu(s) \qquad -2.03 \text{ V}$$
$$Zn^{2+} + 2e^- \rightarrow Zn(s) \qquad 0.34 \text{ V}$$

Reluctantly, you construct a prototype under standard conditions. Annotate the cell drawing on the right to show the cell potential, direction of electron, cation, and anion flow, and label the cathode and anode. (Note: that's a total of six things you need to show.)

Show your work for determining the cell potential.

Zn(s)   Pu(s)

1 *M* Zn^{2+}(aq)   1 *M* Pu^{3+}(aq)
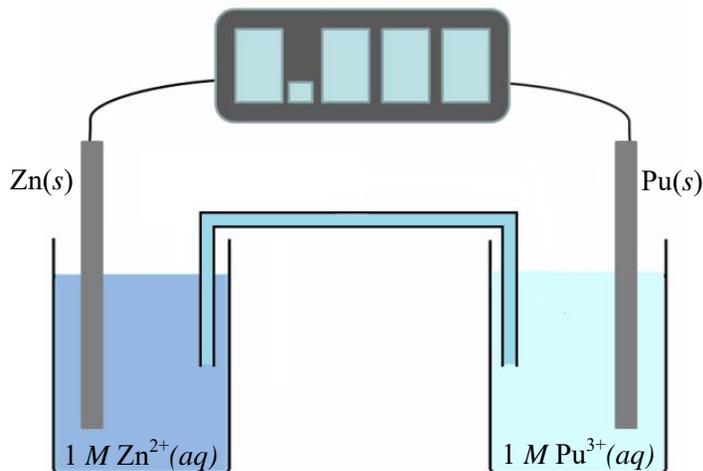
C. Someone from corporate gets wind of your plans to market a voltaic cell containing plutonium, generally considered the most toxic element* on the periodic table. You are about to post your resume on Monster.com when it occurs to you that your plutonium voltaic cell can be reconfigured to measure unknown concentrations of Pu^{3+}. As a "proof of concept" you remove the beaker containing 1 *M* Pu^{3+} and replace it with a beaker containing an unknown amount of Pu^{3+}, and the reading on the voltmeter changes to 2.48 V.
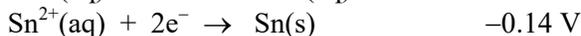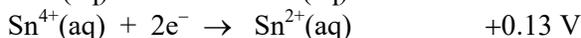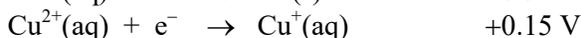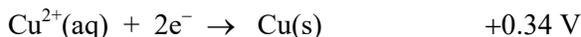
> *Plutonium: A History of the World's Most Dangerous Element*, Jeremy Bernstein, Cornell University Press, **2009**.

1. First write the mathematical equation you are going to use to solve for [Pu^{3+}] showing all the substitutions you made ([Pu^{3+}] should be the only variable left in the equation).

2. Now solve for [Pu^{3+}].

30. (*Sp08*) A voltaic cell can be constructed based on the redox reaction

$$2Cu^{2+}(aq) + Sn(s) \rightarrow 2Cu^+(aq) + Sn^{2+}(aq)$$
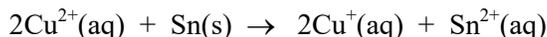
In the back of your book you found the following standard half-cell potentials at 298 K containing some form of copper (Cu) or tin (Sn):

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad +0.34 \text{ V}$$
$$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq) \qquad +0.15 \text{ V}$$
$$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq) \qquad +0.13 \text{ V}$$
$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \qquad -0.14 \text{ V}$$

A. What is the standard cell potential (E°$_{cell}$) for the reaction

$$2Cu^{2+}(aq) + Sn(s) \rightarrow 2Cu^+(aq) + Sn^{2+}(aq)$$
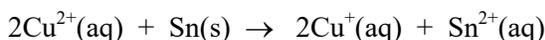
B. In the above redox reaction….

    what reactant is oxidized?   _____

    what reactant is reduced?   _____

    what reactant acts as the oxidizing agent?   _____

    what reactant acts as the reducing agent?   _____

    how many electrons are transferred?   _____

C. Do you expect the equilibrium constant for the above reaction to be greater than one or less than one under standard conditions? Explain your reasoning.

D. Calculate K_{eq} for the reaction.