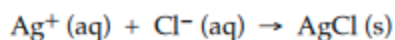**Thermodynamics**

Spontaneity and Entropy

1) Fill out the chart below to show how different values of enthalpy and entropy affect chemical spontaneity. An example is shown in the first column.

Delta H	Delta S	Temperature	Delta G	Spontaneity
-	+	Low	-	Always Spontaneous
				Always Spontaneous
				Never Spontaneous
				Never Spontaneous
				Not spontaneous at low Temperatures
				Spontaneous at Low temperatures
				Not Spontaneous at high Temperatures
				Spontaneous at high temperatures

2)

Consider the reaction:

$$Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl (s)$$

Given the following table of thermodynamic data,

Substance	ΔH_f° (kJ/mol)	S° (J/mol · K)
Ag^+ (aq)	105.90	73.93
Cl^- (aq)	-167.2	56.5
AgCl (s)	-127.0	96.11

determine the temperature (in °C) above which the reaction is nonspontaneous under standard conditions.

3)

Given the following table of thermodynamic data,

Substance	ΔH_f° (kJ/mol)	S° (J/mol · K)
$TiCl_4$ (g)	-763.2	354.9
$TiCl_4$ (l)	-804.2	221.9

complete the following sentence. The vaporization of $TiCl_4$ is _____.

A) spontaneous at all temperatures

B) spontaneous at low temperature and nonspontaneous at high temperature

C) nonspontaneous at all temperatures

D) nonspontaneous at low temperature and spontaneous at high temperature

E) not enough information given to draw a conclusion

4)

Which one of the following is always positive when a spontaneous process occurs?

A) ΔH_{univ} B) ΔH_{surr} C) ΔS_{surr} D) ΔS_{univ} E) ΔS_{sys}

5)

What can be said about a chemical system that has reached a minimum in free energy?

A) The reaction is complete.

B) The system entropy is zero.

C) The system has achieved equilibrium.

D) The temperature is OK.

E) The reaction is very fast.

6) A reaction that is not spontaneous at low temperature can become spontaneous at high temperature if ΔH is _____ and ΔS is _____.

A) +, + B) -, - C) +, - D) -, + E) +, 0 13)

7)

Of the following, the entropy of gaseous _____ is the largest at 25°C and 1 atm.

A) C_2H_2 B) H_2 C) C_2H_6 D) CH_4 E) C_2H_2

8) For a reaction to be spontaneous under standard conditions at all temperatures, the signs of ΔH and ΔS must be _____ and _____, respectively.

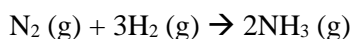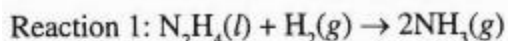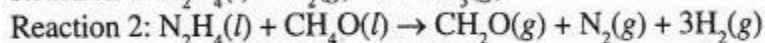A) +, +   B) +, -   C) -, +   D) -, -   E) +, 0

9) The equilibrium constant for the following reaction is 5.0×10^{-8} at 25deg C.

$$N_2 (g) + 3H_2 (g) \rightarrow 2NH_3 (g)$$

The value of ΔG for this reaction is _____ kJ/mol.

Reaction 1: $N_2H_4(l) + H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = ?$

Reaction 2: $N_2H_4(l) + CH_4O(l) \rightarrow CH_2O(g) + N_2(g) + 3H_2(g)$ $\Delta H = -37$ kJ/mol$_{rxn}$

Reaction 3: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = -46$ kJ/mol$_{rxn}$
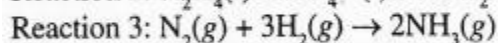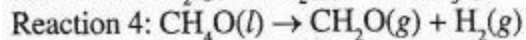
Reaction 4: $CH_4O(l) \rightarrow CH_2O(g) + H_2(g)$ $\Delta H = -65$ kJ./mol$_{rxn}$

10) What is the enthalpy change for reaction 1?

11) If reaction 2 were repeated at high temperature, how would the ΔG of the reaction be affected and why?

12) Under what conditions would reaction 3 be thermodynamically favored?

13) A 2.0Lflask hold 0.40g of helium gas, and is evacuated into a larger container whilst holding a constant temperature, what will be the effect on the entropy of the helium and why?

14) For each statement, decide if it is always true, sometimes true, or never true.

- A spontaneous process will have an entropy of the system increase
- A spontaneous process will have an entropy of the universe increase
- A reaction favoring the reverse direction will have a ΔG that is positive
- An endothermic process that results in a decrease in the entropy of the system will not be spontaneous
- An exothermic process in which the entropy of the system will be spontaneous above some temperature
- An endothermic system where entropy of the system increases will always be spontaneous above some temperature
- An exothermic process where entropy of the system increases is always spontaneous
- A combustion reaction is always spontaneous
- An exothermic process where the entropy of the system decreases must be driven by enthalpy
- ΔG for some reaction will decrease if the concentration of reactants increases
- The entropy of the universe can sometimes be negative
- Freezing is always a nonspontaneous process
- Iodine has less entropy than bromine
- The formation of water increases the entropy of the system
- The entropy of the universe must always increase
- The entropy of a system is never constant
- For an exothermic process, $q_{sys} < 0$ and $\Delta S_{surr} > 0$
- Sublimatino will not increase the entropy of the system

A plot for a chemical process showing ΔG against absolute temperature will have
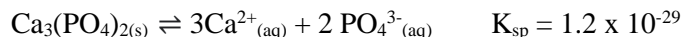
$\Delta H > 0 \ \Delta S > 0$

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

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

$\Delta H < 0 \ \Delta S < 0$

The solubility product constant for the following reaction is given as follows:

$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2\ PO_4^{3-}_{(aq)}$ $K_{sp} = 1.2 \times 10^{-29}$

Determine ΔGrxn in kJ at 25 deg C when $[Ca^{2+}] = 5.2 \times 10^{-4}$ M and $[PO_4^{3-}] = 8.6 \times 10^{-5}$ M.

## Electrochemistry

Redox Reactions

1. What is the **oxidation number of chromium** in the ionic compound ammonium dichromate, $(NH_4)_2Cr_2O_7$?

   a. +3
   b. +4
   c. +5

   d. +6
   e. +7

2. What is the **oxidation number of carbon** in the ionic compound potassium carbonate, K_2CO_3?

   a. +3
   b. +4
   c. +5

   d. +6
   e. +7

3. What are the **oxidation numbers for nickel, sulfur, and oxygen** in $Ni_2(SO_4)_3$?

   a. Ni +3; S +6; O -2
   b. Ni +2; S +4; O -2
   c. Ni +3; S +4; O -2

   d. Ni +2; S +2; O -2
   e. Ni +2; S +4; O -1

4. When hydrogen reacts with calcium metal, **what are the oxidation numbers** of the calcium and hydrogen in the CaH_2 product?

$$Ca(s) + H_2(g) \rightarrow CaH_2(s)$$

   a. -2 and +1
   b. +1 and -2
   c. +2 and -1

   d. 0 and 0
   e. +2 and -2

5. What **are the original and final oxidation numbers for iron** in the smelting of iron from iron oxide?

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$
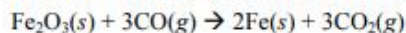
   a. +2 → 0
   b. +3 → 0
   c. 0 → +2

   d. +6 → 0
   e. No change

Cobalt is one of many metals that can be oxidized by nitric acid. Balance the following the reaction. How many electrons are transferred, and what would be the coefficient for H_2O in the balanced reaction?

$$Co + NO_3^- + H^+ \rightarrow NO + H_2O + Co^{2+}$$

   a. 3 electrons; 2 H_2O
   b. 6 electrons; 6 H_2O
   c. 4 electrons; 2 H_2O

   d. 6 electrons; 4 H_2O
   e. None of the above

What was **oxidized** and what was **reduced** in the following reaction?

$$2Hg^{2+} + N_2H_4 \rightarrow 2Hg + N_2 + 4H^+$$

   a. Hg^{2+} was oxidized; N_2H_4 was reduced
   b. Hg^{2+} was reduced; N_2H_4 was oxidized
   c. Hg^{2+} was oxidized; N_2H_4 was oxidized

   d. Hg^{2+} was reduced; N_2H_4 was reduced
   e. None of the above

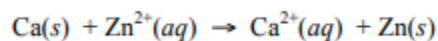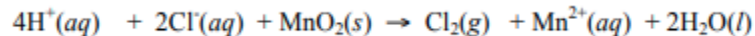Balance the Redox reaction in acidic aqueous solution

$BrO^{3-}_{(aq)} + N_2H_{4(g)} \rightarrow Br^-_{(aq)} + N_{2(g)}$
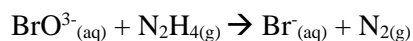
Balance the redox reaction in basic aqueous solution

$Cl_{2(g)} \rightarrow Cl^-_{(aq)} + ClO^-_{(aq)}$
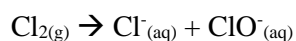
Oxidation and Reduction

What is the reducing agent for these reaction?

$4H^+(aq) + 2Cl^-(aq) + MnO_2(s) \rightarrow Cl_2(g) + Mn^{2+}(aq) + 2H_2O(l)$

$Ca(s) + Zn^{2+}(aq) \rightarrow Ca^{2+}(aq) + Zn(s)$

Choose the strongest reducing agent and oxidizing agent from the list of half reactions:

+1.22 V	$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$
+0.61 V	$Hg_2SO_4(s) + 2e^- \rightarrow 2Hg(l) + SO_4^{2-}(aq)$
-0.95 V	$SnO_2(s) + 2H_2O() + 4e^- \rightarrow Sn(s) + 4OH^-(aq)$
-1.48 V	$Cr(OH)_3(s) + 3e^- \rightarrow Cr(s) + 3OH^-(aq)$
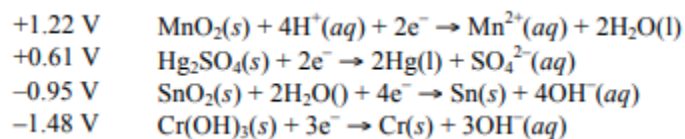
Which of the following metal cation is the best oxidizing agent?

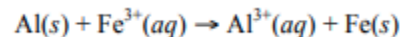Pb^{2+} Cr^{3+} Fe^{2+} Sn^{2+}

Which metal is the best reducing agent?

Mn   Al   Ni   Cr

Ecell Calculations

Calculate the Ecell for the following reactions:

$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$

$Al(s) + Fe^{3+}(aq) \rightarrow Al^{3+}(aq) + Fe(s)$

$4H^+ (aq) + Fe(s) + NO_3^-(aq) \rightarrow Fe^{3+}(aq) + NO(aq) + 2H_2O(l)$
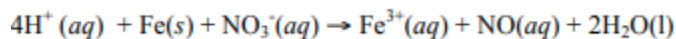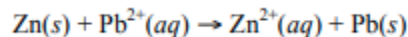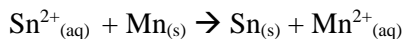
The oxidation of hydrogen by oxygen is one of the most-used reactions in fuel-cell technology. The overall reaction, which is given below, has a $\Delta G°$ value of –474 kJ/mol. What is the standard cell potential for this fuel cell?

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta G° = -474 \text{ kJ/mol}$$

The value of E° for the following reaction is 1.260 V. What is the value of E_{cell} given the concentrations shown?

$$\underset{0.1 \text{ M}}{2Al(s) + 3Cd^{2+} (aq)} \rightarrow \underset{0.6 \text{ M}}{3Cd (s) + 2Al^{3+} (aq)} \qquad E° = 1.260 \text{ V}$$
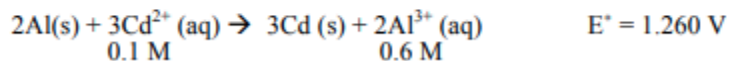
A voltaic cell employs the following redox reaction:

$$Sn^{2+}_{(aq)} + Mn_{(s)} \rightarrow Sn_{(s)} + Mn^{2+}_{(aq)}$$

Calculate the following at 25 deg C under each set of conditions

a) Ecell at Standard condition

b) Ecell where $[Sn^{2+}] = 0.0100M; [Mn^{2+}] = 2.00M$

c) Ecell where $[Sn^{2+}] = 2.00M ; [Mn^{2+}] = 0.0100M$

d) Ecell at equilibrium

e) ΔG at standard conditions

f) ΔG under conditions of part b

g) K at standard conditions

Electrolysis

Chromium often is electroplated on other metals and even plastics to produce a shiny metallic appearance. **How many grams** of chromium (51.996 g/mol) would plate out from a solution of $Cr(NO_3)_3$ when 10 amps of current are passed through the electrolytic cell for 5.36 hours?

If in using a lead-acid battery to start a car, 1.00 gram of Pb (207.2 g/mol) is consumed on the anode, **how long will it take** to recharge the battery, using a current of 0.500 amperes to turn the $PbSO_4$ that was produced back into Pb?

What products are produced in the electrolysis of a molten mix of KI and KBr?

Write the equations for the half-reactions that occur at the anode and cathode for the electrolysis of each aqueous solution:

NaBr

Na_2SO_4

$Ni(NO_3)_2$

KCl

CuBr

Will Nickel dissolve in HCl?   What about Tin?

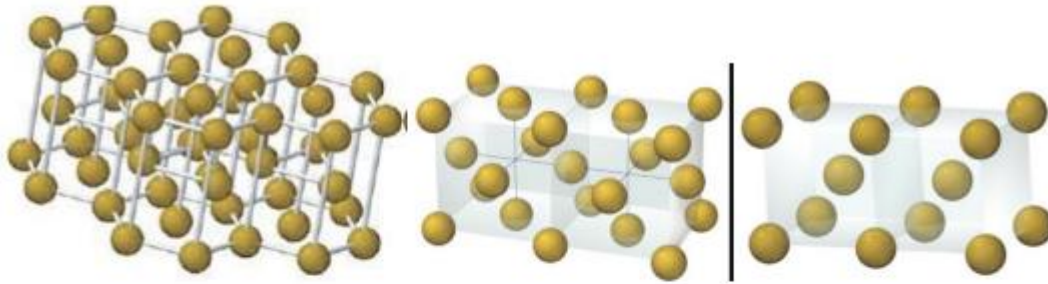Will gold dissolve in HCl? What about HNO_3?

Summarize the difference between

Voltaic Cells

Electrolytic Cells
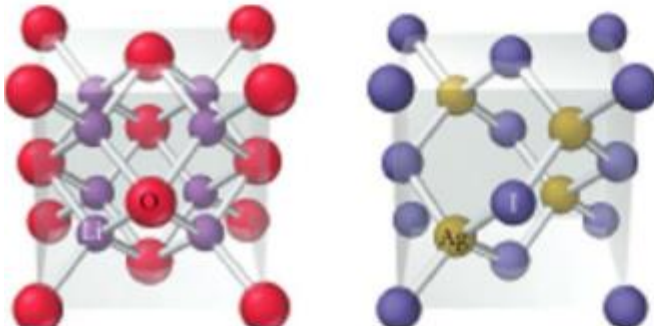
Coordination Compounds

1) For each of the structures below, determine the coordination number

2) Determine the number of atoms per unit cell

3) Based on the structure, name these two molecules

P-type of N-type indicator?

Silicon doped with Gallium	Germanium doped with antimony	Tin Doped with Arsenic
Antimony doped with Tin	Germanium doped with Phosphorous	Silicon doped with Aluminum

Rank by largest band gap: N, P, As, Sb