You are allowed 2 consecutive hours (no cutting classes) for this test. You may use your calculator but NO extra "scratch paper". Use the back of pages if necessary.

LECTURE: Multiple Choice -- 3 points each.
Choose the BEST answer and write the letter in the left margin next to the question.

1. We have made the statement that an absolute value for a system's Internal Energy, E, cannot be obtained. What is the principal reason for this?
   a) Too much confusion in measuring a system's average kinetic energy.
   b) There can be different forms of work involved
   c) Lack of knowledge of all possible potential energy interactions
   d) Heat effects could be exothermic or endothermic and you may not know which beforehand
   e) The initial statement is incorrect; you can in theory always determine a system's absolute energy because of the Third Law of Thermodynamics

2. A consequence of the Third Law of Thermodynamics is:
   a) Absolute entropy values cannot be determined
   b) Absolute enthalpy values can be determined
   c) The entropy of the universe is constantly increasing for any real change
   d) A system above absolute zero cannot have perfect order.
   e) 2 of the above

3. We've introduced a property of the system known as enthalpy, H. What is the chief advantage to be gained by introducing this property?
   a) It is possible to determine an absolute value for H whereas an absolute value for E cannot be determined.
   b) H permits all energy transfers between the system and the surroundings to be attributed to heat effects only.
   c) H is a state function
   d) H permits the use of Hess' Law, whereas an analogous calculation employing E could not be done.
   e) When calculating changes in H, the path used to determine the change will not matter.

4. A famous statement associated with the Second Law of Thermodynamics is that it is the only physical law which demonstrates the direction of time. Which of the following is most responsible for this assertion?
   a) The second law introduces the concept of Entropy
   b) The second law avoids the problem with E which led to the introduction of H
   c) The second law preserves the conservation of energy
   d) The second law is expressed as an inequality
   e) The second law is the one invoked with talking about engines

5. We've also said it is possible to measure ΔG value in lab for a system. What is the most direct thing that we can measure to achieve this?
   a) Temperature
   b) pH of a solution
   c) a reaction's Heat of reaction
   d) $E_{cell}$ for a galvanic cell
   e) Heats associated with phase changes, like Heat of Fusion or Heat of Vaporization
Given the reaction which describes the combustion of ethane, \( \text{C}_2\text{H}_6 \):

\[
2\text{C}_2\text{H}_6 (g) + 7\text{O}_2 (g) = 6\text{H}_2\text{O} (aq) + 4\text{CO}_2 (g) \quad \Delta H_{\text{rxn}} = -3100 \text{ KJ}
\]

The next 4 questions pertain to this reaction.

6. What is the system here?
   a) the \( \text{C}_2\text{H}_6 \), since it is the compound which is combusted
   b) the reactants
   c) the products
   d) only the gases substances
   e) the whole reaction

7. What is the criterion by which we decide whether or not this reaction is spontaneous?
   a) \( \Delta H_{\text{rxn}} \) must be negative (-)
   b) \( \Delta G_{\text{rxn}} \) must be negative (-)
   c) \( \Delta S_{\text{univ}} \) must be positive (+)
   d) \( \Delta G_{\text{rxn}} \) must be positive (+)
   e) \( \Delta S_{\text{surr}} \) must be positive (+)
   f) two of the above will act as the desired criterion

8. What would you predict would be the sign to be attributed to \( \Delta S_{\text{surr}} \)?
   a) positive (+)
   b) negative (-)
   c) no change
   d) there is not enough information here to make this prediction

9. Which category fits this reaction when predicting its spontaneity?
   a) Spontaneous because entropy of system and entropy of surroundings both increase
   b) Not spontaneous because entropy of system and entropy of surroundings both decrease
   c) Maybe spontaneous, depending on temperature, because entropy of system decreases,
      but entropy of surroundings increases
   d) the only way to even make a prediction is by knowing the \( \Delta H_f \) for all the individual
      substances

10. A redox couple is
    a) the same as a half cell
    b) a half cell plus an electrode
    c) an element in 2 different oxidation states
    d) present only while a redox reaction is occurring and does not exist otherwise
    e) two of the above

11. When a solution of \( \text{CuSO}_4 \) has added to it a piece of \( \text{Zn} \) metal, a reaction occurs. The
    explanation for the reaction is that
    a) The \( \text{Cu}^{2+} \) - Cu reduction potential is higher than that for the \( \text{Zn}^{2+} \) - Zn.
    b) The copper redox couple is a better oxidizing agent than the zinc redox couple
    c) \( \text{Zn}^{2+} \) is poorer at taking on two electrons and becoming \( \text{Zn} \) than \( \text{Cu}^{2+} \) is in becoming Cu.
    d) The Nernst equation gives a lower value for the zinc couple than it will for the copper couple
    e) All of the above
    f) only 2 of the above
12. Given 2 redox couples, $A^{+3}, A^{+2}$ and $X^{+4}, X^{+2}$ What, if anything, is needed to produce a half cell?
   a) nothing is needed in either case; you already have a redox couple 
   b) to act as the appropriate electrode you also need the species in the zero oxidation state in each case; that is, metallic $A$, and metallic $X$
   c) to act as the appropriate electrode you also need the species in the zero oxidation state for the redox couple which is going to be reduced. The other redox couple can have an inert electrode, such as Pt or Au
   d) you need a chemically inert metallic electrode, such as Pt or Au, in both cases
   f) you need to keep the two redox couples physically separate and connect them with a wire and a salt bridge

13. Why is it necessary to use a battery when determining the $E_{\text{cell}}$ value for a galvanic cell?
   a) A battery can provide the extra potential needed to make the signal register on a voltmeter
   b) The battery will speed up the galvanic cell, making the measurement quicker and surer.
   c) The battery assures electroneutrality.
   d) The battery balances out the galvanic cell, so that its potential won’t change due to a chemical reaction
   d) The battery switches the anode and cathode.
   e) 2 of the above

14. Given two half cells, how will you know which will be the ANODE if the two half cells are physically connected together by a salt bridge and a wire in a lab?
   a) The ANODE will be the half cell with the greater reduction potential
   b) The ANODE will be the half cell with the lesser reduction potential
   c) The ANODE will be the half cell on the right
   d) The ANODE will be the half cell with the greater concentration of oxidized species
   e) It’ll all depend on whether you have physically generated a galvanic cell or an electrolytic cell and you’re not told that here
   f) 2 of the above

15. Recall the final step in your Cu determination. It involves the titration of $I_2$ with $S_2O_3^{-2}$ to produce $I^-$ and $S_4O_6^{-2}$. If this reaction were to be run by means of a galvanic cell, what would be the relationship between the reduction potentials for the two redox couples above?
   a) $E$ for the $I_2 - I^-$ redox couple is greater than $E$ for the $S_4O_6^{-2} - S_2O_3^{-2}$ redox couple
   b) $E$ for the $I_2 - I^-$ redox couple is less than $E$ for the $S_4O_6^{-2} - S_2O_3^{-2}$ redox couple
   c) $E$ for the $I_2 - I^-$ redox couple is greater than 0 (positive) while $E$ for the $S_4O_6^{-2} - S_2O_3^{-2}$ redox couple is less than 0 (negative)
   d) For a redox titration, the reduction potential for the titrant has to be greater than the reduction potential for the analyte in the flask being titrated.

16. After the calculation of the reduction potential of a half cell, using the Nernst Equation, you get a value of 0.899 V. Which of the following can you deduce from this value?
   a) This redox couple can only be an oxidizing agent because of its high value.
   b) This redox couple has a poorer inherent tendency to take electrons than the Hydrogen redox couple.
   c) Since this redox couple can only be oxidized, you are in practical terms restricted to only using part of the Standard Reduction Potentials table.
   d) None of the above
The wet-chemical Copper determination you’ve been carrying out in the lab is a complicated procedure, more complicated than any of your previous titrametric determinations. Luckily, it is possible to watch the progress of this determination through the many color changes which occur as the determination proceeds. It is, however, also possible to use your old friend (or enemy) the pH line in this determination and designate different stages of the determination by changes in where you find yourself on the pH line. All the stages of this determination are presented below. In each stage, identify the stage by the color of the solution to be expected at this stage and also by the position (I through V) at which this stage would be found on the pH line. Note that in describing a pH line position a possible answer is “No position on pH line”

STAGE 1  -  Solid Copper unknown is weighed into a titration flask and covered with a little bit of water.
Color =  ___________________________________
Position on pH line:  __________________________

STAGE 2:  Concentrated Nitric Acid is added to begin the dissolution process
Color =  ___________________________________
Position on pH line when process is over:  __________________________

STAGE 3:  Once the sample has completely dissolved, concentrated ammonia (NH₃  MW = 17.00,  
Kₜ = 1.85x10⁻⁵) is added until all the excess nitric acid has been neutralized with a few drops of excess ammonia present.
Color =  ___________________________________
Position on pH line when process is over:  __________________________

STAGE 4:  As it is necessary to have a mildly acidic solution later on, it is necessary to neutralize any excess ammonia with glacial acetic acid (HOAc  MW = 60.00,  pKₐ = 4.74), then add 3 mL of excess acetic acid.
Color =  ___________________________________
Position on pH line when process is over:  __________________________

STAGE 5:  This involves the addition of solid KI followed by the subsequent titration. At this stage there are no longer any acid issues to be addressed but merely RedOx ones.

Color of solution just after KI addition =  __________________________
Position on pH line at this stage and throughout the titration process:  __________________________
STAGE 6: The titration with the titrant.
Identify the titrant being used AND the species being titrated at this stage: _____________________

Identify all the ensuing color changes from this point on through the titration to its conclusion AND explain what is happening in each case.

PROBLEMS: (53 pts) NO ‘MAGIC’ ALLOWED. SHOW ALL WORK.

1. (6 pts) Since we’ve just been talking about the Iodometric Copper Determination, this calculation seems to fit perfectly. Here is data from an iodometric determination of copper, such as you carried out in lab. A 1.2437 g sample of dried copper ore is dissolved in Nitric Acid. After the appropriate wet chemistry is carried out, excess KI (MW = 166.01) is added and the liberated I₂ (MW = 254.0) is titrated with a 0.1006 N solution of Na₂S₂O₃. It requires 34.29 mL to reach the final end point. What is the %Cu (AW = 63.54) in the sample?

2. (27 pts) Consider two redox couples, the Permanganate, Manganese redox couple, (MnO₄⁻, Mn²⁺) which has a Standard Potential of 1.51 Volts and a Titanium redox couple, (TiO²⁺, Ti³⁺) which has a Standard Potential of 0.10 V.
   a) We’ve used two special terms above, redox couple, and Standard Potential. Define BOTH terms
b) Suppose the intent is to combine these two redox couples in such a way that a galvanic cell will be formed. What must be done in a physical sense?

c) When a galvanic cell is formed and allowed to operate, a redox reaction will result. **Assume for the moment that the concentrations of all species present in the solution do not matter.** Under this condition give your prediction as to what this redox reaction will be. Your answer should be in the form of a balanced reaction. You may assume this reaction is being run under acidic conditions.

d) Give a clear explanation as to how you came to your decision above as to what this redox reaction would be. **NO CREDIT FOR ANY ANSWERS WITHOUT THIS EXPLANATION.** What would be the value for $E_{cell}$ under this set of circumstances?

e) Where would you expect to find the Cathode associated with this reaction? What would be its polarity?

f) Finally, assume that the concentrations of species involved in this redox reaction do matter. If $[\text{MnO}_4^{-}] = 0.050 \text{ M}$, $[\text{Mn}^{2+}] = 0.10 \text{ M}$, $[\text{TiO}^{2+}] = 0.050 \text{ M}$, $[\text{Ti}^{3+}] = 0.050 \text{ M}$, and the pH in both half cells = 2.00, what now would be the $E_{cell}$ of the resulting galvanic cell?
3. (14 pts) Consider the following two reactions:

\[
\begin{align*}
\text{S}_8 & \quad + \quad 8\text{O}_2 & \quad = \quad 8\text{SO}_2 & \quad \Delta H_{\text{rxn}} = -2376 \text{ kJ} \\
2\text{SO}_2 & \quad + \quad \text{O}_2 & \quad = \quad 2\text{SO}_3 & \quad \Delta H_{\text{rxn}} = -193 \text{ kJ}
\end{align*}
\]

a) Of the four different substances present (S\textsubscript{8}, SO\textsubscript{2}, O\textsubscript{2}, and SO\textsubscript{3}) which substances have heats of formation already known to you without your having to do any kinds of calculations? (NOTE: S\textsubscript{8} is considered to be the standard state for sulfur) What is the heat of formation value (\(\Delta H_f\)) for each of these already-known cases?

b) Calculate the heats of formation (\(\Delta H_f\)) for the remaining cases from the information provided.

c) Finally, USING TWO DIFFERENT ROUTES (the Hess’ Law route and the Heats of Formation route) calculate the heat of reaction, \(\Delta H_{\text{rxn}}\), for the unbalanced reaction:

\[
\_ \text{S}_8 \quad + \quad \_ \text{O}_2 \quad = \quad \_ \text{SO}_3
\]
4. (6 pts) The following problem is presented to you so you can impress all those seated around the Easter Dinner table who might be wondering about how useful your W&L LIBERAL ARTS EDUCATION actually is. Suppose the question arises as to how long it would take to defrost the Easter Turkey (wishbone and all) prior to baking? Well, thanks to Good Old PS 215A, you are in a position to resolve this issue and answer this question, with grace and elegance yet. What you need to know is the following: Weight of turkey = $1.14 \times 10^4$ g (about 25 lbs), Initial frozen temp = -7.0 deg C, Final thawed temp = 22.0 deg C, Specific heat of frozen turkey = 0.500 cal / g deg, Specific heat of thawed turkey = 1.00 cal / g deg, Melting point of frozen turkey = 0.0 deg C, Heat of Fusion of turkey = 44.4 cal / g, and the Heating Transfer Efficiency of the Microwave Oven = $1.20 \times 10^4$ cal / min

Please write and sign the pledge: