Name (please print): ___________________________

Allow two consecutive hours (but not at a time when you have another scheduled class) for taking this test. You may use your personal hand-calculator and your blue Statistical Handout-Helper page, but NO extra scratch paper at the backs of these test-pages should suffice.

LECTURE: Multiple choice 33 pts. (3 pts each)
For each question, choose the BEST answer and write the letter in the left margin next to the question.

1. What is the distinguishing feature of a counter ion?
   a) It is a base
   b) It is the “leftover” part of a weak acid
   c) It is negatively charged
   d) It can neither compete for nor lose a proton
   e) all of the above

   2Fe(s) + 3H₂O(l) = Fe₂O₃(s) + 3H₂(g) ; ΔH_{rxn} = +64 KJ

The next 4 questions pertain to the reaction given above:

2. What is the system here?
   a) the whole reaction
   b) the reactants
   c) the products
   d) only the solid substances

3. What is the criterion by which we decide whether or not this reaction is spontaneous
   a) ΔH_{rxn} must be positive (+)
   b) ΔG_{rxn} must be positive (+)
   c) ΔS_{system} must be positive (+)
   d) ΔG_{rxn} must be negative (-)
   e) ΔS_{surr} must be positive (+)
   f) ΔH_{rxn} must be negative (-)

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

5. 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) Maybe spontaneous, depending on temperature, because entropy of system increases, but entropy of surroundings decreases.
6. Of the laws of thermodynamics, which is concerned with the notion that all energy changes must be accounted for?
a) the First Law  
b) the Second Law  
c) the Third Law  
d) they all insist that all energy changes be accounted for

7. Of the laws of thermodynamics, which involves the notion of time?
a) the First Law  
b) the Second Law  
c) the Third Law  
d) they all are concerned with the notion of time

8. If $\text{HXO}_4^{2-}$ has a $\text{pK}_b = 3.10$, what else do you know to be NOT NECESSARILY true?
a) $\text{HXO}_4^{2-}$ is a weak base  
b) the $K_b$ for $\text{HXO}_4^{2-} = 8.0 \times 10^{-4}$  
c) the $\text{pK}_a$ for $\text{HXO}_4^{2-} = 10.90$  
d) the conjugate is $H_2\text{XO}_4^-$  
e) $H_2\text{XO}_4^-$ also has acid/base properties

9. The following question refers to the vinegar analysis you performed in lab. In which of the following situations would the presence of water cause an error in your results?
a) Washing the tip of the buret with distilled water right before the equivalence point is reached. (This decreases the $[\text{H}_3\text{O}^+]$ and causes a low %HOAc.)  
b) Failing to dry the 250.0 mL volumetric flask before adding your 25.00 mL of original vinegar sample. (You’re going to add water anyway.)  
c) Failing to dry the beakers in which you received your 2 vinegar samples in the first place. (You’re going to dilute the vinegar samples with water anyway.)  
d) Failing to rinse the water out of your buret with your standardized NaOH solution. (After all, a titration only depends on the #mmoles.)  
e) 2 of the above

10. Given these values of $\Delta H$ and $\Delta S$ for 4 chemical reactions, which one reaction will NOT be spontaneous at constant T and P?
a) $\Delta H = +25$ kJ, $\Delta S = -5.0$ J/K, $T = 300$ K  
b) $\Delta H = +25$ kJ, $\Delta S = +100.0$ J/K, $T = 300$ K  
c) $\Delta H = -10$ kJ, $\Delta S = +5.0$ J/K, $T = 298$ K  
d) $\Delta H = -10$ kJ, $\Delta S = -40$ J/K, $T = 200$ K

11. When an aqueous solution is prepared by mixing 0.50 mmoles of $\text{NH}_4\text{NO}_3$ and 0.40 mmoles of $\text{HNO}_3$, what must be known to determine the pH of the solution?
a) only the number of mmoles of $\text{HNO}_3$ present  
b) the ratio of mmoles of $\text{HNO}_3$ and $\text{NH}_4\text{NO}_3$ and the $\text{pK}_a$ value for $\text{NH}_4^+$ 
c) the number of mmoles of $\text{HNO}_3$ and the final volume of the solution  
d) the total number of mmoles of the acids and the final volume of the solution.  
e) the number of mmoles of $\text{NH}_4\text{NO}_3$ and the final volume of the solution.
LECTURE: Short answers (8 points)
1. In the region to the right, draw the Reaction Predictor Plot (which was discussed in class) for a Minor Reaction.

2. For the Reaction Predictor Plot, what is plotted at the Left-hand end of the X axis? On the Right-hand end?

3. For the Reaction Predictor Plot, what did we finally determine should be plotted on the Y axis?

4. Explain how the Reaction Predictor Plot works in explaining the behavior of a Minor reaction.

PROBLEMS (84 pts): Show All Work; Method must be clear; Sig Figs and Units count.

1. (8 pts) Given the postulated reaction: \(2\text{AgCl(s)} + \text{Br}_2(\text{l}) = 2\text{AgBr(s)} + \text{Cl}_2(\text{g})\)

If AgCl(s) has a standard Free Energy of 54.6 kcal/mole and AgBr(s) has a standard Free Energy of 48.7 kcal/mole, calculate \(\Delta G\) for this postulated reaction and state whether this reaction would be spontaneous or not.
2.(44 pts) You find yourself asked to titrate an unknown for an exotic acidic species, Mystery Acid. Its formula can be written as HMys. Its $K_a = 8.3 \times 10^{-7}$ and it has a Molecular Weight of 66.00. In preparation for the unknown sample which is to come in next week’s mail, you acquire for study 250.0 mL of 0.10 M Mystery Acid from the National Institute of Standards. You need to learn which indicator would be the proper choice for this titration before you actually titrate the unknown which is to come. You have on hand a standardized solution of 0.10 M NaOH titrant.

**Using the methodology we’ve used in class when constructing a titration curve (i.e, 100 mL of 0.10 analyte being titrated with 0.10 M titrant):**

PART A. (8pts) Determine the pH at the equivalence point when you titrate Mystery Acid with NaOH.

PART B. (12 pts) Determine the “region of 0.1% accuracy” for this titration. (NOTE: this answer will require calculation of specific pH values as well as a conclusion statement).

PART C. (6 pts) Explain CLEARLY how to employ the calculations above with an Indicator’s “window” in deciding the proper choice of indicator for this titration. (Define what is meant by Indicator’s “window”)

PART D. (6 pts) Explain the important distinction between an \textbf{end point} and an \textbf{equivalence point}, and how this distinction applies in the work you are doing in this determination.

PART E. Finally, when the unknown sample arrives in the mail and you perform your titration, you find that in order to “make your titration fit properly”, you need to dilute 25.00 mL (by a pipet) of the unknown to a volume of 250.0 in a volumetric flask. When you subsequently titrate a 50.00 mL portion of this now-diluted unknown, you find the titration requires 27.50 mL of a standardized 0.09927 M NaOH titrant.

i) (4 pts) What is meant by the above phrase “make your titration fit properly”? What are you trying to make “fit” and Why? (For full credit you need to answer both parts of this question)

ii) (8 pts) What is the \% (wt/vol) of Mystery Acid in the actual unknown sent to you in the mail? (NOTE: The units here are the same as in your vinegar unknown)
3. (32 pts) Below are 4 descriptions of Acid/Base systems. Calculate the final pH in each case.

Case I. 75.00 mL of 0.25 M Benzoic Acid (HOBz, MW = 122.12, pKₐ = 4.20) to which has been added 50.00 mL of 0.35 M NaOH. (MW = 40.00)

Case II 75.00 mL of 0.25 M Benzoic Acid (HOBz, MW = 122.12, pKₐ = 4.20) to which has been added 50.00 mL of 0.35 M Sodium Benzoate, NaOBz. (MW = 144.10)

Case III 75.00 mL of 0.25 M Methyl amine, CH₃NH₂ (MW = 31.00, pKₐ = 3.30) to which has been added 50.00 mL of 0.05 M NaCl (MW = 58.50)

Case IV. 90.00 mL of 0.40 M HCl (MW = 36.50) to which has been added 40.00 mL of 0.45 M Ca(OH)₂ (MW = 74.00)

Pledge: I have neither given nor received any unacknowledged aid on this test.
Signed: ______________________________