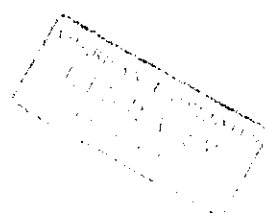


AMERICAN UNIVERSITY OF BEIRUT  
Chemistry 216  
Final Examination

Jan. 24, 1996



Time: 3 hours  
 Calculators allowed  
 Periodic Tables Provided

Name: \_\_\_\_\_ Section: (Day) \_\_\_\_\_

Answer clearly and to the point.  
 Perform calculations to the appropriate number of significant figures.  
 Diagrams should be simple and neatly labeled.  
 Use Pencil.  
 Graphs should be neat and have a suitable title and scale.  
 Give units.

|        |       |             |
|--------|-------|-------------|
| Score: | I.    | /15         |
|        | II.   | /15         |
|        | III.  | /30         |
|        | IV.   | /20         |
|        | V.    | /20         |
|        | VI.   | /20         |
|        | VII.  | /10         |
|        | VIII. | /20 + Graph |
| <hr/>  |       |             |
| TOTAL: |       | /150        |

Equivalent ionic conductances:

$H^+$  350     $Cl^-$  76     $Na^+$  50  
 $OH^-$  198     $HCOO^-$  55     $K^+$  74

EDTA complexes:

$Zn^{2+}$   $\log K_f = 16.5$

$Mg^{+2}$   $\log K_f = 8.7$

$Mn^{++}$ ,  $\log K_f = 13.8$

f.(15%) Answer the following in the space provided:

(a) Outline the theoretical basis of Beer's Law in spectrophotometry.

(b) Give four different examples of deviation from Beer's Law.

(c) Suppose that in a certain spectrophotometer, the incident radiation has a wide spectral band ( $\lambda' - \lambda''$ ), and that under certain conditions the transmittance is 50.0% at  $\lambda'$ , and 40.0% at  $\lambda''$ . Compare the absorbance observed for this non-monochromatic radiation with the absorbance of the monochromatic wavelength  $\lambda = \frac{1}{2}(\lambda' + \lambda'')$ , assumed to be the mean (average) of absorbance at the limits  $\lambda'$  and  $\lambda''$ . Comment on the result.

II.(15%) This question deals with spectrophotometric instrumentation:  
(a) Distinguish between the two types of monochromators (light dispersers) used in spectrophotometers and list the advantages and disadvantages of each.

(b) Discuss the effect of the slit width on the resolution of a spectrophotometer and the adherence to Beer's Law.

(c) Compare the operations of a single beam spectrophotometer, and a double beam spectrophotometer.

11. (30%) For each of the following 15 multiple-choice questions, circle the part(s) which gives the best answer.

1. The third overall formation constant of a complex ion,
  - a. is defined as  $k_3$
  - b. is defined as  $(k_3)^3$
  - c. must be very large
  - d. cannot be greater than the third stepwise formation constant.
  - e. None of the above is true.
  
2. In a solution containing a metal cation and a ligand,
  - a. the fraction of free cation =  $(1 + \beta_1 L + \beta_2 L^2 + \dots)$
  - b. the fraction of unprotonated ligand =  $(1 + K_1/H + K_1 K_2/H^2 + \dots)$
  - c. the fraction of each species present is independent of the total concentration of the cation and its complexes
  - d. at least one chelate is formed
  - e. None of the above is true.
  
3. For the formation of a metal-ligand complex,
  - a.  $\log K$  must be greater than 10
  - b. the charge on the central metal must be +2
  - c. the ligand must have a charge of -4
  - d. the equilibrium constant is larger than the conditional (apparent) formation constant
  - e. it is necessary to have an auxiliary complexing agent
  
4. In an analytical complexometric titration,
  - a. EDTA must be used
  - b. the reaction need not be fast
  - c. the ligand must form a complex with the indicator
  - d. multidentate ligands are superior to monodentate ligands
  - e. the use of a masking agent is recommended even if only one metal is being titrated.

5. Consider the complexes  $MgY^-$  and  $MgE^-$  (E=Erio-chrom black-T indicator)

- As pH increases, the stability of both  $MgY^-$  and  $MgE^-$  increases
- As pH increases, the stability of  $MgY^-$  increases while that of  $MgE^-$  decreases.
- The stability of these complexes is independent on pH.
- $MgE^-$  should be more stable than  $MgY^-$  for the complexometric titration of  $Mg^{++}$  to be possible.
- None of the above.

6. An example of a determinate error in this experiment, the complexometric titration of  $Mg^{++}$  will be:

- An impurity in EDTA.
- An impurity in Mg metal used as the primary standard.
- Errors involved in reading the meniscus while making volume readings.
- Errors involved in estimating the color of the solution at the equivalence point of a titration.
- All of the above.

7. An important reason why Eriochrome Black T can be used as an indicator in a titration involving EDTA as titrant for divalent action  $Mg^{++}$  determination is:

- $MgY^-$  is more stable than  $MgE^-$ .
- $MgY^-$  stability increases as pH increases.
- $MgY^-$  stability increases as the equivalence point is approached.
- $Mg^{++}$  ion acts as a strong oxidizing agent at pH 10.
- The formation constant of the complex involving the indicator is much larger than the formation constant of the complex  $MgE^-$ .

8. The ultraviolet absorption spectrum of a gaseous compound,

- shows more vibrational fine structure than does the spectrum of its aqueous solution.
- is not related to electronic excitation.
- cannot be measured in a spectrophotometer.
- does not follow Beer's Law.
- is not useful in chemical analysis.

9. A  $5.00 \times 10^{-3}$  M solution of a compound placed in a 5.00 cm cell of a spectrophotometer shows a transmittance of 26.8% at 455 nm.
- The solution is probably blue.
  - The compound cannot fluoresce.
  - The absorbance of the solution is 0.434 .
  - If placed in a 2.50 cm cell the solution would transmit 53.6%.
  - None of the above is true.
10. In a double-beam spectrophotometer,
- there are two sources of radiation.
  - the optics include a rotating mirror.
  - there is no transducer.
  - there is no blank.
  - only a narrow range of wavelengths can be covered.
11. The molar conductivities at infinite dilution of  $\text{KCl}$ ,  $\text{KNO}_3$  and  $\text{AgNO}_3$  are 149.9, 145.0, and  $133.4 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  respectively at  $25^\circ\text{C}$ .  
The molar conductivity of  $\text{AgCl}$  at infinite dilution is:
- $161.5 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .
  - $138.3 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .
  - $128.5 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .
  - $428.3 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ .
  - none of the above.
12. Following question 11, the conductivity of a saturated solution of  $\text{AgCl}$  in  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$  was found to be  $1.887 \times 10^{-6} \text{ } \Omega^{-1} \text{ cm}^{-1}$ . What is the solubility product of  $\text{AgCl}$  at this temperature?
- $1.36 \times 10^{-10}$
  - $1.86 \times 10^{-10}$
  - $2.16 \times 10^{-10}$
  - $1.94 \times 10^{-11}$
  - $1.75 \times 10^{-10}$

13. A cell contains 0.10 M aqueous KCl, which at that concentration has a molar conductivity of  $129 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Its measured resistance was  $28.44 \text{ } \Omega$ . When the same cell was filled with 0.05 M NaOH aqueous solution, the resistance was  $31.6 \text{ } \Omega$ . The molar conductivity of aqueous NaOH is:

- a.  $180 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
- b.  $90 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
- c.  $230 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
- d.  $580 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
- e. none of the above.

14. The intensity of a light beam is halved on traversing a 1.00 cm thickness of absorbing medium. What thickness must be traversed to reduce the emergent intensity to one-tenth of the incident radiation?

- a. 2.00 cm.
- b. 1.68 cm.
- c. 4.96 cm.
- d. 6.64 cm.
- e. 3.32 cm.

15. The absorbance of a 0.250 M solution of a weak acid HA were measured in a 2.00 cm cell with distilled water as a blank. These measurements were taken:

| <u>Solvent:</u>  | <u>Absorbance (405 cm)</u> |
|------------------|----------------------------|
| 0.50 M HCl       | 0.852                      |
| H <sub>2</sub> O | 0.703                      |
| 0.50 M NaOH      | 0.000                      |

The  $pK_a$  of the acid is:

- a. 4.75
- b. 3.92
- c. 2.03
- d. 1.62
- e. 5.16

IV.(20%) a. Calculate the pH of a solution obtained by mixing  $10.00\text{cm}^3$   $0.020\text{ F HCl}$  and  $15.00\text{ cm}^3$   $0.20$  formic acid. ( $\text{pK}_a = 3.75$ )

b. Calculate the conductance of the above solution. If measured using a cell of cell constant =  $1.00\text{ cm}^{-1}$ .

c. If  $0.50\text{ cm}^3$  of  $1.0\text{M KOH}$  is added to the above solution, calculate the conductance of the resulting solution.

d. On the back of this sheet draw (qualitatively) the expected conductance-titration for  $50\text{ cm}^3$  of a mixture of  $0.10\text{ F HCl}$  and  $0.10\text{ F}$  formic acid titrated with  $1\text{ F KOH}$ . Label each part of the curve.



V.(20%) \* A mixture of  $Mn^{+2}$ ,  $Mg^{+2}$ , and  $Zn^{+2}$  was analyzed as follows: The 25.00 ml sample was treated with 0.25 g of  $NH_3OH^+Cl^-$  (hydroxyl ammonium chloride, a reducing agent that maintains manganese in the +2 state), 10 ml of ammonia buffer (pH 10), and a few drops of eriochrome black T indicator and then diluted to 100 ml. It was warmed at  $40^\circ C$  and titrated with 39.98 ml of 0.04500 M EDTA to the blue end point. Then 2.5 g of NaF was added to displace  $Mg^{++}$  from its EDTA complex. The liberated EDTA required 10.26 ml of standard 0.02065 M  $Mn^{+2}$  for complete titration. After this second end point was reached, 5 ml of 15% (W/W) aqueous KCN was added to displace  $Zn^{++}$  from its EDTA complex. This time the liberated EDTA required 15.47 ml of the standard  $Mn^{+2}$ .

a. Write the chemical reactions scheme of the above procedure.

b. Calculate the number of milligrams of each in the 25.00 ml sample of unknown (A.W.: Mn = 54.94, Mg = 24.31, Zn = 65.38).

c. What are the advantages/disadvantages of Erio-T as a metallochromatic indicator.

- d. Comment on the feasibility of this titration if
- (i) too much  $\text{NH}_3/\text{NH}_4^+$  buffer is used, and
  - (ii) no  $\text{NH}_3/\text{NH}_4^+$  buffer is used.

VI. (20%) a) Consider the definition of  $K^{\theta} = a_{H^+} \cdot (B/HA)$  where the ratio of molar concentrations of base and acid forms can be expressed in terms of absorbance ( $A_a$ ,  $A$ ,  $A_b$ ). Show how one can derive a relation which gives a linear plot to obtain the dissociation constant from the data by a graphical method.

(b) One millimole portions, each of <sup>the</sup> weak acid (HA) and its salt (NaA), are dissolved in one-liter volumes of various buffer solutions. The absorbances of the resulting solutions are measured at 650 nm in 2.00 cm cells and found to be:  
0.950 (pH 12.00), 0.950 (pH 10.00), 0.677 (pH 7.00), 0.00 (pH 2.00),  
0.00 (pH 1.00). Calculate by showing your reasoning the molar absorptivities of HA,  $A^-$ , and find  $K_a$ .

(c) The following data are taken from two reports on the spectrophotometric determination of the  $K_a$  of the acid at 650 nm, measured in aqueous acetate buffer solutions of low ionic strength at room temperature.

| <u>pK<sub>a</sub>(1) (650nm)</u> | <u>pK<sub>a</sub>(2)(650nm)</u> |
|----------------------------------|---------------------------------|
| 4.957                            | 5.068                           |
| 4.868                            | 5.059                           |
| 4.871                            | 4.888                           |
| 4.844                            | 4.876                           |
| 4.831                            | 4.867                           |
| 4.918                            | 4.895                           |
| 4.913                            | 4.924                           |
| 4.977                            | 4.925                           |
| 4.892                            | 5.084                           |

\* Inspect the above results and decide on the mean and standard deviation for pK<sub>a</sub> (you can reject some points if you want!)

\*Suggest, on the basis of your work, why the two sets give somewhat different results.

\* Estimate the uncertainty in pK<sub>HCl</sub> expected on the basis that pH was measured to  $\pm 0.002$  and absorbance to  $\pm 0.002$

VIII(10%) A solution contains a colored substance (X) and a colorless one (Y). A colorless reagent (L) reacts quantitatively with Y to form a colored compound (YL), but does not react with X. The molar absorptivities of X and YL are 250 and  $3.40 \times 10^3$ . A 10.00 ml portion of the solution is diluted to 250 ml and the diluted solution gives an absorbance of 0.532 in a 2.00 cm cell. Another 10.00 ml portion is also diluted to 250 ml after addition of excess L, and the absorbance of the diluted solution is 0.975 in the 2.00 cm cell. By showing your reasoning calculate the concentrations of X and Y in the original solution.

VIII(20%) Stock solutions of  $M^{+2}$  ( $5.00 \times 10^{-3}M$ ) and a chelating ligand L ( $5.00 \times 10^{-3}M$ ) were used to prepare a series of solutions. The solutions were prepared in  $25.00 \text{ cm}^3$  volumetric flasks and diluted to the marks with distilled water. Absorbances at 520 nm were measured in a 1.00 cm cell with  $H_2O$  blank.

| $M^{+2}$<br>( $\text{cm}^3$ ) | L<br>( $\text{cm}^3$ ) | A<br>(520 nm) |
|-------------------------------|------------------------|---------------|
| 4.00                          | 0.00                   | 0.000         |
| 4.00                          | 1.00                   | 0.092         |
| 4.00                          | 2.00                   | 0.190         |
| 4.00                          | 4.00                   | 0.368         |
| 4.00                          | 6.00                   | 0.565         |
| 4.00                          | 8.00                   | 0.727         |
| 4.00                          | 9.00                   | 0.517         |
| 4.00                          | 10.00                  | 0.376         |
| 4.00                          | 12.00                  | 0.002         |
| 4.00                          | 14.00                  | 0.000         |

a. Plot the data in a suitable form to find the formula of the complex which absorbs at 520 nm.

b. Suggest an explanation for the decrease in A at high ligand concentrations.

c. Find the molar absorptivity for the absorbing complex.

d. Find its formation constant.