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February 4, 2000
Time: 2 hours

CHEMISTRY 215
Final Examination

Name: _____

- Answers clearly and to the point.
- Perform calculations to the appropriate number of significant figures.
- Starts by the question you know best.
- Give units.

Score:

| | |
|-------|-------|
| I | / 10 |
| II | / 15 |
| III | / 10 |
| IV | / 20 |
| V | / 10 |
| VI | / 10 |
| VII | / 10 |
| VIII | / 15 |
| Total | / 100 |

Good Luck

(10%) I. In two sections of Chemistry 215 the final grades distributed as follows:

Section 1: 55, 70, 70, 70, 75, 75

Section 2: 60, 65, 65, 75, 80, 85

Is there a significant difference between the average for the two sections?
Explain.

(15%) II. A solution contains 0.080 F BaCl_2 and 0.035 F KCl .

a) Find the ionic strength of the solution.

b) Find f_{Cl^-} using a suitable equation.

c) Calculate the solubility of PbCl_2 in this solution, including activity corrections.

d) On the same plot, show (qualitatively) the variation in f_{Cl^-} (actual) and f_{Cl^-} (calculated) with ionic strength.

(10%) III. Answer briefly the following in the space provided:

a) Give three examples explaining deviation from Beer's Law.

b) What are the intercept and slope corrections due to in a pH potentiometric titration?.

c) Give the electrochemical representation of a cell, which can be used to routinely measure pH. What is the relationship between Ecell and pH.

d) List the different types of monochromators in a single beam UV-Vis spectro photometer.

(20%) IV. An aqueous solution contains two salts, 0.025M KH_2X and 0.025M K_2HX . The pH, measured with a glass electrode against a calomel electrode in a saturated KCl, is 6.860 at 25°C. The acid H_3X has $\text{pK}_{\text{a}1} = 2.13$, $\text{pK}_{\text{a}2} = 7.21$ and $\text{pK}_{\text{a}3} = 12.32$.

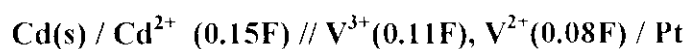
a) Showing your reasoning, calculate the approximate pH expected for this buffer solution.

b) Why is the experimental pH different from the calculated value?

c) Suppose that HCl is added to the above buffer such that the added acid amounts to 0.010M. Calculate the expected resulting pH approximately.

d) Suppose that KOH is added to the original buffer, but that the added base was 0.0260 M. Calculate the resulting approximate pH, and comment.

(10%) V. Given the following cell:



and the standard reduction potentials are:

$$E^\circ(\text{Cd}^{2+} / \text{Cd}) = -0.403\text{V}, E^\circ(\text{V}^{3+}, \text{V}^{2+}) = -0.255\text{V}$$

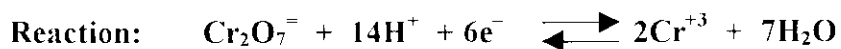
a) Write down the $\frac{1}{2}$ - reactions at the cathode and anode and the overall cell reaction.

b) Calculate the emf of the cell.

c) Calculate the equilibrium constant for the cell reaction.

(10%) VI. A perchlorate ion-selective electrode immersed in 50.0ml of unknown perchlorate solution gave a potential reading of 358.7mV versus standard calomel electrode ($E^\circ(\text{Hg}_2\text{Cl}_2, \text{Hg}) = 0.246 \text{ V}$). When 1.00ml of 0.050 M NaClO_4 was added, the potential changed to 346.1 mV. Assuming, the perchlorate to behave ideally, and that the electrode has a good Nernstian response (slope = 0.05915 V), find, by showing your reasoning, the concentration of ClO_4^- in the unknown.

(10%) VII. A standard chromium (III) solution was prepared by reduction of 5.00ml of 1.00N $\text{K}_2\text{Cr}_2\text{O}_7$ followed by dilution to 100ml. This solution showed an absorbance of 0.310 when measured at 440nm in a 1.00cm cell. A 1.000g sample of a chromium ore was dissolved, treated to ensure that all the chromium was in the trivalent state (Cr^{3+}), and diluted to 100ml. This solution showed an absorbance of 0.336 when measured in the same cell under the same conditions.



- Calculate the Molarity (M) of $\text{Cr}_2\text{O}_7^{\ominus}$.
- Find the molar absorptivity of the standard $\text{Cr}_2\text{O}_7^{\ominus}$.
- Calculate the unknown concentration of $\text{Cr}_2\text{O}_7^{\ominus}$ in the ore sample.
- Hence, calculate the % of Cr in the unknown.

(15%) VIII. A Ag/AgCl indicator electrode was used to monitor Cl⁻ concentration during titration of 100.00cm³ 0.20F KCl with 0.20 F AgNO₃. Assume that the reference is a standard hydrogen electrode.
 $E^{\circ}(\text{Ag}/\text{AgCl}) = +0.222\text{V}$.

a) Write down the electrochemical representation of the cell.

b) Show how the cell emf depends on (Cl⁻).

c) Calculate E cell at the following stages in the titration: After adding 99.50 cm³ AgNO₃.

d) At the equivalence point.

e) After adding 100.50cm³ AgNO₃.