Chem 210 Second Hour Exam Answers

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Some possibly useful equations: $2.3RT/F = 0.05916$ V

$\Delta\lambda^*_{min} = 1/(2\cdot d_m)$ $f = 2v\lambda^*$ $F = 2.3kP_o\Phi_f\epsilon bC$

$\Delta E = E_{cat} - E_{an} + E_{lj} = E_{IND} - E_{REF} + E_{lj}$

$E = E^o - (2.3RT/nF)\log(Q)$ $E_{SCE} = +0.244$ V $E_{Ag/AgCl} = +0.199$ V $\Delta E = K + S\cdot\log(a_A)$

% rel. error $= \pm 100\%\cdot(10^X - 1)$ where $X = \Delta E_{err}/S$ $S = +(2.3RT/zF)$

Calculations: SHOW ALL OF YOUR WORK! Points will be deducted if I cannot see how you got your final answer. Underline or circle your final answers. Include the correct units or lose a point per answer.

1. (6) The cell potential of the following cell is 0.000 V. Calculate the concentration of the Cu^{2+} ion.

SHE $||$ Cu^{2+} (? M) $|$ Cu $\qquad$ $Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^0 = +0.337$ V

$\Delta E = E_{cat} - E_{an} = E(Cu^{2+/0}) - E_{SHE}$ ($E_{SHE} = 0$ V by definition)

$E_{cat} = E^0 - (0.05916/n)\log(1/[Cu^{2+}])$

$\Delta E = 0.000 = (+0.337) - (0.05916/2)\log(1/[Cu^{2+}]) - 0$

$\log(1/[Cu^{2+}]) = \{(0.000) - (0.337)\}/(-0.02958) = 11.4$

$1/[Cu^{2+}] = 10^{11.4} = 2.5\times10^{-11}$; $[Cu^{2+}] =$ **4×10^{-12} M**

2. (6) A sodium ISE and a SCE were immersed in a solution containing 2.0×10^{-3} M Na^+. The cell potential was $+0.347$ V. The ISE and SCE were then transferred to a sample of river water; the resulting cell potential was $+0.386$ V. Calculate the molar sodium concentration in the river water.

Single point calibration; assume ideal $S = 0.05916/(+1) = +0.05916$ V

$\Delta E = K + (0.05916)\log([Na^+])$

$+0.347 = K + (0.05916)\log(2.0\times10^{-3})$; $K = +0.347 - (0.05916)(-2.70) = +0.507$ V

$+0.386 = +0.507 + (0.05916)\log([Na^+])$

$\log([Na^+]) = \{(0.386) - (0.507)\}/(0.05916) = -2.05$; $[Na^+] = 10^{-2.05} =$ **9.0×10^{-3} M**

3. (6) Given the following calibration date for an iodide ISE + Ag/AgCl REF, calculate the concentration of the unknown iodide solution.

$[I^-]$	ΔE
3.0×10^{-5} M	+125 mV
1.0×10^{-3} M	+46 mV
[?]	+60 mV

Calibration curve; do NOT assume S is ideal.

$+125 = K + S \log(3.0 \times 10^{-5})$

$+46 = K + S \log(1.0 \times 10^{-3})$

Subtract: $+79 = S(-4.52) - S(-3.00) = S(-1.52)$; $S = +79/(-1.52) = -52.0$ mV

$+46 = K - (52.0)(-3.00)$; $K = -110$ mV

$+60 = (-110) - (52.0)\log([I^-])$; $\log([I^-]) = \{(+60) - (-110)\}/(-52.0) = -3.27$

$[I^-] = 10^{-3.27} =$ **5.4×10^{-4} M**

4. (4) Convert −0.699 V vs Ag/AgCl to V vs SHE.

$-0.699 \text{ V} = E - E_{Ag/AgCl}$

$+0.199 \text{ V} = E_{Ag/AgCl} - E_{SHE}$

Add: **-0.500 V** $= E - E_{SHE}$

5. (6) If the uncertainty in a cell potential is ±2 mV for a measurement using a Ca^{2+} ISE, what is the % relative error in the calculated Ca^{2+} concentration?

% rel. error $= \pm 100\% \cdot (10^X - 1)$ where $X = \Delta E_{err}/S$

$S_{ideal} = +59.16 \text{ mV}/(+2) = +29.58$ mV

% rel. error $= \pm 100\% \cdot (10^{+2/(29.58)} - 1) = \pm 100\% \cdot (10^{+0.068} - 1) =$ **±17%**

6. (6) A biological sample was analyzed by Raman spectroscopy using a HeNe laser (632.8 nm) for excitation. The sample exhibited a Raman peak at 1450 cm^{-1}. What was the corresponding wavelength in nm?

$\lambda^*_{ex} = (10^7 \text{ nm/cm})/(632.8 \text{ nm}) = 15803 \text{ cm}^{-1}$

Stoke's shift: $15803 \text{ cm}^{-1} - 1450 \text{ cm}^{-1} = 14353 \text{ cm}^{-1}$

$\lambda_{Stoke's} = (10^7 \text{ nm/cm})/(14353 \text{ cm}^{-1}) =$ **696.7 nm**

Credit given also for anti-Stoke's shift: $15803 \text{ cm}^{-1} + 1450 \text{ cm}^{-1} = 17253 \text{ cm}^{-1}$

$\lambda_{anti\text{-}Stoke's} = (10^7 \text{ nm/cm})/(17253 \text{ cm}^{-1}) =$ **579.6 nm**

Short answer: Provide a word, phrase, formula, or short sentence.

7. Why do dispersive IR spectrometers have a grating change during a scan?
(4)

To improve throughput. A blazed grating has high throughput from 2/3 λ_B to 2 λ_B. That is not large enough to cover the IR spectral domain (4000 – 400 cm^{-1})

8. What factors affect the fluorescence quantum yield of a molecule?
(5)

Molecular flexibility, the presence of heavy atoms, solvent viscosity and paramagnetic molecules. Increased molecular flexibility, the presence of heavy atoms or paramagnetic molecules decrease fluorescence quantum yield, increased solvent viscosity increases fluorescence quantum yield.

9. Why does the excitation spectrum resemble (but not match) the absorption spectrum of the
(4) molecule?

The excitation spectrum resembles the absorption spectrum because fluorescence is proportional to the molar absorptivity of the molecule (F ϵ). The fluorescence is also proportional to the excitation intensity (F P_0) , which is wavelength dependent, so there is not an match between the excitation and absorption spectrum.

10. What instrumental method allows concentrations of several elements be determined simultaneously?
(4)

Atomic emission spectroscopy.

11. Sketch a Ag/AgCl reference electrode and label the parts.
(4)

The sketch should show an internal silver wire coated with silver chloride. The internal solution is saturated KCl also saturated with AgCl. A frit forms the liquid junction to the sample.

12. Convert this cell notation into 2 half-reactions and the cell reaction.: Pt * Fe^{2+}, Fe^{3+} ** Ag^+ * Ag
(5)

Anode: $Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$ (oxidation)
Cathode: $Ag^+ + e^- \rightleftharpoons Ag(s)$ (reduction)
Cell rxn: $Fe^{2+} + Ag^+ \rightleftharpoons Fe^{3+} + Ag(s)$

13. In potentiometry, why is a TISAB added to samples? What does the acronym stand for?
(5)

TISAB = total ionic strength adjustment buffer. It is a concentrated salt solution which is added to samples so that all samples have a high and nearly constant ionic strength. This makes the activity coefficients constant and allows the determination of molar concentrations, rather than activities.

14. What gas is used in a ICP?
(3)

Argon.

Discussion: Give as much detail as possible. Each question is worth 16 points.

15. Sketch a FT-IR based on a Michelson interferometer and discuss how it obtains interferograms and converts them to spectra. What two detectors could be used in this instrument? Include in your discussion the relationship between mirror velocity and modulation frequency of the light. Why are FT-IR's often purged with dry nitrogen? What are the advantages of an FT-IR over the dispersive instrument?

4 points: Correct sketch showing source, collimated beam, interferometer (beam splitter, fixed mirror, moving mirror), sample and detector (DTGS or MCT).

5 points: Operation: A given wavelength periodically undergoes constructive and destructive interference as the moving mirror slides along. Consequently, the intensity of that wavelength oscillates at a frequency given by $f = 2v\lambda^*$ (where λ^* is the corresponding wavenumber). All wavelengths reach the detector simultaneously. The detector signal vs time is the interferogram (sketch). The computer uses the Fast Fourier transform to convert the interferogram to a spectrum of light intensity vs frequency. A blank spectrum must be recorded first and stored in computer memory. Then the sample is run and the computer uses both spectra to calculate the desired spectrum.

3 points: Because the FT-IR is inherently single beam in operation, changes in water vapor and carbon dioxide vapor concentration between the blank and sample causes the H_2O and CO_2 bands to show up in the final spectrum. Purging the FT-IR with dry nitrogen eliminates these vapors.

4 points: The advantages are: Fellgett's advantage (all wavelengths measured simultaneously);

Jacquinot's advantage (high throughput); constant effective bandwidth over the entire spectrum, high precision in peak positions, and absence of stray light problems.

16. Sketch a graphite furnace and discuss how it works. Describe the temperature program of a graphite furnace and what happens at each temperature. Sketch a block diagram of an atomic absorption spectrometer which contains the graphite furnace. Sketch the hollow cathode lamp and discuss how it works. What is the role of the chopper and the monochromator?

4 points: The sketch should show the graphite tube with electrical leads to a power supply. The tube is in a box purged with argon. Light passes through two windows and down the axis of the tube. Samples are introduced through a hole in the box and the top of the graphite tube.

4 points: A sketch of the temperature program is helpful. The sample, a solution with a volume of 10-100 μL, is injected into the tube. The tube is heated to 100 C for a minute to dry the sample. The tube is then heated to 300-500 C for 30 s to ash the sample (break down organics). Then the tube is heated rapidly to 2000-2500 C to vaporize and atomize the sample; absorbance is measured at this point. The tube is heated to 3000 C for a few seconds to clean it and then cooled.

4 points: The block diagram should show the hollow cathode lamp, a chopper, the graphite furnace, the monochromator, and the PMT detector. The chopper alternately sends light through the graphite tube and around it. The chopper helps the instrument to distinguish light from the hollow cathode lamp from the light due to the furnace. The monochromator picks one of the many emission lines from the hollow cathode lamp so that Beer's law is valid, and also protects the PMT from the light emitted by the graphite furnace.

4 points: The sketch of the hollow cathode lamp should show an anode wire and a cathode cup inside a glass chamber filled with argon. The cup is lined with the element to be detected. Roughly 300 V between the anode and cathode sends a stream of electrons through the argon. The argon is ionized to Ar^+. The argon ions blasts the element lining the cathode into the gas phase and excites the elemental atoms. Light is emitted at precisely the wavelengths absorbed by ground state atoms in the vapor phase for that element.