/95

CHEM 212; Fall 2014
Exam 3

Name key

PART 1: Do all questions 1-3.

PART 2: Do 2 of the ~~3~~4 questions. It is essential YOU indicate the problems you want graded. Otherwise, I will grade the first two with writing.

1	2	3	4
2	10	5	9

$[Cu^{2+}] = 0.02M$

$[Cr^{3+}] = 0.07M$

Write CLEARLY and show your work (full points will not be awarded for the correct answers with inadequate work shown).

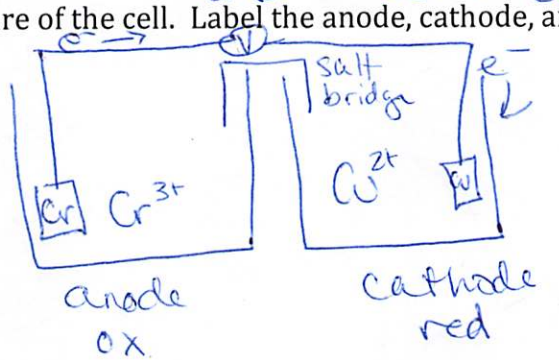
20 2. (~~25~~ pts) Given a voltaic cell made from the following components:

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $E^0 = 0.34$ V

$Cr^{3+} + 3e^- \rightarrow Cr_{(s)}$ $E^0 = -0.74$ V

$Cr_{(s)} \rightleftharpoons 3e^- + Cr^{3+}$ $E^\circ = 0.74V$

a. (3) Draw a picture of the cell. Label the anode, cathode, and the direction of electron flow on the picture.



b. (3) Write the line notation for the cell

$Cr^0 | Cr^{3+} \,||\, Cu^{2+} | Cu^0$

c. (2) Write each of the balanced half reactions in the appropriate direction with E°.

$3Cu^{2+} + 6e^- \rightleftharpoons 3Cu^0_{(s)}$ $E^\circ = 0.34V$

$2Cr^0_{(s)} \rightleftharpoons 6e^- + 2Cr^{3+}$ $E^\circ = 0.74V$

d. (2) Write the balanced equation and calculate E°_{cell}.

$3Cu^{2+} + 2Cr^0_s \rightleftharpoons 3Cu^0_s + 2Cr^{3+}$ $E^\circ_{cell} = 1.08V$

/10

e. (5) Calculate the cell potential for the following conditions:
~~$[Fe^{2+}] = 0.31M$~~ ~~$[Fe^{3+}] = 0.02M$~~ ~~$[Ce^{3+}] = 0.45M$~~ $[Cr^{2+}] = 0.02\,M$; $[Cr^{3+}] = 0.07\,M$

$$Q = \frac{\text{products}}{\text{reactants}} = \frac{[Cr^{3+}]^2}{[Cr^{2+}]^3}$$

$$E_{cell} = E^\circ - \frac{0.05916V}{n} \log Q$$

$$E_{cell} = 1.08\,V - \frac{0.05916V}{6e^-} \log \underbrace{\frac{(0.07)^2}{(0.02)^3}}_{612.5},\ 8\times10^{-6}$$

$$E_{cell} = 1.08\,V - 0.027$$

$$E_{cell} = 1.05\,V$$

f. (2) What voltage will be produced by this cell at equilibrium?

$E_{cell} = 0V$ at equilibrium, no current flows the battery is dead

g. (3) Calculate the equilibrium constant for this cell.

$$K = 10^{\frac{E^\circ n}{0.5916}} = 10^{\frac{1.08V \cdot 6}{0.05916}} = 10^{109.53}$$

2. (11pts) Draw a Jablonski Diagram. Label absorption, fluorescence, phosphorescence, nonradiative decay, internal conversion and intersystem crossing.

See figure 17-15

shape 4 inc S_0, S_1, T_1
terms 6
freebie 1

$$\nu = \frac{c}{\lambda} = \frac{3\times10^{8}\ m/s}{560\times10^{-9}\ m} = 5.35\times10^{14}\ /s$$

a. (3 pts) Calculate the energy and frequency of a 560 nm photon.

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.63\times10^{-34}\ J\cdot s \cdot 3\times10^{8}\ m/s}{560\times10^{-9}\ m} = 3.55\times10^{-19}\ J$$

$E = 3.55\times10^{-19}$ J

c. (3 pts) Why does fluorescence occur at lower wavelengths than the absorbed excitation energy?

because of energy loss due to nonradiative decay

d. (3 pts) Consider a UV-Vis absorption experiment. If A=2, what is T? If $\varepsilon = 3\times10^{4}$ $cm^{-1}M^{-1}$, what is the concentration of analyte in the solution?

$b = 1$ cm

$A = -\log T$

$T = 0.01$

$\%T = 1\%$

$A = \varepsilon b c$

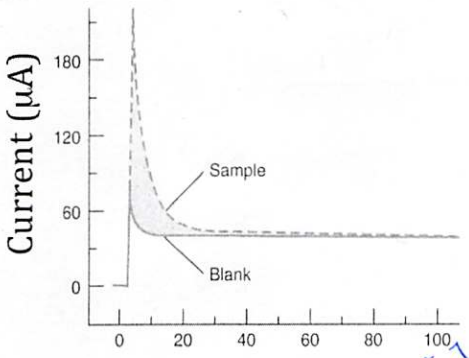
$c = \frac{A}{\varepsilon b} = \frac{2}{3\times10^{4}\cdot 1} = 6.7\times10^{-5}\ M$

/20

SA: 2pt ea 10 pts 1 freebie

fill in: 1pt ea 4pts

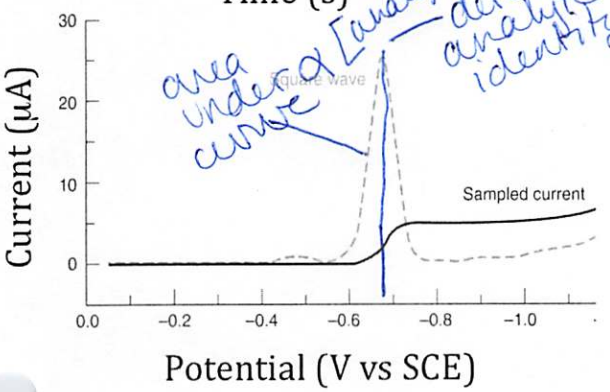
3. (15 pts,) Consider the following images and associated techniques.



Technique: Constant voltage coulometry

What is the technique used for?

determining the concentration of analyte in solution using ~~during~~ a titration

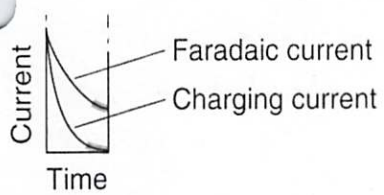


area under curve ∝ [analyte] determine analyte identity

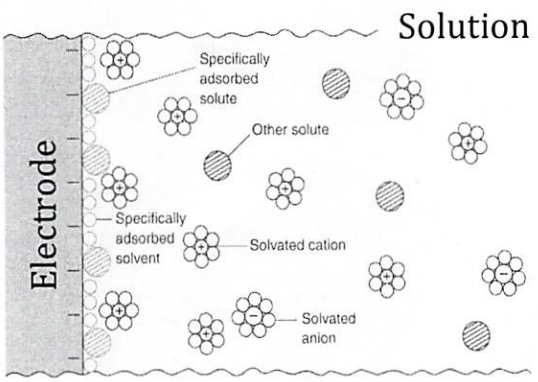
These techniques are exampled of what general type of electrochemistry: voltametry

What are these types of techniques generally used for?

determining the concentration of analyte(s) in solution.



In a measurement, the faradaic current is proportional to the concentration of analyte in solution. The charging current is generated by the phenomena shown in the figure below and is the reason that there is a pause before measuring current in this kind of experiment.



Phenomena: electric double layer

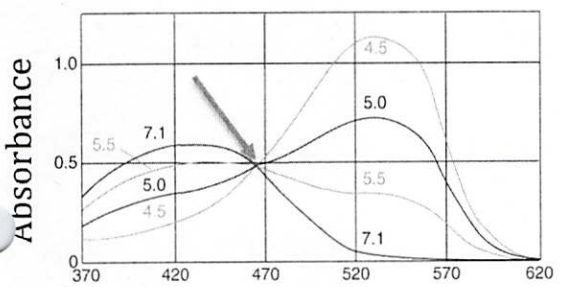
Why does a charging current develop?

diffusion of analyte to electrode surface is slower than the rxn at the electrode surface.

∴ solution @ electrode ≠ bulk soln

Why does the charging current decay faster than the faradaic current?

diffusion is a fast process



What term describes the point on the figure indicated by the arrow? isobestic point

What is this type of analysis used for?

determining the relative amounts of each species in a 2 component mixture

--PART 2—

Do 2 of the following 4 questions. It is essential YOU indicate on the first page of the exam the problems you want graded. Otherwise, I will grade the first two with writing.

4. (20 pts) Consider an electrochemical cell:

2 a. What is the purpose of the indicator electrode?

to measure the potential in an a. solution of interest.

2 b. What are two of the most common materials for inert electrodes to be made from?

C, Pt, Au

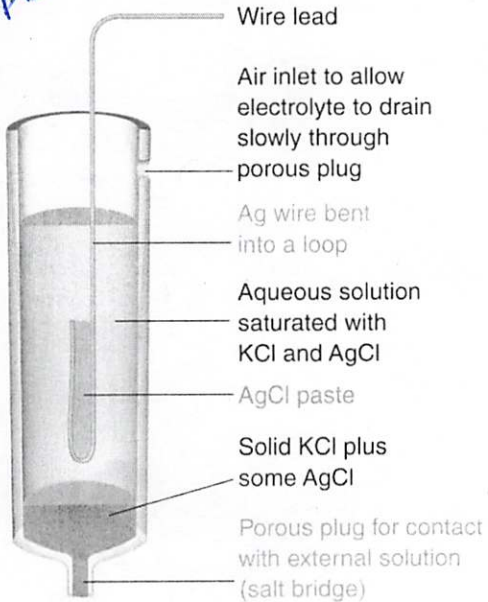
2 c. What is the purpose of a reference electrode?

to maintain a constant potential

d. Describe how an Ag-AgCl reference electrode works with reference to the figure below

14 pts

See text pg 310



5. Consider the following instrument components.

a. (10 pts) Diagram and label a monochromator. Briefly state the function of each component in the diagram.

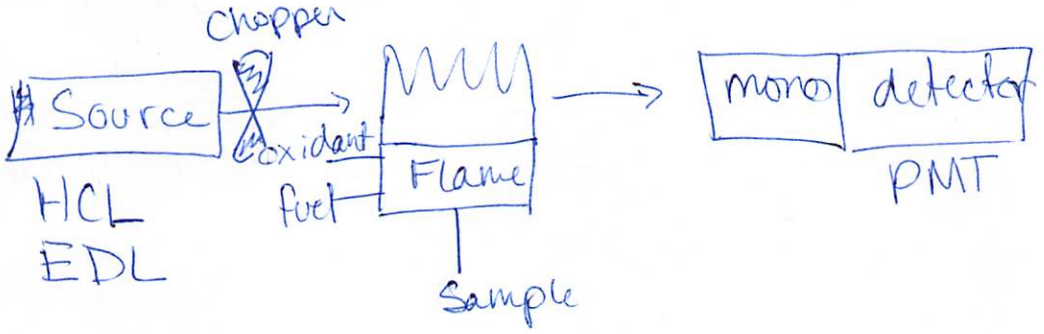
See spectroscopy worksheet

b. (10 pts) Diagram and label a PMT. Briefly state the function of each component in the diagram.

See spectroscopy worksheet

6. (20 pts) Consider the suite of atomic spectrometers

a. (12 pts) Draw a box diagram and label a flame Atomic Absorption Spectrophotometer. Briefly explain the role of each component. Suggest what components might be (e.g., detector= PMT) if these were featured in class or videos.



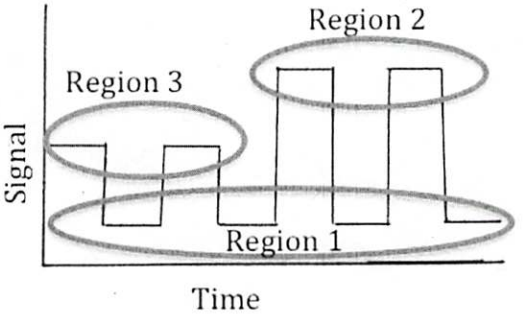
geometry 5
labels 5
HCL & PMT 2

b. (3 pts) What is the purpose of a monochromator in a Flame AA instrument?

to reduce stray light contributed by the flame

c. (2 pts) Consider the output signal of a Flame AA. What component of the instrument gives rise to the square wave shape?

the chopper



d. (3 pts) Explain the signal contributing to the signal in each region.

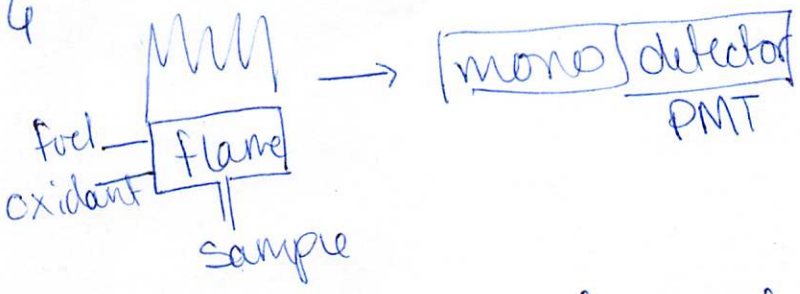
Region 1: flame only

Region 2: blank solution + HCL + flame

Region 3: sample + HCL + flame

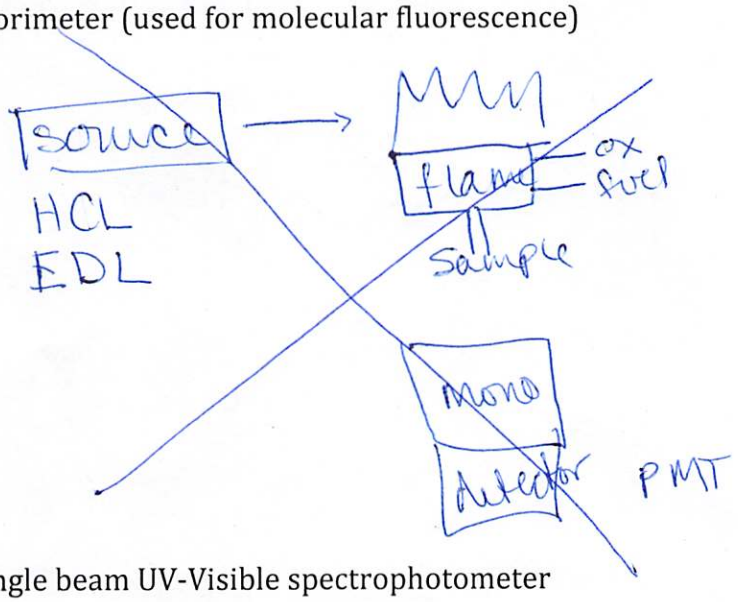
7. (20 pts) Diagram and label the following instruments. Briefly explain the role of each component. Suggest what components might be (e.g., detector= PMT) if these were featured in class or videos.

a. Atomic emission spectrophotometer



flame fuel - generally acetylene
oxidant - generally air

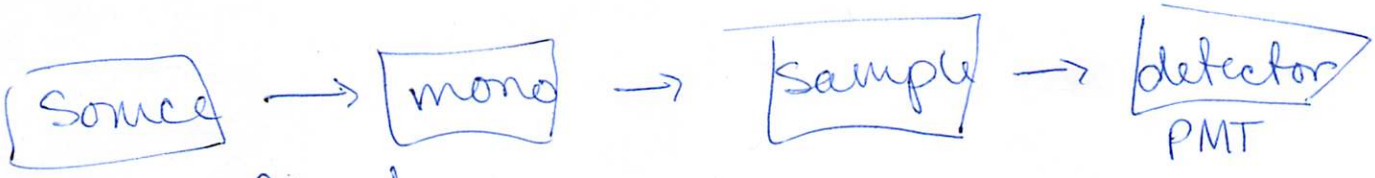
b. Florimeter (used for molecular fluorescence)



source → tungsten filament deuterium arc

excitation mono – sample → emission mono → detector PMT

c. Single beam UV-Visible spectrophotometer



tungsten filament
deuterium arc