Exam 2 – Chem 454 – March 7, 2018

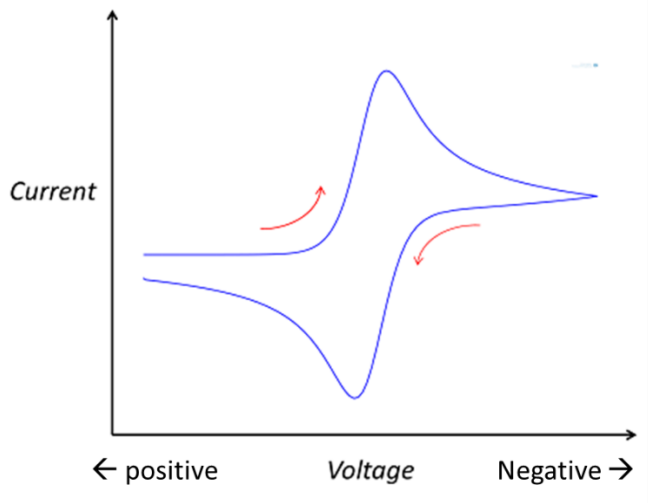
1. Describe why voltammetric cells require 3 electrodes. What are those 3 electrodes called and what purpose does each fill? A diagram may help in you explanation (10 points). [1]
2. Why is the hydrogen evolution reaction (HER) such a bothersome phenomenon in anodic stripping voltammetry (ASV)? Discuss the specific example of iron analysis. In your discussion consider the following half reactions.(10 points) [2]

   $2H^+ + 2e^- = H_2(g)$ $\quad E^0 = 0.00$ V

   $2Fe^{2+} + 2e^- = Fe(s)$ $\quad E^0 = -0.44$ V

3. A solution of unknown Pb^{2+} concentration gave an ASV signal of 35.0µA. A spike of standardized Pb^{2+} increased that concentration by 6.0 µM and gave an ASV signal of 70.0 µA. What is the concentration of Pb^{2+} in the sample? (10 points) [3]
4. (10 points) Label the major features of the following cyclic voltammogram. Assume that it is for

   $A + e^- \rightarrow A^-$



Include the following features. [4]

   a) faradaic current
   b) capacitive current
   c) anodic peak current for $A^- \rightarrow A + e^-$
   d) cathodic peak current for $A + e^- \rightarrow A^-$
   e) approximate E^0

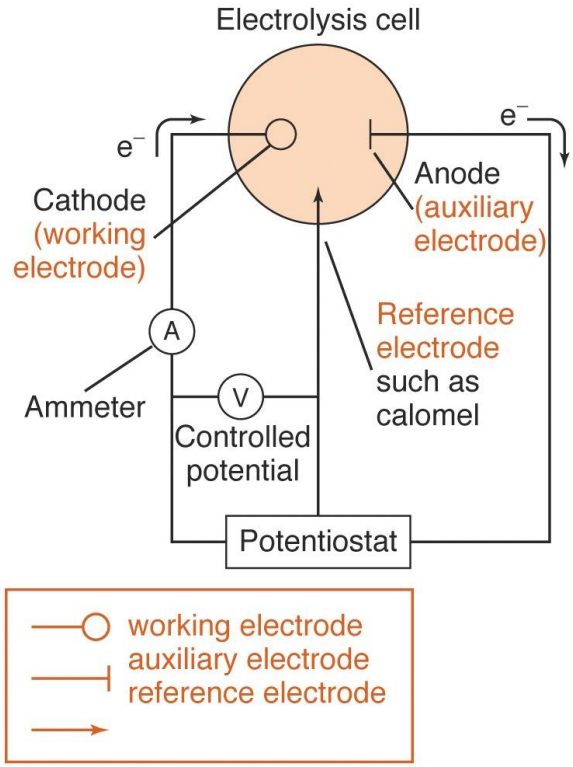
5. Sketch a Jablonski diagram illustrating the following: (20 points) [5]
   a. Absorption
   b. Internal Conversion
   c. Intersystem crossing
   d. Vibrational Relaxation
   e. Fluorescence
   f. External Conversion
   g. Internal Conversion

h. Phosphorescence
i. Label which states are singlet and which are triplet.
j. Label which radiationless relaxations.

6. What are flicker, 60 Hz, and shot noises, how does appear in a power density vs. frequency spectrum. (10 points) [6]
7. UV analysis of an analyte yielded an absorption signal of 0.115 for a 10.0 mL sample. A spike of 1.00 mL of 0.112 mM added to that sample yielded an absorption of 0.202. What is the concentration of the analyte in the sample? (10 points) [7]

---

[1]



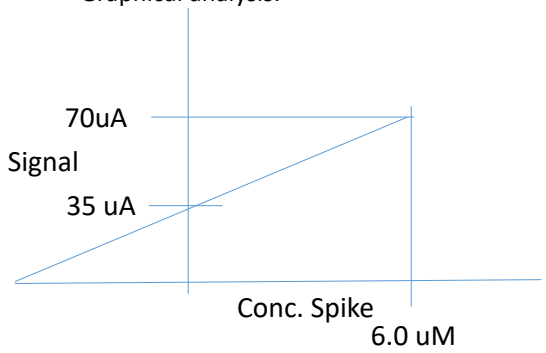
(1) Working electrode – where the current is measure. Held at a specific potential relative to a (2) chemical reference electrode, e.g. Ag/AgCl or SCE. The (3) counter electrode allows for a current flow across the working electrode. It is same magnitude but opposite in flow of the working electrode.

[2] ASV requires electrochemical deposition of metal on a conductive substrate. For iron that requires a potential more negative than -0.44 V, probably -0.8 V from a practical standpoint. This results in vigorous HER giving gas bubbles that may delaminate the Fe metal deposits from the conductive substrate. Next as that deposition stops and the scan moves to more positive potentials the HER will persist and interfere with the ASV signal for Fe.

At the accumulation step: $2H^+ + 2e^- = H_2(g)$ & $2Fe^{2+} + 2e^- = Fe(s)$
At the ASV step (positive of -0.44 V): $2H^+ + 2e^- = H_2(g)$ & $Fe(s) = 2Fe^{2+} + 2e^-$

The 2 currents in the ASV will interfere reducing the signal of $Fe(s) = 2Fe^{2+} + 2e^-$

3 Graphical analysis:

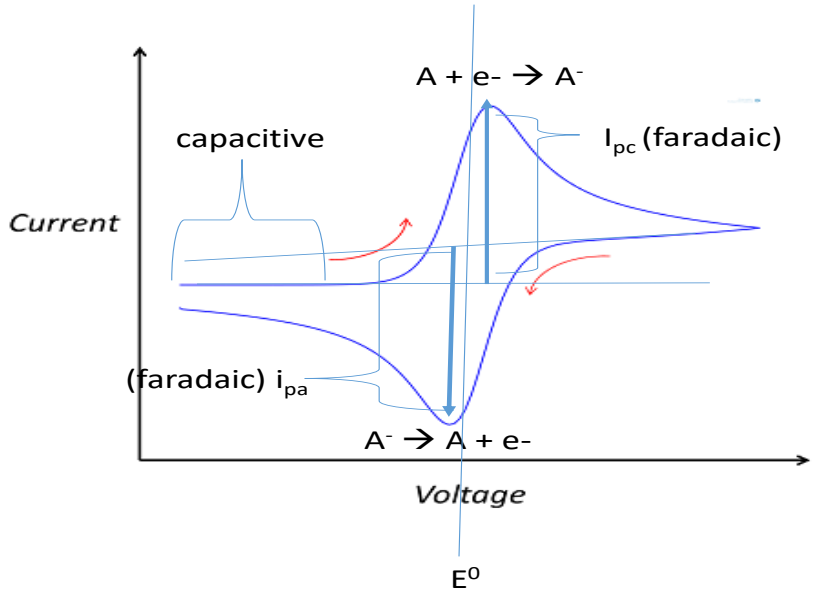


slope = (70 – 35)uA / 6.0 uM = 5.83 y-int = 35 uA

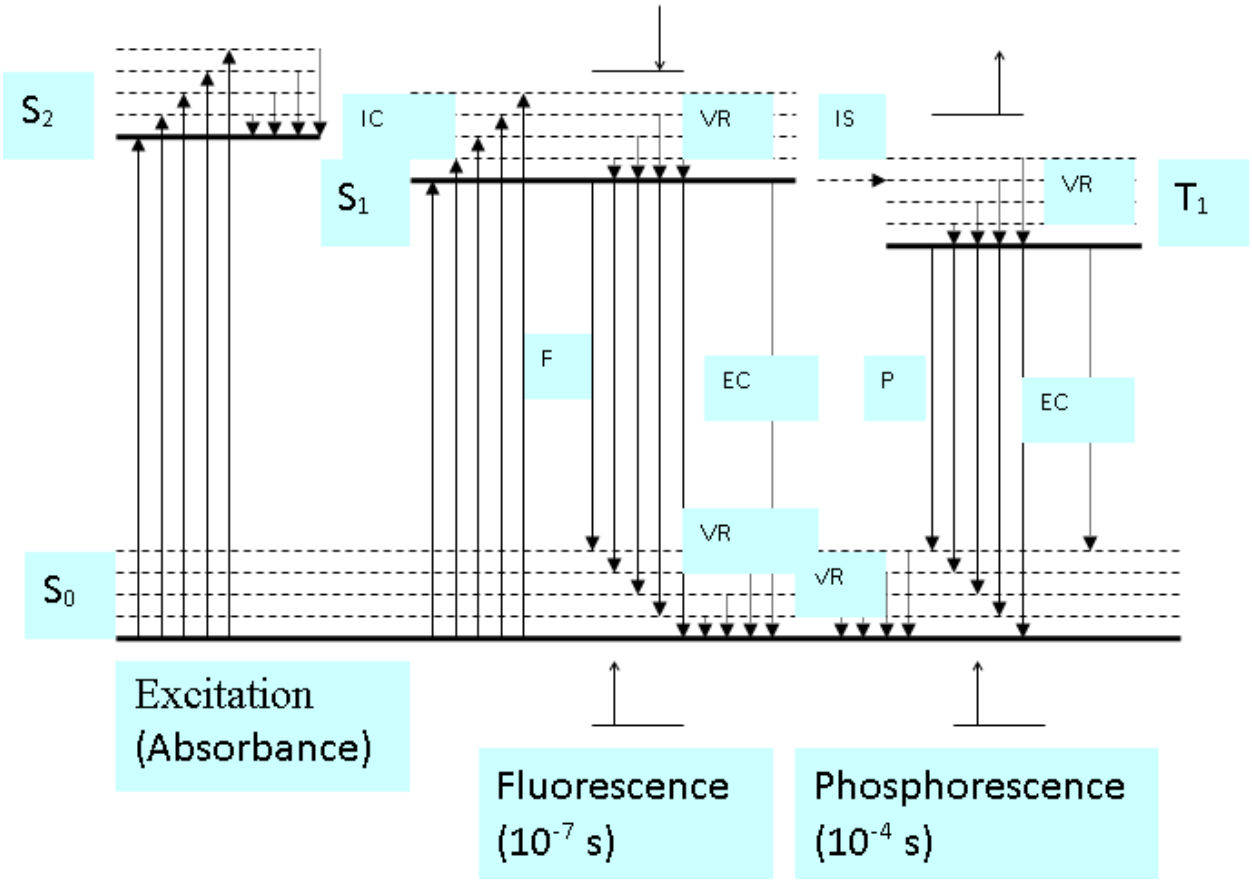
line: y = mx + b y = 5.83 (x) + 35 find x-int

0 = 5.83 (x) + 35 x = - 6.00 uM

4



[5]

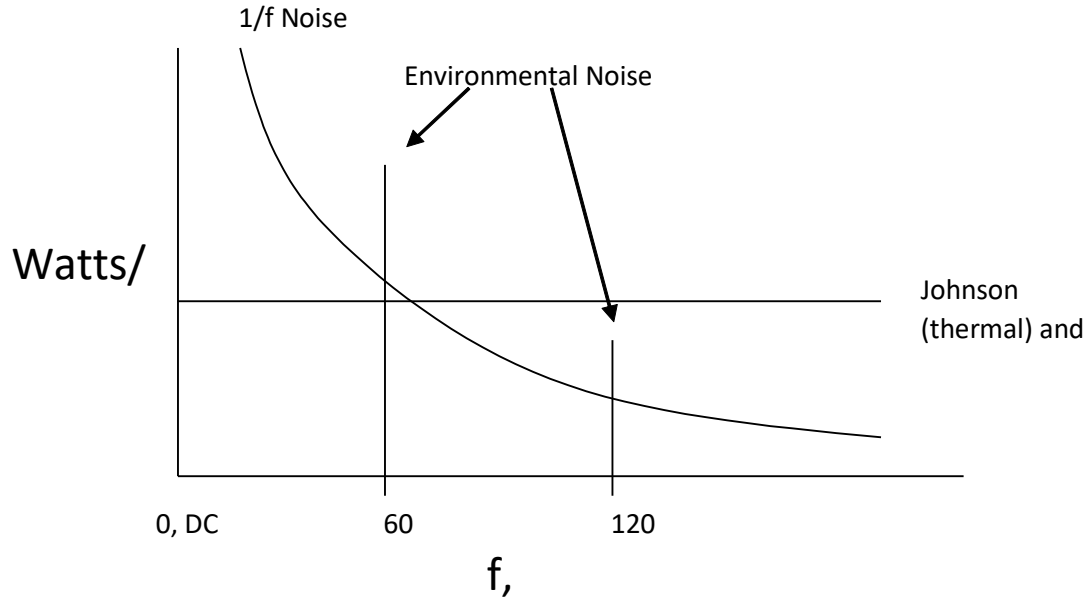


Radiationless – VR and EC

[6] *Flicker – Is low frequency noise whose origins are not clearly understood.*

Shot Noise - Arises from the statistical flucuations across electrical junctions, e.g N-P juction of a transistor. It occurs at all frequencies.

60 Hz – Is a form of environmental noise that comes from AC wiring.



7 We know that A α C Therefore: $A_1/A_2 = C_1/C_2$

let x = conc analyte in mM

conc in spiked sample = (1/11)*0.112 + (10/11)*x

0.115/0.202 = x/((1*0.112/11) + (10*x/11))

0.569 = x / (0.0102) + 0.909 x

0.517 x + 0.00580 = x

0.00580 = 0.483 x

x = 0.0121 mM