CHEM 3390 Final 2015 ANSWERS.

1. acceptable:
a, (b), c, e → (although IR maybe a problem with –OH groups)

2. $Cl^- : \frac{1}{35}$ $F^- : \frac{1}{19}$ $SO_4^{2-} = \frac{2}{96} = \frac{1}{48}$ $ClO_4^- = \frac{1}{99}$

$\ominus$ $ClO_4^{\ominus}$ $SO_4^{(2-)}$ $Cl^{\ominus}$ $F^{\ominus}$ $\oplus$

(4) EOF (3) (2) (1)

answer is (C).

3 d

5 $2Na^+ + 2e \rightarrow 2Na(s)$ $E^\circ = -2.71$

$ClO_4^- + 2e + H_2O \rightarrow ClO_3^- + 2OH^-$ $E^\circ = 0.17$

$E^\circ = -2.71 - 0.17 = -2.88$ V (e)

6 $\text{slope} = \frac{-0.0562 + 0.0795}{\log(0.15) - \log(601)} = \frac{0.0233}{1.176} = 0.0198 \cong \frac{0.0592}{3}$

$\Rightarrow n = 3$, either Al^{3+} or Fe^{3+}

for Al^{3+}, $E^\circ = -1.66 - 0.244 = \sim -0.4$
for Fe^{3+}, $E^\circ = -0.04 - 0 = -0.04$

(d) measurements are in the range of the Fe^{3+} system.

12 (C)

13 $t = 5\,min$ moles $= 0.250\,L \times 8\times10^{-6}\,M$

$= 2\times10^{-6}$ mole

$i = \frac{Q}{t} = \frac{2\times10^{-6}\,mole \times 96368\,C/mole}{5\times60\,s} = 6.42\times10^{-4}\,A.$

$= 642\times10^{-6}\,A,$

or 642 μA. (C)

14 (C)

15 (b) (C also accepted).

16 a) pH 3: $\log \alpha_2 = -11$, $\alpha_2 = 10^{-11}$

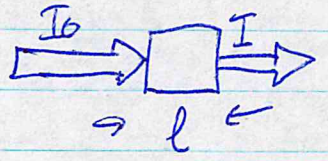
$[Ca^{2+}] = \sqrt{\frac{K_{sp}}{\alpha_2}} = \sqrt{\frac{5\times10^{-9}}{10^{-11}}} = \sqrt{5\times10^{2}} = 22.4\,M$

does not make much sense!

b) $SHE \| [Ca^{2+}] = x\,M | Ca(s)$

$E^0 = -2.76\,V$ for $Ca^{2+} + 2e \rightarrow Ca(s)$

17 a) • UV-vis: absorbance experiments $A = \varepsilon l c$

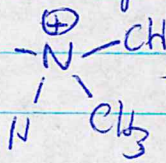


$A = -\log \frac{I}{I_0}$

• fluorescence: λ_{exc} is constant, λ_{em} is scanned to obtained the fluorescence spectrum. At a fixed λ_{exc}, λ_{em} pair, $I_f \propto$ conc.

• OES: light comes from excited atoms and ions in the plasma torch. Based on different λ_{em} for each element,

b) UV-vis: tungsten lamp / xenon lamp
Fluorescence: excitation is also by a tungsten/xe lamp
emission is by the sample at 90°.
OES: Emission of light by the sample.

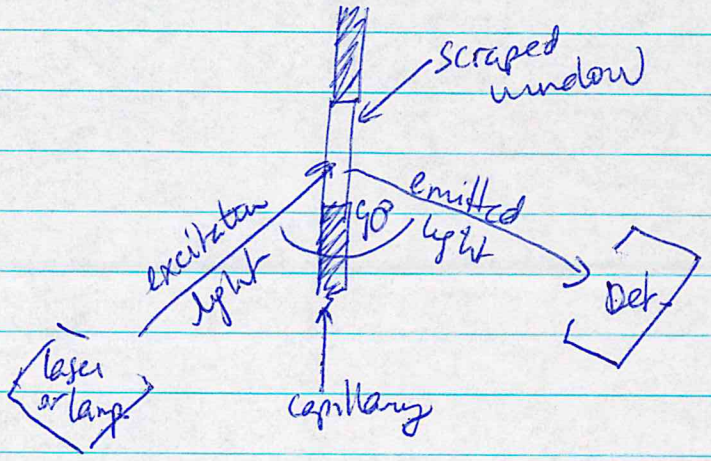
18 a) Charge and mobility would be affected. The amino acids would lose their possibly positive $H_3\overset{\oplus}{N}-$ end, but would gain a  group.

pI would change but maybe not that much.

Larger compounds → less mobility.

Overall migration times would be a bit larger.

b)



21 Tyr pI 5.66, Lys pI 9.74

↑ less basic, less ⊕ ↑ more basic, more ⊕

Cation exchange: Lys retained more
Anion " : Tyr retained more
CE, ⊕ → ⊖ : Lys would move faster.

22

a) Seems to be DB-1 column, as compounds elute in order of b.p. DB1 is non polar, polymethyl siloxane.

b) Looks like polarity becomes important. Isooctane has no hydroxyl and elutes first, then both polar MeOH and octanol elute in b.p order.
Column maybe DB 5, more polar than @, and polarity + b.p. count.

23

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$ $\quad K_{sp} = [Al^{3+}][OH^-]^3$

$Al(OH)_3 + 3e^- \rightarrow Al(s) + 3OH^-$ $\quad E^0 = ?$

$Al^{3+} + 3e^- \rightarrow Al(s)$ $\quad E^0 = -1.66\ V$

At equilibrium,

$$0 = E^0_? + 1.66 - \frac{0.0592}{3} \log [OH^-]^3 + \frac{0.0592}{3} \log \frac{1}{[Al^{3+}]}$$

$$0 = E^0_? + 1.66 - \frac{0.0592}{3} \log \underbrace{[OH^-]^3 [Al^{3+}]}_{K_{sp}}$$

$$E^0_? = -1.66 + \frac{0.0592}{3} \log 1.8 \times 10^{-33} = -2.31\ V$$

24

With all ^{13}C, the MW would be 138 instead of 128 for the normal molecule.

Method 1: ^{13}C Naphth. Could be used as internal standard in GC/MS analysis. Retention time would be slightly different and peak areas could be compared.

24 Cont'd

Method 2: One could do direct MS (without prior separation) by spiking a mixture of PAH with this standard, and by directly comparing peak areas at m/z 128 and 138.

25 Cu^{2+} is easiest reduced → the best oxidizing agent.
Ba^{2+} is the best reducing agent.

e.g. if we had the

$$Cu^{2+} + Ba(s) \rightarrow Cu(s) + Ba^{2+}, \text{ reaction}$$

it would be spontaneous as

$$E^{\circ}_{Cu^{2+}} - E^{\circ}_{Ba^{2+}} = \sim -0.1 - (-2.0) = +1.9V$$