CHEN 3590 final - 2017 - answers

1. $[M^{2+}] = \sqrt{\frac{K_{sp}}{\alpha_2}} = 5 \times 10^{-3}$ M.

at pH 8 on graph, $\log \alpha_2 \simeq -2.2 \Rightarrow \alpha_2 = 10^{-2.2} = 6.3 \times 10^{-3}$

$K_{sp} = \alpha_2 [M^{2+}]^2 = 6.3 \times 10^{-3} \times (5 \times 10^{-3})^2$
$= 1.58 \times 10^{-7}$

the closest is MCO_3 (1.3×10^{-7}) (d)

2.

$T = 0.3$ $A = -\log T = -\log(0.3) = 0.52$

On the graph, $A = 0.52$ corresponds to 4.25 mg/L (b)

3. (a) argon of higher quality, fewer impurities, less background noise $\Rightarrow$ better sensitivity.

4 (b)

5 (c)

6 Aniline: aromatic base pka > 7 (9.4) ⊕ at pH 7
ASA, organic acid, pka < 7 (2.7) ⊖ at pH 7
acetone: organic molecule, no pka. neutral
phenylalanine: zwitterionic compound (pI 5.91) ⊕ at pH 7

6 cont'd

The most basic compound is Aniline, will be the most positive at pH 7
followed by Phenylalanine
Acetone (neutral)
ASA (negative)

⇒ for cation exchange at pH 7: retention order is

ASA, acetone, Phe, Aniline
↑ least retained ↑ most retained,

8 (b)

11 $E^\circ = E^\circ_{Ag^+/Ag} - E^\circ_{Zn^{2+}/Zn} = 0.80\,V - (-0.76\,V)$

$= +1.56\,V$ (a)

12 (b)

13 $E_x - 0.199\,V = E_{cell} = E^\circ_x - 0.199V + \frac{0.0592}{n}[M^{n+}]$

$\text{Slope} = \frac{0.138 - 0.12}{0 - (-0.6)} = \frac{0.018}{0.6} = 0.03 \simeq \frac{0.0592}{2}$

$\Rightarrow n = 2$

$0.13 = E^\circ_{M^{2+}} - 0.199$

↑ one of the measurements

$E^\circ_{M^{2+}} \simeq 0.33\,V$ → corresponds the best to Cu^{2+}.

13 cont'd $Cu^{2+} + 2e \rightarrow Cu(s)$: $E^\circ = 0.34V$
$Fe^{2+} + 2e \rightarrow Fe(s)$: $E^\circ = -0.41$
$Ca^{2+} + 2e \rightarrow Ca(s)$: $E^\circ = -2.76V$

$\Rightarrow$ Only Cu^{2+} is suitable. (d)

14 (e)

15 (a) end of multiple choice questions.

16 for each element, the closer an electron to the nucleus, the higher the binding energy.
for In for example, 3p > 3d > 4d
As : 2p > 3p > 3d.

If we compare the same orbital between two elements, O 1s, and C 1s, the larger nucleus attracts more force on 1s electrons and binding energy is higher for O 1s.

Comparison of In 3p and As 3p also leads to the same conclusion:
In (↑ 49) As (↑ 33)

binding energy is higher for larger Z In > As.

17 C_2 = final concentrations

$C_{2A} = 20 \mu g/mL$ $C_{2B} = 10 \mu g/mL$ $C_{2C} = 5 \mu g/mL$

C_1 = original conc.

17 cont'd.

$C_{1A} = 1\ mg/mL \quad C_{1B} = 1\ mg/mL \quad C_{1C} = 1\ mg/mL$

$V_2 = 2\ mL \quad (A, B, C)$

$$V_{1A} = \frac{C_{2A} V_{2A}}{C_{1A}} \qquad V_{1B} = \frac{C_{2B} V_{2B}}{C_{1B}} \qquad V_{1C} = \frac{C_{2C} V_{2C}}{C_{1C}}$$

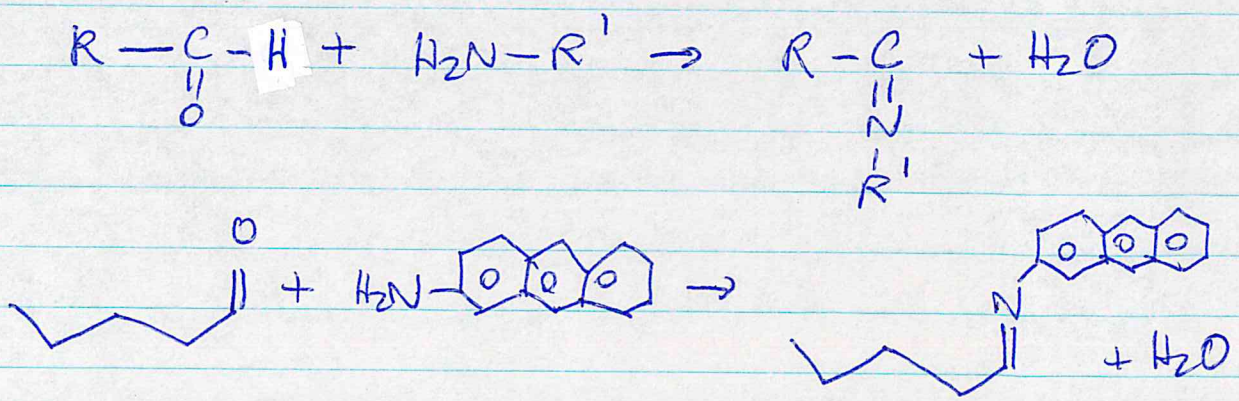
$$V_{1A} = \frac{20\ \mu g/mL \times 2\ mL}{1000\ \mu g/mL} = 0.04\ mL = 40\ \mu L$$

$$V_{1B} = \frac{10\ \mu g/mL \times 2\ mL}{1000\ \mu g/mL} = 0.02\ mL = 20\ \mu L$$

$$V_{1C} = \frac{5\ \mu g/mL \times 2\ mL}{1000\ \mu g/mL} = 0.01\ mL = 10\ \mu L$$

↑ these volumes are reasonable for pipettes.

19 a) formation of a Schiff base:



19 cont'd.

b) labelling with 2-aminoanthracene would give a lot more hydrophobicity to the aldehydes.

In normal phase HPLC, they would come out with a non polar solvent, better if aromatic, e.g. toluene.

c) all compounds will be detected at the same λ_{exc}, λ_{em} and fluorescence intensity will be directly proportional to concentration.

20 $3ClO_3^- \rightarrow 3ClO_4^-$

↓ oxidation

$2NO_3 \rightarrow 2NO$ reduction

real reactions from table:

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

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \quad E^\circ = 0.90$

$E^\circ = 0.90 - 0.17 = 0.73\ V.$

21 a) polystyrene, PVC, polyethylene and copolymers of all three types.

b) clean up injector with solvent, and cut top off column to remove polymer deposit.

c) Reversed phase HPLC VC (most polar), ethylene, styrene (styrene is more hydrophobic than ethylene).

23 Hydrodynamic injection, 2 modes.

i) by pressure; sample is injected by pressure at one end of capillary

ii) by siphoning: Injection end of capillary is higher, then sample solution is sucked in by gravity.

Electrokinetic injection:

A high voltage is applied (higher than normal separation voltage) and mobile analytes are moved into the capillary by electrophoretic motion.

24 first let's look at different reduction potentials:

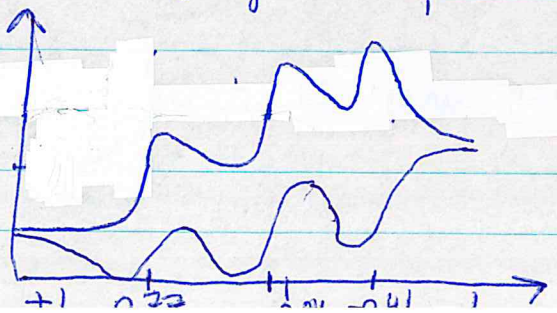
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^0 = 0.77\ V$

$Fe^{2+} + 2e^- \rightarrow Fe(s)$ $E^0 = -0.41\ V$

$Fe^{3+} + 3e^- \rightarrow Fe(s)$ $E^0 = -0.04\ V$

Range of potentials covered is +1 to -1

If the original solution contains Fe^{3+} and Fe^{2+},
The first reduction will occur at 0.77 V, and most Fe^{3+} will turn into Fe^{2+}.
Then at −0.04V, any remaining Fe^{3+} will turn solid.
at −0.41V, Fe^{2+} (original + from 1st reaction) will turn solid.



Reversible? depends if solid is on the electrode or fell off.