CHEM 3590

fall 2018

Final examination

Answers

1. a) 10ppm Cu = 10 mg/L of Cu in solution

Total sample: 100 mg

Total volume: 25 mL

Amount of Cu in solution: $10 mg/L \times 0.025 L = 0.25 mg$

$$\% Cu = \frac{0.25 mg}{100 mg} \times 100\% = 0.25\%$$

b) • From literature values, check for emission lines of potential contaminants at other λ values..

• Or do a standard additive curve of the sample to a water blank, and see if the curve goes through zero, if not there is an interference

interference ←
no interference ←

interference ↑

volume of sample added
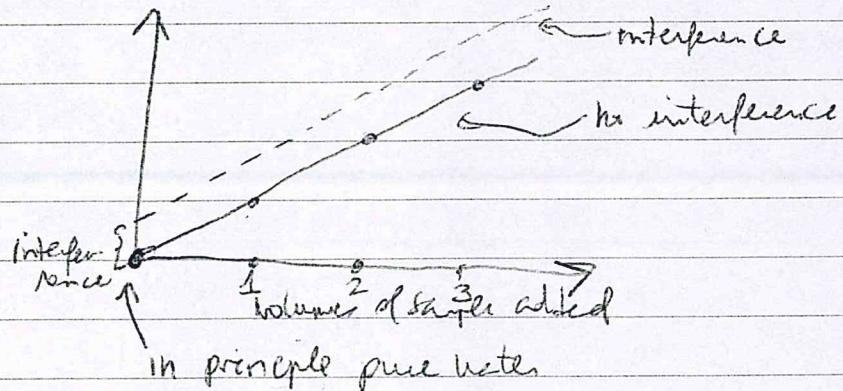
in principle pure water
sample should not emit at λ_{Cu} if there is no interference

2. $AgCl + e^- \rightarrow Ag + Cl^-$ $\quad E^0 = 0.199 V$ cathode
(flip) $Ag^+ + e^- \rightarrow Ag$ $\quad E^0 = 0.80 V$ anode
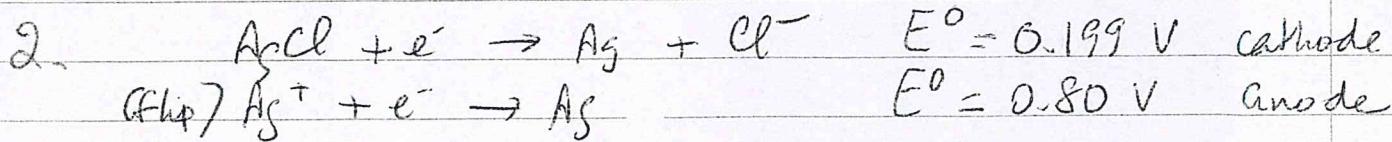
$E_{cath} - E_{an} = 0 = 0.199 - 0.0592 \log [Cl^-] - 0.80 + 0.0592 \log \frac{1}{[Ag^+]}$
$= 0.199 - 0.80 - 0.0592 \log k_{sp}$

$$0 = 0.199 - 0.80 - 0.0592 \log k_{sp}$$

$$\log k_{sp} = \frac{0.199 - 0.80}{0.0592} \implies k_{sp} = 7.05 \times 10^{-11}$$

3. a) pH 4.5   the only $\ominus$ species present is $H_2AsO_4^-$

$$C_T = [H_2AsO_4^-]$$

pH 9.2 $$C_T = [HAsO_4^{2-}]$$ } mass balance

Charge balance at pH 4.5

$$[H_3O^+] = [H_2AsO_4^-] + [Cl^-] + [OH^-]$$

   ↑
   if HCl is used to acidify

at pH 9.2

$$[H_3O^+] + [Na^+] = 2[HAsO_4^{2-}] + [OH^-]$$

   ↑
   if NaOH is
   used to increase the pH

b) Arsenic acid is V and more ionizable than As III. This makes As easier to capture on membrane devices in the water purification procedure.

4- a) a plausible reaction could be : $Ce^{4+} + e \rightarrow Ce^{3+}$

$$E^0 = 1.44 V$$
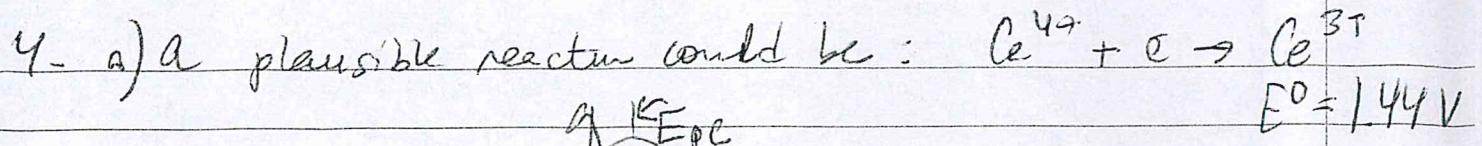
b)
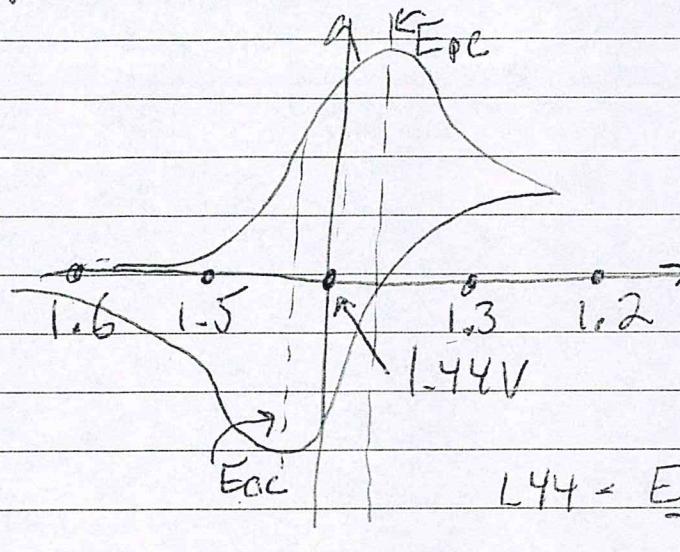
$$1.44 = \frac{E_{pc} + E_{ac}}{2}$$

c) • we can plot a calibration curve, i_{pc} vs conc, and determine the conc. of an unknown.
• we can tell if the reaction is reversible, ie. if the whole material gets oxidized after reduction.
  if $i_{pc} = i_{pa}$, it is reversible.

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	C_2	C_1		V_2	V_1
x	20 µg/mL	50 µg/mL		2 mL	0.8 mL
y	0.1 mg/L	100 mg/100mL = 1 mg/mL		2 mL	0.2 mL
z	0.2 mg/L	100 mg/100mL = 1 mg/mL		2 mL	0.4 mL

x : pipet 0.8 mL (or 800 µL) using the 100-1000 µL pipet
y : pipet 0.2 mL (or 200 µL) using the 20-200 µL pipet
z : pipet 0.4 mL (or 400 µL) using the 100-1000 µL pipet

total volume 1.4 mL, complet to 2 mL by adding 600 µL with the 100-1000 µL pipet.

6. As volumes increase, total signals must be multiplied by dilution factors to provide for linear relationship (graph given is not linear)

So the table becomes

Vol standard added (mL)	Conc. std* ppm	Signal Cd
0	0	11.5 (×1)
1	1	13.79 (×1.1)
2	2	16.09 (×1.2)
3	3	18.40 (×1.3)
4	4	20.69 (×1.4)

*e.g. for $\dfrac{4mL \times 10ppm}{10\,mL} = 4\,ppm$ → these are also corrected with dil. factor.

$$Slope = \dfrac{20.69 - 11.5}{4 - 0} = 2.30$$
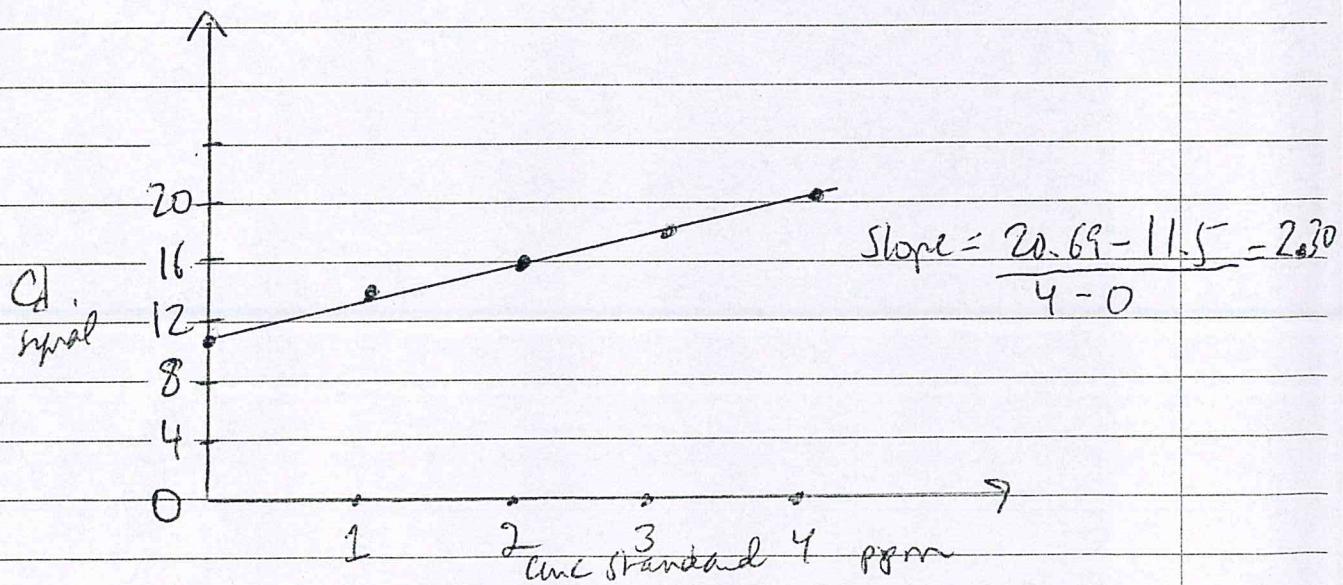
The graph equation becomes:

→ $Cd_{signal} = slope\,(Conc\,Cd)_{std} + 11.5$

at intercept:

$0 = slope\,(-\,conc\,unk) + 11.5$

$= 2.30\,(x) + 11.5$

$\boxed{Conc = 5\,ppm}$

$x = -\dfrac{11.5}{} = -5\,ppm$

7.   a) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
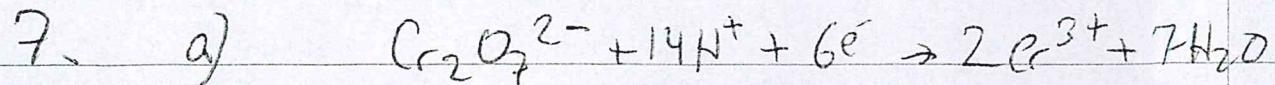
stays in the same direction.

$2Br^- \rightarrow Br_2 + 2e^-$ was reversed
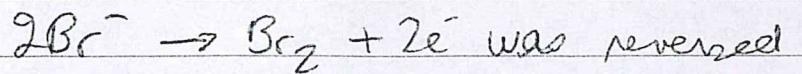
so that $E_{0cell} = 1.49 - 1.07 = 0.42 \, V$

with balancing : make up for $6e^-$

$Cr_2O_7^{2-} + 14H^+ + \cancel{6e^-} \rightarrow 2Cr^{3+} + 7H_2O$
$6Br^- \longrightarrow 3Br_2 + \cancel{6e^-}$

$Cr_2O_7^{2-} + 14H^+ + 6Br^- \rightarrow 2Cr^{3+} + 3Br_2 + 7H_2O.$
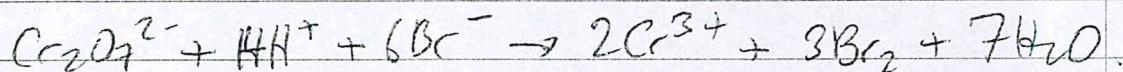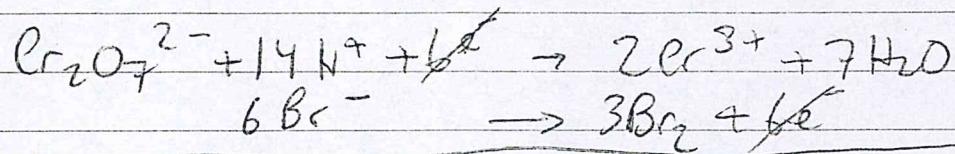
b) the reaction would keep on going until the concentrations attain equilibrium values.

$$k_{eq} = \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}[Br^-]^6}$$

or when $E_{cath} - E_{an} = 0$ (no more current passes).

8. q : charge of the ion
      f : friction coefficient of analyte
      μ_{ep} : electrophoretic mobility
      η : viscosity of separation medium
      r : effective radius of analyte molecules.

effects. It is reasonable to assume that the more friction (f), the lower the velocity is.

In turn, f is proportional to η, and r.

$\Rightarrow$ The more viscous and the larger the molecules, the slower they are

However charge (q) has the opposite effect, as the higher q, the higher the velocity.

This is why $v_{ep} \propto \dfrac{z}{m}$ (charge/mass)

9. a) The chromatograms indicate that molecules elute ~30s though the fluorescence detector earlier than through the MS.

In 30s, the volume eluted is $\dfrac{1 \, ml}{min} \times 0.5 \, min = 0.5 \, ml$

The radius of the tube is 0.5mm or 0.05 cm.

If $0.5 \, cm^3 = \pi (0.05 cm)^2 L$,

$$L = \dfrac{0.5 \, cm^3}{\pi (0.05)^2} = 64 \, cm$$

b) In fluorescence, as all amino acids are derivatized with dansyl chloride, signals are proportional to conc. In MS, different amino acids have different ionization efficiencies, so one cannot compare signals directly.

10. a) lysine pI 9.74   negative above pH 9.74
ethylene diam pka = 10.7   neutral above pH 10.7
pyridine   pka = 8.75   neutral above pH 8.75
propylamine   pka = 10.67   neutral above pH 10.67

pH 8.75 is the threshold value. Under that pH all molecules are ⊕ charged.

b) If we work at say, pH = 8, the most ⊕ charged is the most basic = ethylene diamine.

least ⊕ charged is pyridine.

Elution order: pyridine, lysine, propylamine, ethylene diamine.

c) Yes, at high pH silanols are $\boxed{}$tonated, giving the possibility of formation of a layer of cations adjacent to the $SiO\Theta$ wall. These are attracted to the cathode at the detection end, causing EOF

11. a) These detectors are made of a system of 2 electrodes, one made of radioactive Ni, undergoing a steady current of β (electrons) emission. These ē are captu$\boxed{}$ at the other electrode, which establishes a current between the two electrodes.
When analytes go through and capture these electrons, the current is interrupted and a signal is obtained.

b) There would be too much friction and solvent movement to allow efficient electron capture, if this were to be done in the liquid phase. Also, a steady current b/w the electrodes would not be established.

12- a) BE: energy necessary to pull out a core electron from the nucleus.

b) BE $\uparrow$ with $\uparrow$ oxidation number.

A higher oxidation number means fewer electrons felt by the nucleus, therefore more force exerted on each core electron and more energy needed to pull them out.

c) X ray photo electron Spectroscopy.

Solid Sample is bombarded with mono λ X-Rays, and core electrons are pulled out of surface atoms.

The K.E. of these core electrons is used to derive BE's.

$$h\nu = BE + KE + \text{Instrument work fundon.}$$
$$\uparrow$$
$$Xrays$$

K.E. is measured on an electric field sector, as K.E. $\propto$ Electric field.

13. a) $I = \frac{1}{2}\left[(0.01 \times 3^2) + (0.03 \times 1^2)\right] = 0.06 \, M$

activity coefficients can be found for both La^{3+} and Cl^{-} from table at Ionic strenght between 0.05 and $10^{-1} M$.

for $La^{3+} : \gamma \approx 0.23 \Rightarrow a_{La^{3+}} = 0.23 \times 0.01 M = 2.3 \times 10^{-3}$
for $Cl^{-} : \gamma \approx 0.79 \quad a_{Cl^{-}} = 0.79 \times 0.03 M = 2.37 \times 10^{-2}$

b) $\qquad A = \varepsilon l c$

$\qquad\qquad\qquad\uparrow$

$\qquad\qquad$ conc La^{3+}

The effective conc of La^{3+} is 2.3×10^{-3}
The analytical conc is $\qquad$ 0.01 M

$$Error, \% = \frac{0.01 - 2.3 \times 10^{-3}}{2.3 \times 10^{-3}} \times 100\% = 334\%$$

or $error = \frac{0.01 - 2.3 \times 10^{-3}}{0.01} \times 100\% = 77\%$.

$\qquad\qquad\qquad\qquad\qquad$ also accepted.

14. a) Temperature and pressure.
The plasma torch is at several $\times 1000$ K and the interface materials must be resistant to this heat.
Pressure: skimmers are placed at the interface to pump out Ar gas and other plasma components so pressure is reduced for MS.

b) ICP-MS only: there may be interferences from the formation of oxides.

Example: Say we analyse Ca^+ (m/z 40), the CaO^+ compounds has m/z 56, same as Fe^+.

Because light emission is likely to occur at different λ for CaO^+ and Fe^+, the OES detector becomes important to differentiate components according to emission patterns.

11:     Instruments to consider would be:

      ICP (MS)
      HPLC (MS)
      GC (MS)
      Ion exchange
      UV
      Fluorescence
      Conductivity detectors
      gel permeation columns
      Electrochem cells
      voltameters
      etc...