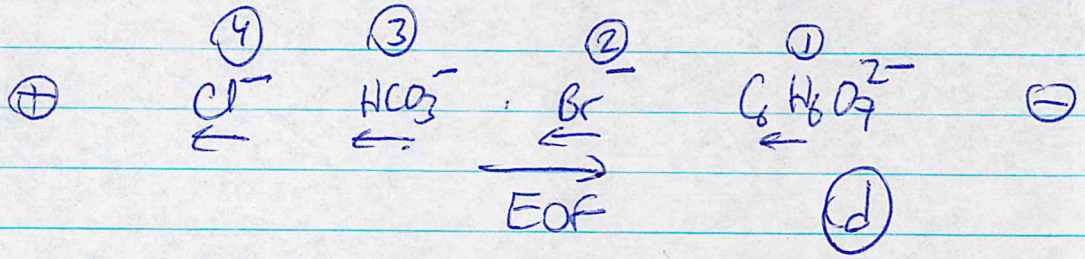
CHEM 3590 final 2016 Answers

2 (b)

3 z/m ratios: $Cl^- = \frac{1}{35}$ $Br^- = \frac{1}{79}$ $C_6H_6O_7^{2-} = \frac{2}{190} = \frac{1}{95}$

$HCO_3^- : \frac{1}{63}$



(d)

5 $Ce^{4+} + e^- \rightarrow Ce^{3+}$ $E^0 = 1.44V$

$Br_2 + 2e^- \rightarrow 2Br^-$ $E^0 = 1.07V$

$E^0 = 1.07 - 1.44 = -0.37\ V$ (a)

6 $Q = nF \times$ moles analyte

UO_2^{2+} : U is +6 U^{4+} : U is +4

$\Rightarrow n = 2$

$$\text{moles analyte} = \frac{Q}{nF} = \frac{5782\ C}{2 \times 96368\ C/mol} = 0.03\ \text{mole}$$

$$\text{Conc.} = \frac{0.03\ mol}{0.200\ L} = 0.15\ M$$ (a)

7 reduction →
oxidation ←

$E_{cell} = E_{red} - 0.199 \Rightarrow E_{red} = E_{cell} + 0.199V$

$E_{cell} = \frac{0.67 + 0.72}{2} = 0.70$

$E_{red} = 0.70 + 0.199V = 0.899V$ (c)

8 The y axis is in milli-absorbance units ⇒ UV detector, LC. Could be c or d, but gel permeation would not separate molecules so close in MW. Only possible answer is (c).

Makes sense as caffeine is less polar than paraxanthine.

9 e.g. for 100 mL of dry gel we get 175 mL of wet gel.

then for 10 mL " " " " " 500 mL of wet gel

$x = 286 mL$ (e)

10 Diethylamine : a strong base ⊕ at pH 7
phosphoric acid : a strong acid ⊖ at pH 7
acetic acid : a weak acid : less ⊖ at pH 7
Glycine: amino acid with pI, less acidic than acetic acid
less basic than DEA.

Retention order, from least retained to most:

① ② ③ ④
Diethylamine, glycine, acetic acid, phosphoric acid (b)

11 Carbons with higher oxidation states have higher 1s binding energies.

CF_3 : C is +3

C=O C is also +3, but O is less e.n. than F. Say C is $\leq +3$

CH_2 : C is −1

CH_3 C is −3

The order is as indicated in (b)

13 (c) (Cd = only absorbance)

14 $$\text{slope} = \frac{0.309 - 0.281}{\log(0.09) - \log(0.01)} = 0.0293 \simeq \frac{0.0592}{2}$$

$n = 2$

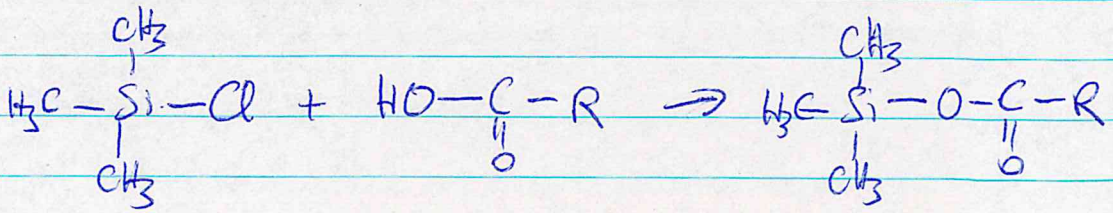
Intercept $= E^0$

$$0.309 = E^0 + \frac{0.0592}{2}\log(0.09) \Rightarrow E^0 = 0.31\,V$$

$M^{2+} = Cu^{2+}$ (c)

15 (b)

16 a)



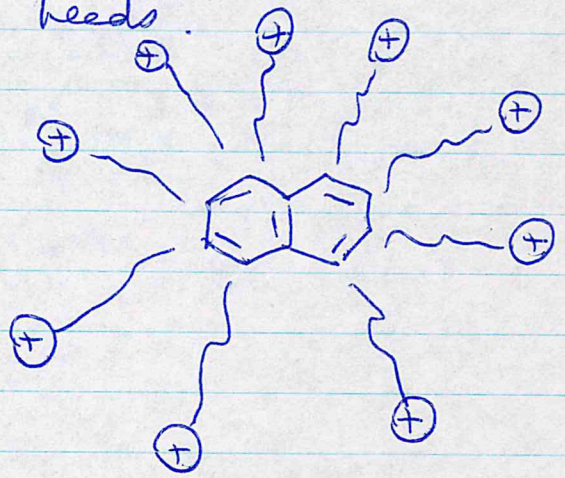
b) Polar compounds are often difficult to elute off a GC column due to low volatility and thermolability. This makes compounds more

17 One method would be to use a higher resolution MS allowing better distinction b/w Ar^+ and Ca^+

One could also use standard additions of Ca^{2+} solutions, if Ar^+ background is constant.

We can also rely on the optical emission properties of Ar^+ and Ca^{2+} for quantitative analysis.

19 MEKC - formation of micelles with charged polar heads.



20 $A + L \rightleftharpoons AL$ Citric acid: $C_6H_8O_7$

a) n.b.
$$C_A = [A] + [AL]$$
$$C_L = [L] + [AL]$$
$$C_{\text{citric acid}} = [C_6H_8O_7] + [C_6H_7O_7^-] + [C_6H_6O_7^{2-}] + [C_6H_5O_7^{3-}]$$

C-B : $$[H_3O^+] + [Na^+] = [OH^-] + [C_6H_7O_7^-] + 2[C_6H_6O_7^{2-}] + 3[C_6H_5O_7^{3-}]$$

b) To calculate the equilibrium constant of complex formation (formation or dissociation constant).

21

1. start of experiment
2. Peak cathodic current of 1st reduction potential
3. " " " of 2nd " "
4. potential reversal
5. peak anodic current for oxidation of component that got reduced in (3) (maybe?)

there is no real visible oxidation peak, so reduction was not reversible in this case and the assumption made for (5) doesn't really hold.

22

a) oxidation

b) the E value for 1st oxidation is ~ 0.35 V = E_{cell}

$$0.35\,V = E_{ox} - 0.199, \quad E_{ox} = 0.549\,V$$

closest value in table is for [redacted]

$$I_2 + 2e^- \rightarrow 2I^- \quad E^\circ = 0.54\,V$$

second oxidation: $E_{cell} \simeq 0.68\,V$

$E_{ox} \simeq 0.879\,V$

this could be $Hg^{2+} \rightarrow Hg_2^{2+}$ $E^\circ = 0.90$

or $ClO^- \rightarrow Cl^-$ $E^\circ = 0.90$

23 NaI, FW = 150 g/mol moles = $\frac{0.005\,g}{150\,g/mol} = 3.33 \times 10^{-5}$ mole

I_2 generated = $\frac{3.35 \times 10^{-5}}{2} = 1.67 \times 10^{-5}$ mole. There are 2 e⁻ consumed per I_2.

a) $Q = 2 \times 96368 \times 1.67 \times 10^{-5} = 3.21\,C$

b) Reaction products can react again w/ H_2O, altering titration