Wilfrid Laurier University, Waterloo, Ontario (**FINAL EXAM**)

Session: Fall 2012 Course No: CH261 Name: _____

Course Title: Analytical Chemistry I ID #: _____

Professor: Dr. Scott Smith Lab. Section: _____

Length of Test: 2.5 hours Examination Aids Allowed: calculators are allowed

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Answer all questions in the booklet provided. All questions are of equal weight and part marks will be assigned. Remember to put your name and id no. on your booklet(s).

Official regulations for Laurier exams are given below:

The doors of the examination room will be opened approximately 10 minutes before the start of the examination. Candidates will be permitted to enter the examination room quietly up to one half hour after the scheduled start of the exam. Candidates arriving late will not be allowed any extra time. Candidates must not begin the examination or attempt to read the examination questions until instructed to do so.

Candidates once having entered, may not leave the exam room before completing and submitting the exam unless accompanied by a Proctor. Candidates are not permitted to submit their examination and leave the examination room until 1 hour after the examination has begun, and in no case before their attendance has been taken. In no case may a candidate leave the room temporarily, for any reason, until 30 minutes after the start of the examination. In order that remaining candidates are not disrupted, candidates must remain seated and may not leave the examination room during the last 15 minutes of the examination session.

At the close of the examination period, candidates must stop writing immediately. The Presiding Officer may seize the papers of candidates who fail to observe this requirement, and a penalty may be imposed at the discretion of the instructor. Candidates must submit all their work, according to the instructions of the Presiding Officer, including all materials and a copy of the examination paper with their name and student ID number written on it. Unused examination booklets may not be taken from the examination room.

A candidate who leaves before the examination is over must hand in all completed and attempted work, notes made during the exam, and a copy of the examination paper with their name and student ID number on it.

Talk or any form of communication between candidates is absolutely forbidden. No information of any kind is to be written on the question paper or on scrap paper for the purpose of assisting other candidates. Responses to questions must not be done in an exaggerated way or in a manner that will involve transmission of information to others. Candidates must remain seated during the examination period. A candidate needing to speak to the proctor (e.g. to ask for additional supplies or to request permission to leave the examination room for any reason) should so indicate by raising his or her hand.

Questions concerning possible errors, ambiguities or omissions in the examination paper must be directed to the proctor who will investigate them through the proper channels. The proctor is not permitted to answer questions other than those concerning the examination paper.

Candidates must not use or attempt to use any improper source of information. No candidates for an examination may bring into the examination room any books, notes or other material containing information pertaining to the examination unless the examiner has given instructions that such material will be allowed and this instruction is specified on the examination paper. Any item brought into the examination room is subject to inspection.

No briefcases, backpacks or other bags and carriers may be brought to the desk site where the candidate is writing the examination. These bags should be left outside the examination room. If books, notes etc. cannot be left outside the examination room, they must be put at the front of the examination room in a place designated by the proctor before a candidate takes a seat. Candidates are advised not to bring valuables to the examination room.

No electronic or communication devices will be allowed in the examination room, including cell phones, blackberries, pagers, etc. Calculators are not allowed unless specified by the instructor and indicated on the examination paper. Only non-programmable models authorized by the instructor will be allowed. It is the candidate's responsibility to ascertain whether the use of calculators is permitted, and, if it is, whether any restrictions are imposed on the types of calculators that may be brought to the examination.

Translation dictionaries (e.g. English-French) or other dictionaries, (thesaurus, definitions, technical) are not allowed unless specified by the instructor and indicated on the examination paper. Electronic dictionaries are never allowed.

Except for bottled water, no food or drink is allowed in the examination room. Candidates with health problems that warrant relaxation of this regulation should provide medical documentation to the presiding officer prior to the beginning of the examination. Such students should restrict themselves to those items and packaging that will least distract other examinees.

Candidates are expected to write their examinations in an honest and straightforward manner. Where there are reasonable grounds for believing a violation of exam protocol has occurred, the candidate will be subject to the disciplinary procedures and sanctions according to the University Calendar.

Only currently registered students will be permitted to write the final exam. Examinations conducted at Wilfrid University will be bound by WLU regulations, regardless of where the candidate is registered.

Approved by Senate (Oct. 27/2003)

monoprotic acid (HL)

$HA \rightleftharpoons H^+ + A^-$

$$[HA] = \frac{A_T[H^+]}{[H^+] + K_a}$$

$$[A^-] = \frac{A_T K_a}{[H^+] + K_a}$$

monobasic base (B)

reaction $B + H_2O = BH^+ + OH^-$

$$[B] = \frac{B_T[OH^-]}{[OH^-] + K_b}$$

$$[BH^+] = \frac{K_b B_T}{[OH^-] + K_b}$$

Buoyancy Correction

$$m = \frac{m'\left(1 - \frac{d_a}{d_w}\right)}{\left(1 - \frac{d_a}{d}\right)}$$

m corrected mass
m' mass read on the balance
d_a density of air (0.0012 g/mL)
d_w density of calibration weights (8.0 g/mL)
d density of of the object being weighed

Henderson-Hasselbalch

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

error propagation functions:

function	Uncertainty
$y = x_1 + x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$
$y = x_1 \cdot x_2$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$
$y = x^a$	$\%e_y = a\%e_x$
$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = e^x$	$\frac{e_y}{y} = e_x$

quadratic equation solution

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

conversion factors and constants

$k_B = 1.38065 \times 10^{-23}\ J \cdot K^{-1}$
$h = 6.62608 \times 10^{-34}\ J \cdot s$
$N_A = 6.02214 \times 10^{23}\ mol^{-1}$
$R = 0.0821\ L{\cdot}atm{\cdot}K^{-1}{\cdot}mol^{-1}$
$R = 8.3145\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$R = 0.083145\ L{\cdot}bar{\cdot}K^{-1}{\cdot}mol^{-1}$
$R = 62.3656\ L{\cdot}torr{\cdot}K^{-1}{\cdot}mol^{-1}$

stats

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

,

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

$$t = \frac{|\bar{x} - \text{reference value}|}{s}\sqrt{n}$$

paired t-test

$$t_{calc} = \frac{|\,\bar{d}\,|}{\bar{s}_d}\sqrt{n}$$

compare replicate measurements

$$t_{calc} = \frac{\bar{x_1} - \bar{x_2}}{s_{pooled}}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$s_{pooled} = \sqrt{\frac{\Sigma_{\text{set 1}}(x_i - \bar{x_1})^2 + \Sigma_{\text{set 2}}(x_i - \bar{x_2})^2}{n_1 + n_2 - 2}}$$

Activities (α in pm units)

$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$

$\mathcal{A}_c = [C]\gamma_C$, $\log\gamma = \frac{-0.51z^2\sqrt{I}}{1 + (\alpha\sqrt{I}/305)}$

Nernst equation

$E = E_0 - \frac{0.0592}{n}\log Q$

Quadratic for ppte. titration curve

solid AB titrate A into B

solve for [A]

a=1, b=B_T-A_T, c=$-K_{sp}$

Quadratic for complex. titrn curve

complex MY titrate Y into M

solve for [M]

a=K', b=$Y_T K' - M_T K' + 1$, c=$-M_T$

EDTA (H_6Y)

$$\alpha_{Y^{4-}} = \frac{Y}{H6Y + H5Y + H4Y + H3Y + H2Y + HY + Y}$$

where

$Y = K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}$

$HY = K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}[H^+]$

$H2Y = K_{a1}K_{a2}K_{a3}K_{a4}[H^+]^2$

$H3Y = K_{a1}K_{a2}K_{a3}[H^+]^3$

$H4Y = K_{a1}K_{a2}[H^+]^4$

$H5Y = K_{a1}[H^+]^5$

$H6Y = [H^+]^6$

pKa1=0.0, pKa2=1.5, pKa3=2.00, pKa4=2.69, pKa5=6.13, pKa6=10.37

diprotic acid (H_2A)

$$\alpha_{H_2A} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_{HA^-} = \frac{[H^+]K_{a1}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_{A^{-2}} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

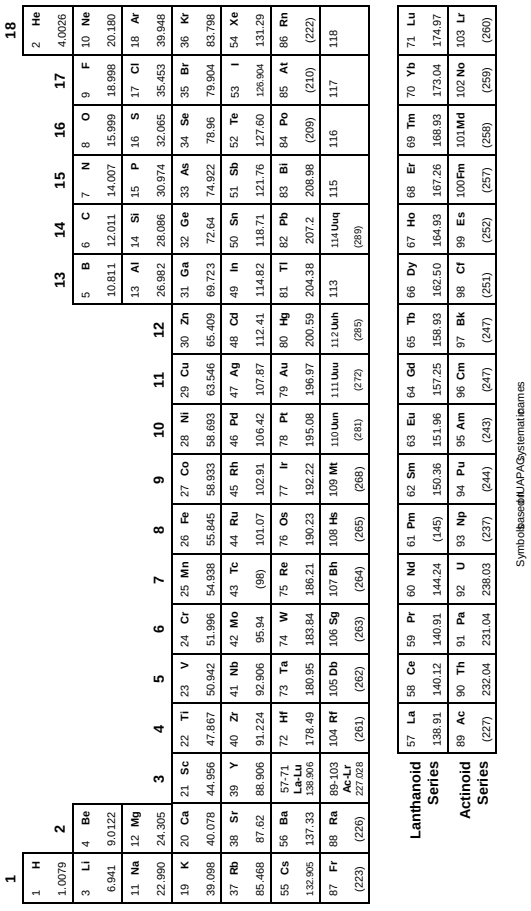
Conditional Formation Constant

$$K' = \alpha K_{thermo}$$

metal	logK$_f$ EDTA
Li^+	2.95
Mg^{2+}	8.79
Ca^{2+}	10.65
La^{3+}	15.36
Cu^{2+}	18.78

Values of Students' t

df	90	95	99.9
1	6.314	12.706	636.578
2	2.920	4.305	31.598
3	2.353	3.182	12.924
4	2.132	2.776	8.610
5	2.015	2.571	6.869
6	1.943	2.447	5.959
7	1.895	2.365	5.408
8	1.860	2.306	5.041
9	1.833	2.262	4.781
10	1.812	2.228	4.587
15	1.753	2.131	4.073
20	1.725	2.086	3.850
25	1.708	2.060	3.725
30	1.697	2.042	3.646
40	1.684	2.021	3.551
60	1.671	2.000	3.460
120	1.658	1.980	3.373
∞	1.645	1.960	3.291



Standard reduction potentials

reaction	E^0 (V)
$Li^+ + e^- \rightarrow Li$	-3.040
$Na^+ + e^- \rightarrow Na$	-2.713
$La^{3+} + 3e^- \rightarrow La$	-2.379
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763
$CO_2(g) + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	-0.49
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.38
$Ag(CN)_2^- + e^- \rightarrow Ag_{(s)} + 2CN^-$	-0.310
$Tl^+ + e^- \rightarrow Tl$	-0.336
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.257
$V^{3+} + e^- \rightarrow V^{2+}$	-0.225
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ *(1 F HCl)*	0.139
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.14
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
$2H^+ + 2e^- \rightarrow H_2$	0.000
$5S_4O_6{}^{2-} + 2e^- \rightarrow 2S_2O_3{}^{2-}$	0.09
$TiO^{2+} + 2H^+ + 2e^- \rightarrow Ti^{3+} + H_2O$	0.10
$S + 2H^+ + 2e^- \rightarrow H_2S$	0.14
$Cu^{2+} + e^- \rightarrow Cu^+$	0.17
$Hg_2Cl_2 + 2e^- \rightarrow 2Cl^- + 2Hg$	0.268
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Cu^+ + e^- \rightarrow Cu$	0.52
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.695
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
$Ag^+ + e^- \rightarrow Ag$	0.799
$Hg^{2+} + 2e^- \rightarrow Hg$	0.86
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.358
$Ce^{4+} + e^- \rightarrow Ce^{3+}$ *(1 F HCl)*	1.47
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.763
$S_2O_8{}^{2-} + 2e^- \rightarrow 2SO_4{}^{2-}$	1.96
$F_2 + 2e^- \rightarrow 2F^-$	2.87

1. (5 points) Define the following terms:

(a) analytical chemistry (b) reducing agent (c) chemical activity

(d) confidence interval (e) standard hydrogen electrode

Answer:

(a) for a sample answering the questions **what and how much?** and establishing confidence interval about the estimates.

(b) a species that is itself oxidized as it reduces some other species. Ox. species + red. agent = reduced species + oxidized reducing agent.

(c) $(C) = \gamma_c[C]$ and define terms

(d)

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

and define terms and explain what it means

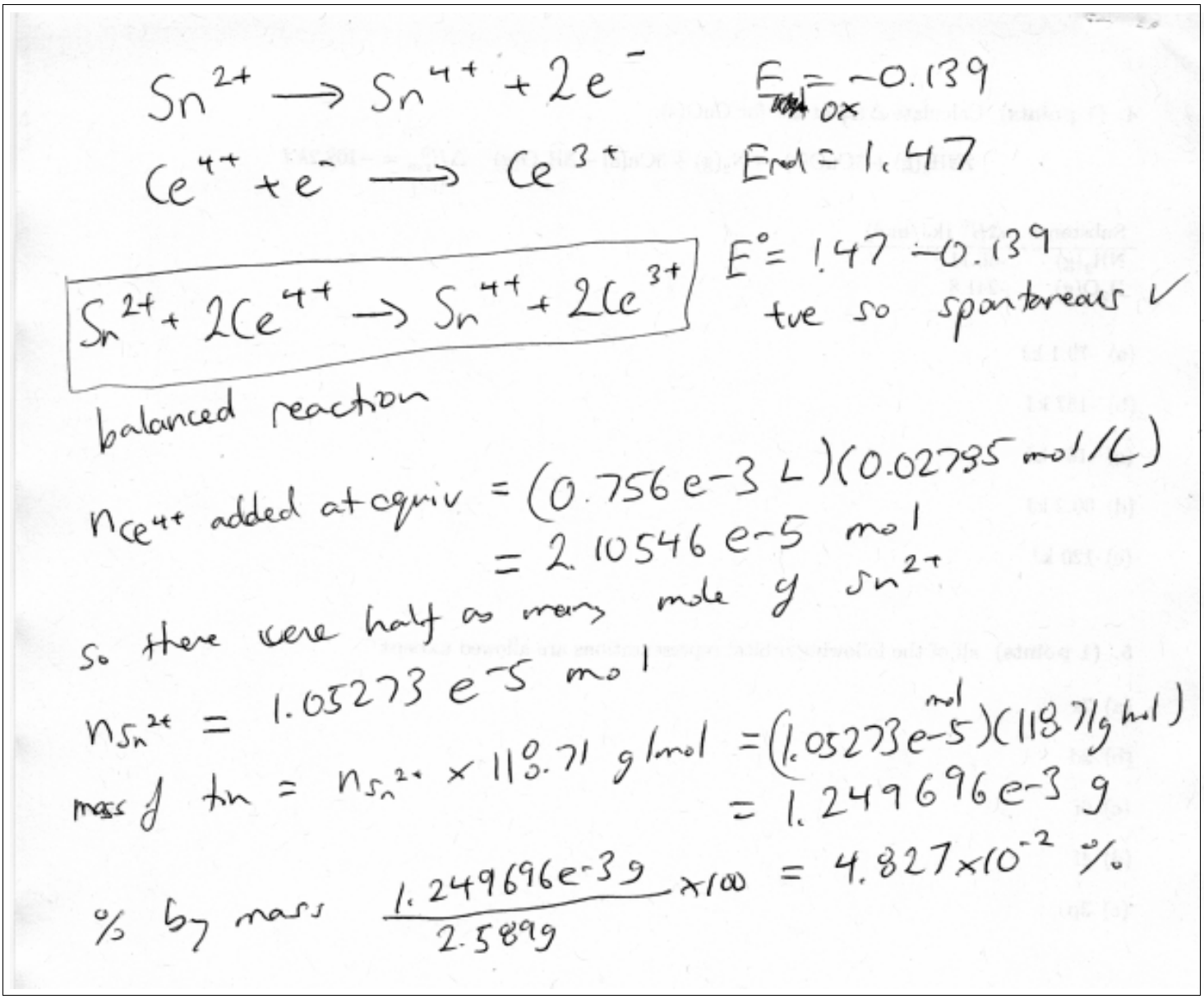
(e) standard hydrogen electrode is defined as zero reduction potential.

$$2H^+ + 2e^- \rightarrow H_{2(g)}$$

constructed with an aqueous solution 1 M activity of H^+ and bubbled with 1 bar pressure of H_2 gas with a Pt electrode to carry electrons around.

2. (5 points) A 2.589 g sample of tin ore is dissolved and completely reduced to the II oxidation state. The final solution for redox titration is dissolved in 1 M HCl. The resulting Sn^{2+} ions are titrated with cerium (IV) nitrate. The end point is reached when 0.756 mL of 0.02785 mol/L cerium has been added to the sample. What is the percent tin by weight in the original ore sample? (Note: it is known that no significant amount of other metals are present in the sample).

Answer:



3. (5 points) Action is taken against Olympic athlete if their urine is found to contain caffeine concentrations above a reference value of 12.00 μg/mL. Five replicate samples from one athlete give values of 12.01, 11.95, 12.56, 12.31 and 12.21 μg/mL. Should action be taken against this athlete?

Answer:

this is comparison to a known value test

need mean and sd $t = \frac{|\bar{x} - \text{ref}|}{s}\sqrt{n}$

$\bar{x} = 12.208$ sd = 0.2449898

$$t_{calc} = \frac{|12.208 - 12.00|}{0.2449898}\sqrt{5}$$

$= 1.898$

t value for comparison select 95% CI

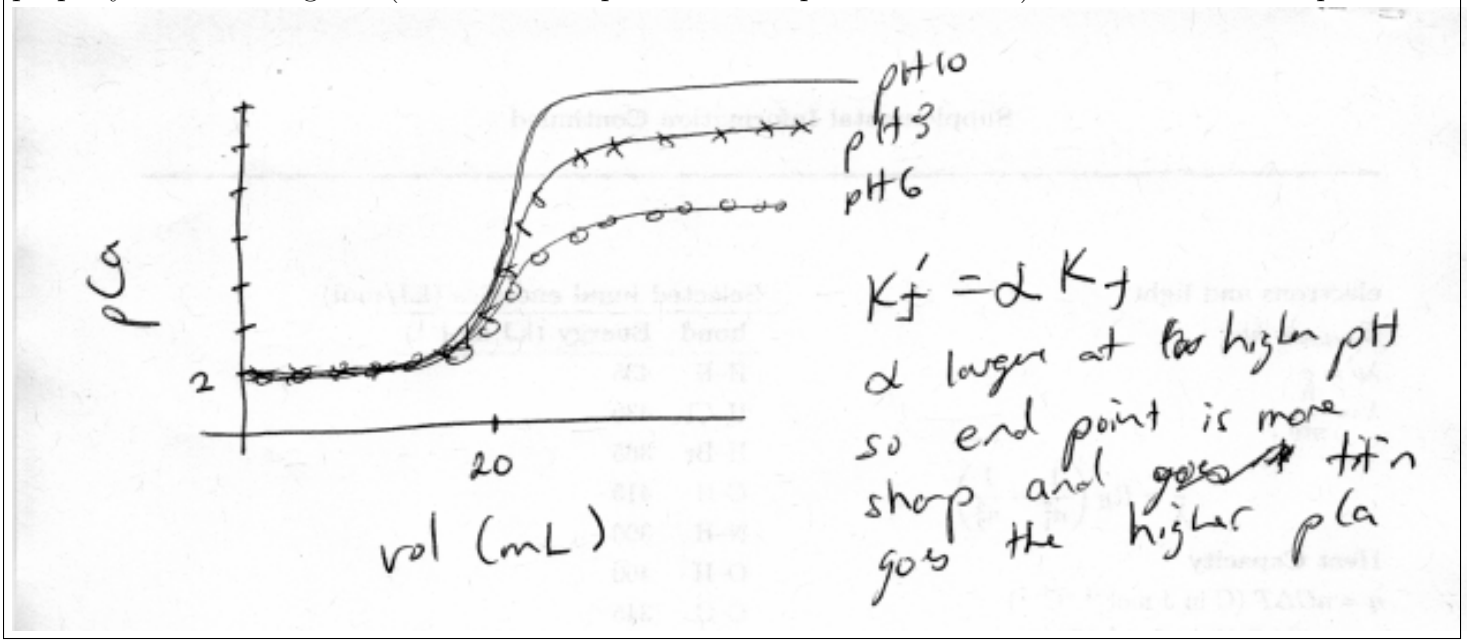
$t = 2.776$ $(df = 4)$

action must be taken. (even if picked other values action must be taken, but a value must be specified)

4. (5 points) Semi-quantitatively sketch titration curves for calcium determination by EDTA titration at pH values of 6, 8 and 10. The titrations start with 100 mL of calcium at 0.01 mol/L and the EDTA titrant is 0.05 mol/L. Sketch all three curves on the same graph. Explain your sketch. (Note: one quantitative point is sufficient for all your sketches).

Answer:

just the pH dependence. pCa lowest for at end for lowest pH but end point always the same volume. properly labelled diagram (vol EDTA vs pCa and end point at 20 mL). should start from pCa of 2.



5. (5 points) 0.60 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$ (FM = 392.13) in 400 mL of 1 M H_2SO_4 titrate with 0.02 M $KMnO_4$. Quantitatively sketch the titration curve using $\frac{1}{2}V_e$, V_e and $2V_e$. (Note: at these low pH values sulfuric acid is monoprotic).

Answer:

0.60 g iron salt

$$n_{Fe^{2+}} = \frac{0.60\,g}{392.13\,g/mol} = 0.00153\,mol$$

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad E^\circ_{red} = 1.51$

$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad E^\circ_{ox} = -0.771\ V$

$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$ balanced rxn

titrant — analyte

before equiv curve determined by analyte half-rxn $E = E^\circ_{red}$ Fe so $= 0.771\ V$ (because $[Fe^{3+}] = [Fe^{2+}]$)

at two Ve potential is from Mn redox couple

$$E = E^\circ - \frac{0.0592}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H]^8}$$

at equiv $Mn^{2+} = \frac{1}{5} n_{Fe\ initial}$ all made from rxn. no new Mn^{2+}

at 2Ve have added $n_{MnO_4^-} = \frac{1}{5} n_{Fe\ initial}$ but lost $\frac{1}{5}$ reacted

so $[MnO_4^-] = [Mn^{2+}]$ they cancel

equiv volume is $\dfrac{\left(\frac{n_{Fe^{2+}}}{5}\right) mol}{0.02\ mol/L} = \dfrac{\frac{0.00153}{5}}{0.02} = 0.0153\ L = 15.3\ mL$

at 2VEe $[H^+] = \dfrac{(1\ mol/L)(0.4\ L)}{(0.4 + 2 \times 0.0153)} = 0.929$

$$E_{2Ve} = 1.51 - \frac{0.0592}{5}\left(\log\left(\frac{1}{0.929^8}\right)\right)$$

$= 1.507$

at equiv ...

analyte equals stoich that

$$n_{Fe^{2+}} = \frac{1}{5} n_{MnO_4^-}$$

and by rxn stoich

$$n_{Fe^{3+}} = \frac{1}{5} n_{Mn^{2+}}$$

we have two potentials to satisfy

$$E_{Fe} = E^\circ_{Fe} - \frac{0.0592}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{Mn} = E^\circ_{Mn} - \frac{0.0592}{5} \log \left(\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8} \right)$$

to cancel stuff out at $E_{Fe} + 5E_{Mn}$

$$6E = E^\circ_{Fe} - 0.0592 \log \left(\frac{[Fe^{2+}]}{[Fe^{3+}]} \right) + 5E^\circ_{Mn} - 0.0592 \log \left(\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8} \right)$$

$$= 0.771 + 5(1.51) - 0.0592 \log \left(\frac{[Fe^{2+}][Mn^{2+}]}{[Fe^{3+}][MnO_4^-][H^+]^8} \right)$$

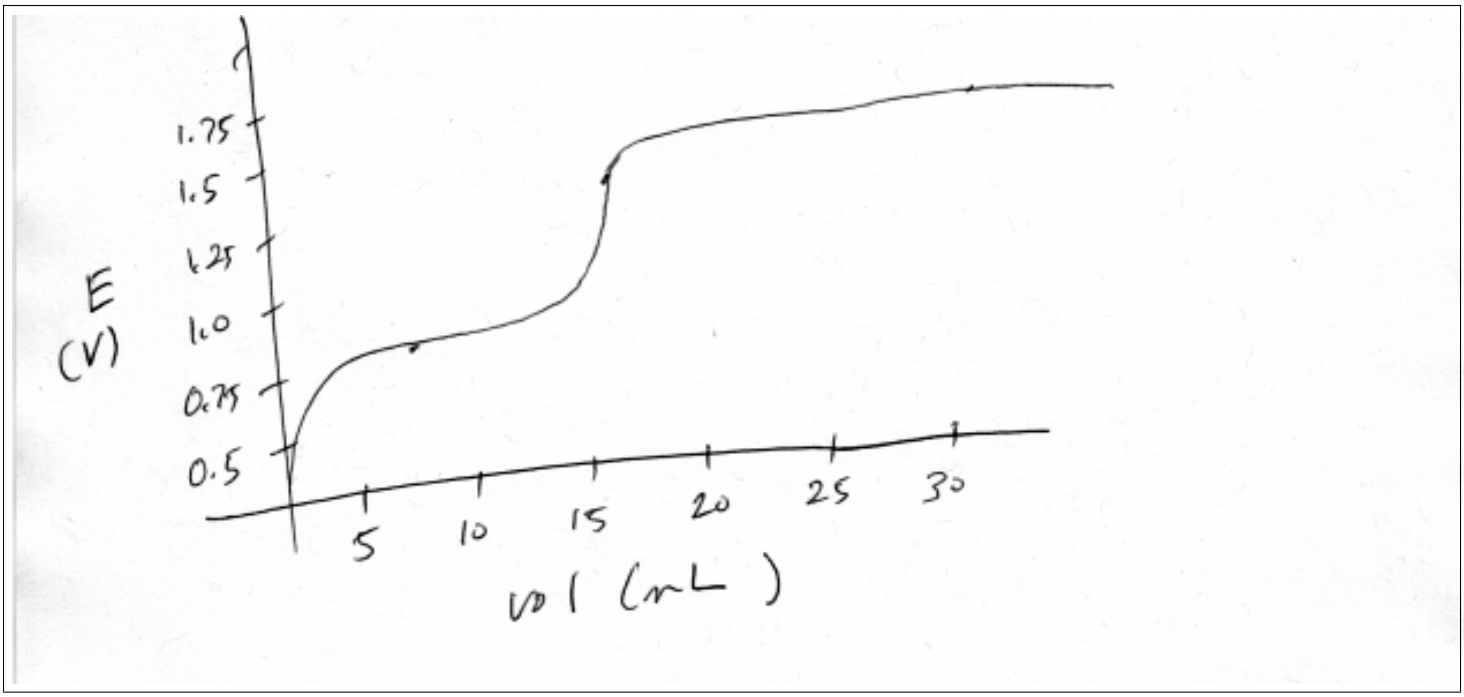
$$= 8.321 - 0.0592 \log \left(\frac{(\frac{1}{5} MnO_4^-)(Mn^{2+})}{(\frac{1}{5} Mn^{2+})(MnO_4^-)[H^+]^8} \right)$$

$$[H^+] = 1 \left(\frac{40}{41.5.3} \right) = 0.963$$

$$6E = 8.321 - 0.0592 \left(\log \left(\frac{1}{0.963^8} \right) \right)$$

$$= 8.313$$

$$E_{equiv} = 1.386$$



6. (5 points) pH=-log(H^+). For a solution of 0.01245 mol/L $CaSO_4$, 0.0025 mol/L $Mg(NO_3)_2$, 10 μM HCl what is the pH? The hydrated radius of hydronium cation is 900 pm.

Answer:

conc [H] is 10^{-5}. calc activity coefficient and determine activity of H+.

ions Ca^{2+}, SO_4^{2-}, Mg^{2+}, NO_3^-, H^+, OH^-, Cl^-

$[H^+] = 10\,\mu M$ from strong acid HCl

$(H^+) = \gamma_{H^+}[H^+]$

need to determine γ from extended debye huckel

first need ionic strength (μ)

$$\mu = \frac{1}{2}\left(0.01245(4) + 0.01245(4) + 0.0025(4) + 0.005(1) + 1e\text{-}5(1) + 1e\text{-}5(1) + 1e\text{-}9(1)\right)$$

(Ca^{2+}, SO_4^{2-}, Mg^{2+}, NO_3^-, H^+, Cl^-, OH^-)

o.k. if forget these b/c conc so low

$= 0.05731$ mol/L

$$\log\gamma = \frac{-0.51(1)^2\sqrt{0.05731}}{1 + \frac{900\sqrt{0.05731}}{305}} = \frac{-0.12209}{1.70641}$$

$= -0.071547799$

$\gamma = 0.84811$

$(H^+) = (0.84811)(1e\text{-}5) = 8.4811e\text{-}6$

$pH = 5.07$

7. (5 points) For argentometric titrations of halogens the equivalence point occurs at

$$pAg = \frac{pK_{sp}}{2}$$

Explain why.

Answer:

at equiv [X]=[Ag] and [X][Ag]=Ksp so $[Ag]^2$=Ksp. take -log of both sides. -2logAg=-logKsp and so pAg=pKsp/2

8. (5 points) How do quantitative titrimetry results (determination of analyte) depends on the initial volume of sample? Explain. (For example, if you dissolved 0.100 g of analyte into 100 mL or 200 mL then titrated, how would your analytical results differ? and why?)

Answer:

titration is amount based so makes no difference as long as can still detect endpoint. end titration when you've added stoichiometric amount NOT stoichiometric concentration. if indicator based endpoint too dilute will make it hard to see the change. and response variable (pH, pCa, ...) would be spread out more if solution was too dilute but equiv point would not change (in terms of amount).