Chemistry 51 F ‘14 | Final Exam | December 15, 2014
Professor Cohen | | Closed book, 3 hours

Student name: ____________________________________ Student ID#: ____________________

GSI name: ______________________

Leave this section blank for grading

MC: _______ / 67 Short answer: _______ / 230??

Total: _____300

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(You can use it for scratch paper, long responses, etc)

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<u>Multiple Choice Questions</u>

1) (5 points) In the Earth's atmosphere the CO_2 mixing ratio is increasing at about 2 ppm/yr and the background CO_2 level is now near 400 ppm (compared to the preindustrial concentration of ~270ppm). Instruments with the precision below for an annual average are available? The cost is inversely proportional to the precision. What is the least expensive instrument that will meets the measurement requirements?

A) 10%

B) 1%

C) 0.1%

D) 0.5%

E) 0.01%

2) (10 points) A team of students attempts to quantify the amount of toxic metals in their hair. Their procedure is:

i. weigh a lock of hair from each partner
ii. dissolve the hair in 1 ml strong acid
iii. neutralize with a strong base, followed by bringing the total volume to 10 mls.
iv. They used MP-AES to measure the concentration of Zn, Cu and Mn in the final solution. They then express their result as moles of metal per gram of hair.

Results were as follows (units are micrograms metal/gram of hair):

	Zn	Cu	Mn
Partner 1:	175	10	0.40
Partner 2:	325	22	1.8
Partner 3:	120	12	0.66

The partners repeat the measurement with two additional locks of partner 1's hair and find their procedure is only reproducible to ~25%. Based on the data, which of the following is true? *Label each answer as true or false*

A) There is a systematic error in the measurements for partner 2.

B) None of the differences between partner 1 and 3 are likely significant

C) Partner 2 dyes his hair.

D) The methods used are not very accurate

E) Most of the differences between the partners are likely significant.

3) (12 points) The partners find the large differences for partner 2 surprising? Which actions should they take next? *Label each answer as true or false*

A) repeat the experiment.

B) assume the data is incorrect present only data for partners 1 and 3

C) review their notebooks and carefully check for errors.

D) develop a new procedure using independent methods of analysis

4) (10 points) HPLC separations can be optimized by: *Label each answer as true or false*

A) Magnetic fields

B) Choice of solvent

C) Column Material

D) Type of Detector

E) Sensitivity of the detector

5) **(10 points)** Which of the following are likely to be effectively separated from molecules that do not interact with the resin by column chromatography using a negatively charged resin? *Circle all correct answers*

A) NH_4^+

B) NH_3

C) CH_3COOH

D) CH_3COO^-

E) Fe^{3+}

6) **(8 points)** Which of the following would be the most effective solution to a matrix effect in quantitative analysis of a sample? *Circle one*

A) Dilute the sample

B) Separate the analyte by HPLC

C) Use the method of standard addition

D) Use calibration standards in the range of the concentration

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7) (12 points) Mass spectrometers use which of the following to effect mass separation *Circle all correct answers:*

A) Magnetic fields

B) Electric fields

C) Gravity

D) RF pulses

E) Lasers

F) GCs

<u>Short Answer Questions:.</u>

<u>#1</u> [15 points total] (a) Explain how a galvanic cell uses a spontaneous chemical reaction to generate electricity.

(b) Calculate E^0 for the electrochemical cell $Ag|Ag^+||Li^+|Li$.

<u>#2</u> [30 points]
A molecule is observed using optical spectrometry. To get the maximum information from the spectrum the observer needs to obtain a spectrum with the narrowest feasible linewidth. List 3 components or parameters of an experiment utilizing an optical spectrometer and describe how they affect the observed linewidth.

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#3 (18 points) A solute S has a partition coefficient of 4.0 between water (phase 1) and chloroform (phase 2). The solute is initially dissolved in 80.0 mL of water. It is then extracted six times with 10.0-mL portions of chloroform.

(a)Find the fraction of solute remaining in the aqueous phase.

(b) Instead of six extractions of 10.0 mL each, a professor tried to save some time by performing one extraction of S from 80.0 mL of water using 60.0 mL of chloroform all at once. Find the fraction of solute remaining in the aqueous phase.

(c) Briefly explain how the results from (a) and (b) above form the basis for chromatography.

#4 (40 points) In class, we estimated the detection limit of a mass spectrometer. Draw a diagram of a mass spectrometer. Estimate the detection limit with specific reference to your figure.

#5 (20 points) You wish to determine the Pb^{2+} concentration in a dilute vinegar solution. To do this you spike your vinegar solution with 3 100 uL aliquots of a 100 ppb Pb^{2+} standard and measure the current creating the standard addition curve below (**O**).

(a)Using this curve, what is the concentration of Pb^{2+} in the vinegar sample? Include the error calculation.

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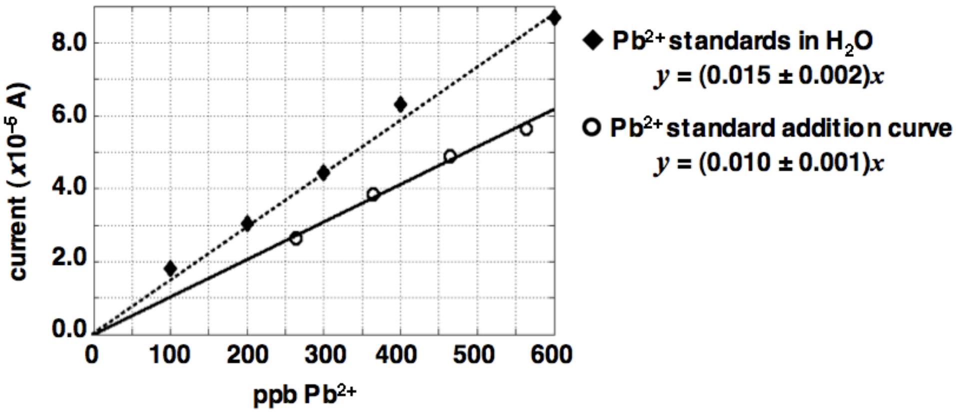

standard addition curve data	
current ($x10^{-5}$ A)	ppb Pb^{2+} added
2.65 ± 0.03	0
3.84 ± 0.02	100
4.89 ± 0.02	200
5.64 ± 0.03	300
6.9 ± 0.04	400

calibration curve in H_2O data	
current ($x10^{-5}$ A)	Pb^{2+} (ppb) in water
1.8 ± 0.01	100
3.03 ± 0.02	200
4.44 ± 0.02	300
6.3 ± 0.01	400
8.71 ± 0.02	600

(b)Give an explanation for the difference in slopes observed from the two curves.

Equations and Tables

Statistics:

$$\bar{x} = \frac{\sum_i x_i}{n}$$

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

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$$

$$\text{Confidence interval} = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

Activities:

$$\mu = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + \cdots) = \frac{1}{2}\sum_i c_i z_i^2$$

$$K = \frac{\mathcal{A}_C^c \mathcal{A}_D^d}{\mathcal{A}_A^a \mathcal{A}_B^b} = \frac{[C]^c \gamma_C^c [D]^d \gamma_D^d}{[A]^a \gamma_A^a [B]^b \gamma_B^b}$$

$$\log \gamma = \frac{-0.51 z^2 \sqrt{\mu}}{1 + (\alpha\sqrt{\mu}/305)} \qquad \text{(at 25°C)}$$

Acid Base Equilibria:

$pH = -\log[H^+]$

$pX = -\log X$

$$pH + pOH = -\log K_w = 14.00 \text{ at } 25°C$$

$$K_a \cdot K_b = K_w$$

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

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$$pH = pK_a + \log \frac{[B]}{[BH^+]}$$ ↙ pK_a applies to *this* acid

With activities:

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

Diprotic/Dibasics:

$$K_{a1} \cdot K_{b2} = K_w$$

$$K_{a2} \cdot K_{b1} = K_w$$

Intermediate form of a diprotic acid:

$$[H^+] \approx \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}}$$, or approximately, $$pH \approx \frac{1}{2}(pK_1 + pK_2)$$

Diprotic Buffers:

$$pH = pK_1 + \log\frac{[HA^-]}{[H_2A]}$$ and/or $$pH = pK_2 + \log\frac{[A_2^-]}{[HA^-]}$$

Thermodynamics and Electrochemistry:

$\Delta G° = \Delta H° - T\Delta S°$

for $aA + bB \rightleftarrows cC + dD$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$\Delta G° = -RT\ln K$

$\Delta G° = -nFE°$

$\Delta G = \Delta G° + RT\ln Q$

$\Delta G = -nFE$

$E° = E°_{cathode} - E°_{anode}$

$E = E° - (RT/nF)\ln Q = E° - (0.05916/n)\log Q$ at 25°C

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Constants:

$N_0 = 6.02214 \times 10^{23}\ mol^{-1}$

$k = 1.38066 \times 10^{-23}\ J\ K^{-1}$

$F = 96{,}485\ C / mol$

$1\ V = 1\ J / C$

$R = 8.31451\ J\ K^{-1}\ mol^{-1}$

$R = 8.20578 \times 10^{-2}\ L\ atm\ K^{-1}\ mol^{-1}$

TABLE 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function[a]	Uncertainty[b]
$y = x_1 + x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
$y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\,\frac{e_x}{x}$
$y = x_1 \cdot x_2$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\,e_x$
$y = Bx$ *(see note below)*	$e_y = \|B\|$	$y = e^x$	$\frac{e_y}{y} = e_x$

a. x represents a variable and a represents a constant that has no uncertainty.

b. e_x/x is the relative error in x and $\%e_x$ is $100 \times e_x/x$.

Note that B is a constant with no uncertainty.

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TABLE 4–1 **Ordinate and area for the normal (Gaussian) error curve, $y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$**

$\lvert z \rvert$[a]	y	Area[b]	$\lvert z \rvert$	y	Area	$\lvert z \rvert$	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5	∞	0	0.5

a. $z = (x - \mu)/\sigma$.

b. The area refers to the area between $z = 0$ and $z =$ the value in the table. Thus the area from $z = 0$ to $z = 1.4$ is 0.419 2. The area from $z = -0.7$ to $z = 0$ is the same as from $z = 0$ to $z = 0.7$. The area from $z = -0.5$ to $z = +0.3$ is $(0.191\,5 + 0.117\,9) = 0.309\,4$. The total area between $z = -\infty$ and $z = +\infty$ is unity.

Harris, *Quantitative Chemical Analysis,* 8e

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TABLE 4-2 Values of Student's *t*

Degrees of freedom	Confidence level (%) 50	90	95	98	99	99.5	99.9
1	1.000	6.314	12.706	31.821	63.656	127.321	636.578
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

In calculating confidence intervals, σ may be substituted for s in Equation 4-6 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s, the value of t to use in Equation 4-6 comes from the bottom row of Table 4-2.

Values of t in this table apply to two-tailed tests illustrated in Figure 4-9a. The 95% confidence level specifies the regions containing 2.5% of the area in each wing of the curve. For a one-tailed test, we use values of t listed for 90% confidence. Each wing outside of t for 90% confidence contains 5% of the area of the curve.

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TABLE 7-1 Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α, pm)	Ionic strength (μ, M) 0.001	0.005	0.01	0.05	0.1
Charge = ±1		*Activity coefficient (γ)*				
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, $H_2citrate^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75
Charge = ±2		*Activity coefficient (γ)*				
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.69	0.52	0.45
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700	0.872	0.755	0.685	0.50	0.425
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(CO_2^-)_2$, $H_2C(CH_2CO_2^-)_2$, $(CH_2CH_2CO_2^-)_2$	600	0.870	0.749	0.675	0.485	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$, $(CHOHCO_2^-)_2$	500	0.868	0.744	0.67	0.465	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, $Hcitrate^{2-}$	450	0.867	0.742	0.665	0.455	0.37
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3		*Activity coefficient (γ)*				
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, In^{3+}, lanthanides[a]	900	0.738	0.54	0.445	0.245	0.18
$citrate^{3-}$	500	0.728	0.51	0.405	0.18	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.16	0.095
Charge = ±4		*Activity coefficient (γ)*				
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1 100	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	500	0.57	0.31	0.20	0.048	0.021

a. Lanthanides are elements 57–71 in the periodic table.

SOURCE: *J. Kielland, J. Am. Chem. Soc. 1937, 59, 1675.*

Reduction Potentials

E^o	Reduction Half-Reaction
+2.890 V	$F_2 (g) + 2e^- \rightarrow 2 F^- (aq)$
+1.396 V	$Cl_2 (g) + 2e^- \rightarrow 2 Cl^- (aq)$
+1.229 V	$O_2 (g) + 4H^+ (aq) + 4e^- \rightarrow 2 H_2O (\ell)$
+1.078 V	$Br_2 (\ell) + 2e^- \rightarrow 2 Br^- (aq)$
+0.799 V	$Ag^+ (aq) + e^- \rightarrow Ag (s)$
+0.771 V	$Fe^{3+} (aq) + e^- \rightarrow Fe^{2+} (aq)$
+0.339 V	$Cu^{2+} (aq) + 2e^- \rightarrow Cu (s)$
+0.222 V	$AgCl (s) + e^- \rightarrow Ag (s) + Cl^- (aq)$
+0.197 V	$AgCl (s) + e^- \rightarrow Ag (s) + Cl^- (aq)$ [saturated KCl]
0 V [defined]	$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$
–0.236 V	$Ni^{2+} (aq) + 2e^- \rightarrow Ni (s)$
–0.762 V	$Zn^{2+} (aq) + 2e^- \rightarrow Zn (s)$
–1.677 V	$A\ell^{3+} (aq) + 3e^- \rightarrow A\ell (s)$
–3.040 V	$Li^+ (aq) + e^- \rightarrow Li (s)$