Chemistry 51 F '14 | Midterm Exam | October 8, 2014

Professor Cohen | Closed book, 50 minutes

Student name: ___________________________________ Student ID#: ____________________

GSI name: ______________________

<u>Leave this section blank for grading</u>

MC: _______ / 40 #1: _______ / 60 #2________/50

<u>Total</u>: _____150

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

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<u>Multiple Choice Questions</u> (10 points each, 40 total)

1) In an open container on the Earth's surface a professor weighs 2.373(5) g of $CaCO_3$ and adds it to 1.0000(7) L of water. Which of the following errors in a calculation of the final molarity CO_3^{2-} is systematic? *Circle all correct answers*

A) The professor weighs the $CaCO_3$ properly but forgets to treat the acid-base properties of CO_3^{2-}.

B) The professor doesn't record the temperature

C) The (5) represents the average of 3 measurements.

D) The water is not distilled and has an initial pH of 6.5.

E) The $CaCO_3$ was hydrated and not dried before using

2) Which of the following would solutions would have the largest activity correction to a simple equilibrium expression for the dissociation of acetic acid, CH_3COOH? *Circle one*

A) 0.1M NaCl

B) 0.1M AgCl

C) 0.1M $MgCl_2$

D) 0.1M sodium citrate

4) pH and titrations: *Circle all correct answers*

A) Using the equipment from the CHEM 15 laboratory, the pKa of an acid can be measured to 0.01%

B) The K_w for water is 10^{-14} under all conditions

C) The end point of any titration is accompanied by a color change

D) At the equivalence point the concentration of an acid and its conjugate base are always equal

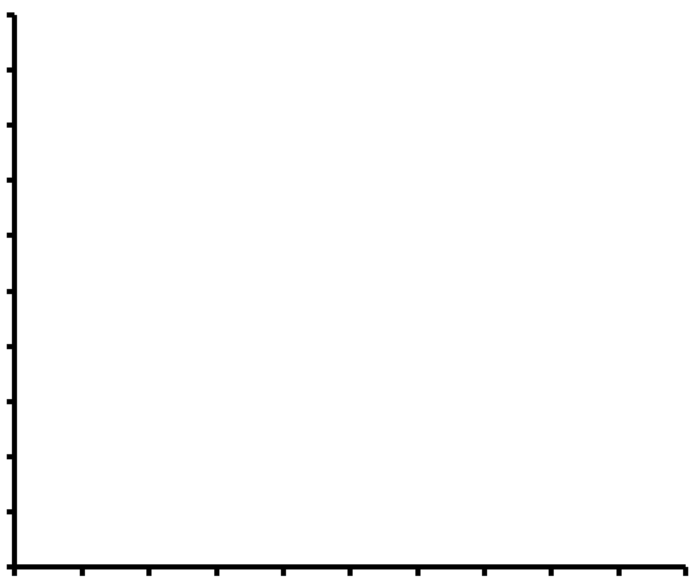
<u>Short Answer Questions:.</u>

<u>#1</u> [60 points total] In this problem, you can assume all the activity coefficients are 1.

(a) You make a solution by adding 0.75 moles of weak base A□ and 0.25 moles of its conjugate acid HA to 1 L of pure water. Express the pH of the resulting solution in terms of the pKa for HA.

(b) Take ½ the solution (0.5L) and add enough of a 1M strong acid solution to the mixture to set the pH equal to the pK_a. What is the volume of the final solution?

(c) Repeat step b, adding the acid solution in 4 equal increments. **Sketch** below the resulting titration curve of pH versus of strong acid added, labeling the axes and unique points along the way as titrant solution is added.



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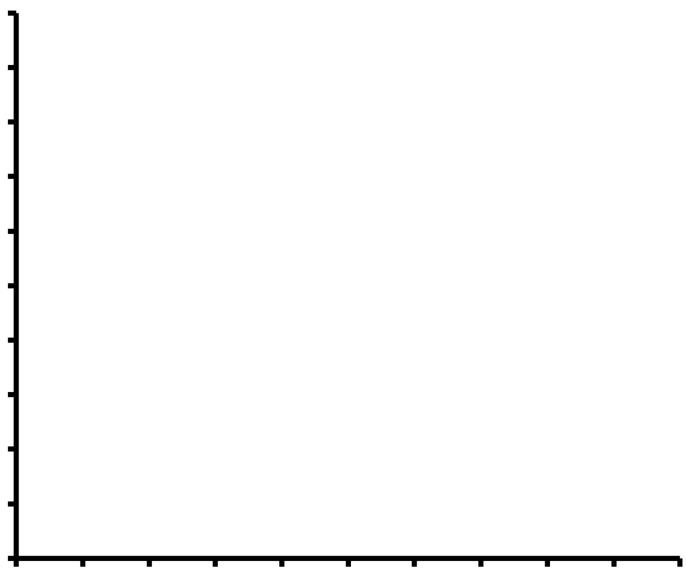
(d) Indicate in the graph below how you would plot the results to arrive at the most accurate estimate of the pKa. Label the axes.



(e) How would you modify the procedure above to get a more accurate result?

#2 [50 points total] Draw a diagram of the Galvanic cell you used in the laboratory. Label all of the key components. Give examples of one choice an instrument designer could make to optimize the measurement of the half cell potential.

Calculate E^0 for the electrochemical cell $Cu|Cu^{2+}||Mg^{2+}|Mg$.

The electrons will flow from _________ to _________ spontaneously.

Use the cell potential to find the equilibrium constant for this reaction at 298K.

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Equations and Tables

Statistics:

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

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

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

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:

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

$pX = -\log X$

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

$$K_a \cdot K_b = K_w$$

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

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{B}]}{[\mathrm{BH}^+]}}$$

$\mathrm{p}K_a$ applies to *this* acid

With activities:

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

Diprotic/Dibasics:

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

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

Intermediate form of a diprotic acid:

$$[\mathrm{H}^+] \approx \sqrt{\frac{K_1K_2\mathrm{F} + K_1K_w}{K_1 + \mathrm{F}}}$$, or approximately, $$\boxed{\mathrm{pH} \approx \frac{1}{2}(\mathrm{p}K_1 + \mathrm{p}K_2)}$$

Diprotic Buffers:

$$\mathrm{pH} = \mathrm{p}K_1 + \log\frac{[\mathrm{HA}^-]}{[\mathrm{H_2A}]} \quad \text{and/or} \quad \mathrm{pH} = \mathrm{p}K_2 + \log\frac{[\mathrm{A_2}^-]}{[\mathrm{HA}^-]}$$

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)*	$e_y = \lvert B \rvert$	$y = e^x$	$\frac{e_y}{y} = e_x$

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.

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

$\|z\|$[a]	y	Area[b]	$\|z\|$	y	Area	$\|z\|$	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.*

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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	$Li^+(aq) + e^- \rightarrow Li\,(s)$