CHEM 222 Exam 4

- You may begin the exam between 8:00 and 9:30 AM Wednesday, April 29, but you will have 90 ٠ minutes to complete the exam and upload scans of your work.
- You may use your book, notes, or online resources, but you MAY NOT receive assistance from anyone other than Dr. Lamp.
- Complete five (5) of the following problems on separate paper. There is no need to print out the exam. You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures. For discussion problems, be concise in your answers.
- Once you have completed the exam, scan your work as pdf and upload it to Blackboard. •
- Submission of your work is your pledge that the exam was completed ethically! Unethical work will result in a grade of zero on the exam and the Student Affairs office will be notified.
- Your exam materials must be uploaded by no more than 90 minutes after you begin the exam. • You may turn the exam in earlier if you wish.

K _w = 1.0 x 10 ⁻¹⁴ = [H ⁺][OH ⁻]	$K_a K_b = K_w$	F = 96485 C mol ⁻¹
$E = E^{O} - \frac{2.303RT}{nF} \log Q = E^{O} - \frac{0.05916V}{n} \log Q$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$	R = 8.31441 Jmol ⁻¹ K ⁻¹
$E = const. + \beta \left(\frac{0.05916V}{n}\right) log A_{ion}$	$\Delta G^{\circ} = -nFE^{\circ} = -RTInK$	A = abc = ε bc = -log T

Possibly Useful Information

values of α_{y4} for EDTA at 20°C and $\mu = 0.10$ M										
рН	α _{γ4-}	рН	α,4-	рН	α _{γ4-}					
0	1.3 x 10 ⁻²³	5	3.7 x 10 ⁻⁷	10	0.36					
1	1.9 x 10 ⁻¹⁸	6	2.3 x 10 ⁻⁵	11	0.85					
2	3.3 x 10 ⁻¹⁴	7	5.0 x 10 ⁻⁴	12	0.98					
3	2.6 x 10 ⁻¹¹	8	5.6 x 10 ⁻³	13	1.00					
4	3.8 x 10 ⁻⁹	9	5.4 x 10 ⁻²	14	1.00					

for CDTA at 20°C and 0 10 84

IA 1A 1 Hydrogen 1.008	2 11A 24					Peri	odic	Fable	of the	e Elen	nents	13 ША 34	14 IVA	15 VA 54	16 VIJ	5 17 A VIII	2 Helium 4.003
³ Li	⁴ Be											5 B	6 Carbon	7 N	° C) ^P Fluori	ne ¹⁰ Ne
6.941 11	9.012	ĺ										10.811	12.011	14.007	15.9	99 18.91 17	20.180 18
Na Sodium 22.990	Magnesium 24.305	3 ШВ 38	4 IVB 48	5 VB 58	6 VIB 6B	7 VIIB 7B	8		10	11 IB 1B	12 IIB 28	Aluminur 26.982	n Silicon 28.086	Phospho 30.974	rus Sulfi 32.0	ur Chlori 66 35.43	I Ar Argon 33 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 CO Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Znc 65.38	31 Gallium 69.723	32 Germania 72.631	m 33 Arsenia 74.922	34 Seleni 78.9	e Bromi 71 79.90	r ne 4 36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92,906	42 Mo Molybdenum 95.95	43 TC Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmiur 112,414	49 In Indium 114.818	50 Sn 118.711	51 Sb Antimor 121.76	y 52 Telluri 127	e I lum 126.9	ve 04 54 Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Thallium 204 383	B2 Pb Lead 207.2	83 Bi Bismut 208.98	84 Poloni [208.5	0 85 Astati 182] 209.9	t Rn Radon 87 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Darmstadtium [281]	111 Rg Roentgenium [280]	Copernicie [285]	m 113 Nihoniur [286]	114 Fl Fleroviur [289]	n 115 Moscovii [289]	am 116 Livermo	prium 3]	sine Dg Oganesson [294]
	Lanth Ser	anide ies	La Contraction 14	Ce rium 0.116 59 Prasec 14	Pr Sdymium 0.908	Id Prom	ethium 1.913	narium 50.36	Eu ropium 51.964	65 olinium 57.25	rbium 58.925	Dy ysprosium 162.500	Ho Holmium 164.930	Erbium 167.259	Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
	Actir Ser	nide ies A	Ac 1 27.028 90 Th 23	orium 2.038 91 Prota 23	Pa 92 L L L L L L L L L L L L L	J nium 1.029	Ip unium 7.048 94 Plu 24	Pu 95 Anium 4.064	Am 96 Ci 43.061 96 Ci 24	2000 97	Sk rkelium \$7.070	Cf alifornium 251.080	ES insteinium [254]	10 Fm Fermium 257.095	nd Md Iendelevium 258.1	102 No Nobelium 259.101	Lr Lawrencium [262]

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Complete five (5) of the following seven (7) problems. 16 points each

- 1. Consider the titration of 25.0 mL of 0.0255 M Cd(NO₃)₂ with 0.0120 M EDTA in a solution buffered at pH 9.00. (log K_f = 16.50 for the Cd²⁺-EDTA complex)
 - a. Calculate pCd²⁺ at two of the volumes below. (12 points)
 - At the equivalence point
 - At a volume half-way to the equivalence point
 - At a volume 11.0 mL after the equivalence point.

First locate the equivalence point:

	25.0 m l	-	Х	0.02	55 me	l Cd²	+	X	1 mol Y	4-	=		1 L		=	53.1 mL
					f			1	. mol C	²⁺		0.01	L20 m	ol ¥⁴-	_	
At the	equivale	nce	point:	[CdY ²	-] = (2	5.0 m	ıL x ().0255 r	nol/L)/(78.1	mL) =	0.008	816 M			
					C	Cd ²⁺	+	Y ⁴⁻	=	C	CdY²⁻					
					i	0		0		0.0	00816					
				(C	+x		+x			-X					
				(9	x		x		0.0	0816-x					
	K _f '	=	$\alpha_{\text{Y4-}}K_{\text{f}}$	= _	[CdY	′ ²⁻]	=	(0.054)	(10 ^{16.5})	=	1.71x	10 ¹⁵	= _0).00816	5-x	
					[Cd ²⁺]	[Y⁴⁻]								(x)(x)		
				Solv	ing fo	r x yie	elds	[Cd ²⁺] =	2.18 x	10 ⁻⁹ N	/l or pC	d = 8	.66			

Half-way to the equivalence point (26.6 mL): we will have consumed half of the (25.0x0.0255 = 0.6375 mmol) Cd^{2+} we started with, so 0.319 mmol remains in a total of 51.6 mL of solution. Since K is large, we can assume that the dissociation of CdY^{2-} is negligible.

0.319 mmol Cd²⁺x 1 =0.00618 M Cd²⁺ or, pCd = 2.21 25.0 + 26.6 mL

11.2 mL after the equivalence point: we will have 12.0 mL unreacted EDTA in a total of 25+53.1+11 = 89.1 mL solution.

$$\begin{split} [CdY^{2-}] &= (25.0 \text{ mL x } 0.0255 \text{ mol/L})/(89.2 \text{ mL}) = 0.00715_5 \text{ M} \\ [EDTA] &= (11.0 \text{ mL x } 0.0120 \text{ mol/L})/(89.1 \text{ mL}) = 0.00148_1 \text{ M} \\ &\quad Cd^{2+} + Y^{4-} = CdY^{2-} \\ &i & 0 & 0.00148_1 & 0.00715_5 \\ &c &+x &+x &-x \\ &e & x & 0.00148_1 + x & 0.00715_5 - x \\ &K_f' &= \alpha_{Y4-}K_f &= \underbrace{[CdY^{2-}]}_{[Cd^{2+}][Y^{4-}]} = (0.054)(10^{16.5}) = \underbrace{0.00715_5 - x}_{(x)(0.00148_1 + x)} \\ &Solving \text{ for x yields } [Cd^{2+}] = 2.82_5 \times 10^{-15} \text{ M or } \textbf{pCd} = \textbf{14.55} \end{split}$$

b. Given that the fraction of the EDTA present as Y⁴⁻ does not reach its maximum until pH is over 12 or so, why would we choose to run the titration at pH 9.00 instead? (4 points) Increasing the pH favors the formation of insoluble metal hydroxides, therefore, the titration must be run at a lower pH or we must use an auxiliary complexing agent to prevent hydroxide formation at higher pH.

2. In our magnesium determination in the laboratory, we added a solution made from ammonia and ammonium chloride to each sample prior to titrating with EDTA. Explain the two primary purposes served by the addition of this solution?

Your discussion should focus on the following two ideas:

- 1. In order for the titration to be effective, it is important to keep as much of the EDTA in its fully deprotonated for as is reasonable. Keeping the pH high results in a larger fraction of all EDTA present as Y⁴⁻. As a result, the conditional formation constant, K_f', will remain large.
- 2. At high pH, many metal ions form insoluble metal hydroxides or hydrous oxides. Should this happen, the analyte would precipitate out of solution and be unavailable for reaction with EDTA. Ammonia serves as an auxiliary complexing agent in the titration by forming a soluble magnesium complex. The tendency for ammonia to bind Mg²⁺ is greater than that for hydroxide, preventing the formation of magnesium hydroxide. However, EDTA binds more strongly than ammonia, allowing the titration reaction to occur.
- A 1.25 g sample of soil containing Cu²⁺ and Zn²⁺ and other nonmetals was digested in acid and diluted to a final volume of 50.00 mL. This solution was treated with 25.0 mL of 0.0452 M EDTA to bind all the metal. The excess <u>unreacted</u> EDTA required 12.4 mL of 0.0123 M Mg²⁺ for complete reaction. An excess of the reagent 2,3-dimercapto-1-propanol was then added to <u>displace the EDTA</u> <u>from zinc only</u>. Another 29.2 mL of Mg²⁺ were required for reaction with the liberated EDTA. Calculate the percent by weight of Cu²⁺ and percent by weight of Zn²⁺ in the original rock sample We need to figure out the mass of both metals in the sample.

25.0 mL x 0.0452 mol EDTA = 1.13 mmol EDTA delivered L

12.4 mL x 0.0123 mol Mg x 1 mol EDTA = 0.1525 mmol EDTA in excess L 1 mol Mg

So, (1.13 - 0.1525)mmol = 0.9775 mmol EDTA was used to bind all of the metal. Therefore, mol Zn²⁺ + mol Cu²⁺ = 0.9775 mmol

We can determine the amount of zinc from the magnesium titration:

So, the difference between the total moles metal and the moles zinc must correspond to the number of moles copper in the sample.

(0.9775 – 0.3592)mmol = 0.6183 mmol Cu²⁺

Now to determine percent composition:

If you have questions email <u>blamp@truman.edu</u> or click on <u>https://zoom.us/j/101470362</u> to Zoom.

4. Consider the electrochemical cell below:

Pt(s) | Br₂(*l*) | HBr (aq, 0.0500 M) || Cr(NO₃)₃ (aq, 0.200 M) | Cr(s)

- a. Calculate E_{cell} for the conditions given. (10 points)
 - **Reaction** (all species are aqueous unless noted) E° (volts) $Br_2(aq) + 2e^- = 2Br^-$ +1.098 $Br_2(\ell) + 2e^- = 2Br^-$ +1.078 $NO_3^- + 4H^+ + 3e^- = NO(g) + 2H_2O$ +0.955 $2H^+ + 2e^- = H_2(g)$ 0.000 $Cr^{3+} + 3e^{-} = Cr(s)$ -0.740 $Cr^{3+} + 3e^{-} = Cr(s)$ $E^{\circ} = -0.740 V$ Cathode: Anode: $Br_2(\ell) + 2e^- = 2Br^-$ E° = +1.078 V E° = -0.740 V - 1.078 V = -1.818 V Cell Rxn: $6Br^{-} + 2Cr^{3+} = 2Cr + 3Br_2$

Nernst equation for each half cell:

$$E_{anode} = +1.078 \text{ V} - \underline{0.05916 \text{ V} \log[\text{Br}^-]^2} = +1.078 \text{ V} - \underline{0.05916 \text{ V} \log[0.0500]^2} = +1.155 \text{ V}$$

$$E_{cathode} = -0.740 \text{ V} - \underline{0.05916 \text{ V} \log 1}_{3} = -0.740 \text{ V} - \underline{0.05916 \text{ V} \log 1}_{3} = -0.754 \text{ V}$$

 $E_{cell} = E_{cathode} - E_{anode} = (-0.754 - 1.155)V = -1.909 V$

Or, you could use the Nernst equation for the entire cell

E _{cell} =-1.818 V-0.05916 Vlog	1	=-1.818 V-0.05916 Vlog	. 1	= -1.909 V
6	[Cr ³⁺] ² [Br ⁻] ⁶	6	[0.200] ² [0.0500] ⁶	

Either approach is acceptable.

b. Is the reaction spontaneous in the direction written in part a? How do you know? (3 points) Since the cell potential is negative, the reaction is not spontaneous.

c. Is the reaction more favorable under standard conditions, or with the conditions given? How do you know? (3 points)

Since E is less negative and therefore ΔG less positive, the reaction is more favorable under standard conditions.

5. Given that $E^{\circ} = +0.796 \text{ V}$ for the reaction $\text{Hg}_2^{2^+}(aq) + 2e^- \Leftrightarrow 2\text{Hg}(\ell)$ and $K_{sp} = 1.2 \times 10^{-18}$ for $\text{Hg}_2\text{Cl}_2(s)$, calculate E for $\text{Hg}_2\text{Cl}_2(s) + 2e^- \Leftrightarrow \text{Hg}(\ell) + 2\text{Cl}^-(aq)$ under <u>standard conditions</u>.

There are several approaches to solving this problem. Here's one:

	Reaction	E°	K	ΔG^{o}
1	$\mathrm{Hg_2}^{2+}(aq) + 2e^{-} \Leftrightarrow 2\mathrm{Hg}(\ell)$	+0.796 V		$\Delta G^{o_1} = -nFE^{o_1}$
2	$Hg_2Cl_2(s) \Leftrightarrow Hg_2^{2+}(aq) + 2Cl^{-}(aq)^{-}$		1.2x10 ⁻¹⁸	$\Delta G^{o_2} = -RTInK$
Net = 1 +2	for $Hg_2Cl_2(s) + 2e^- \Leftrightarrow Hg(\ell) + 2Cl^-(aq)^-$	$E^{o}_1 + E^{o}_2$	K_1K_2	$\Delta G^{o}_{1} + \Delta G^{o}_{2}$

Since we can make our overall equation by summing the two components, we can determine the ΔG° for the reaction from the sum of the ΔG° s for the component reactions.

 $\Delta G^{\circ}_{1} = -nFE^{\circ} = -(2 \text{ mol e}^{-})(96485 \text{ coul/mole e}^{-})(+0.796V) = -153,604 \text{ J}$

 $\Delta G^{\circ}_{2} = -RTlnK = -(8.31441 J/mol K)(298K)ln(1.2x10^{-18}) = 102,240 J$

 $\Delta G^{\circ}_{net} = \Delta G^{\circ}_{1} + \Delta G^{\circ}_{2} = 102240 \text{ J} + (-153604 \text{ J}) = -51364 \text{ J}$

 $E^{o}_{net} = \Delta G^{o}_{net}/(-nF) = -51364 J/[-(2 mol e^{-})(96485 coul/mole e^{-})] = +0.266 V$

Another approach would be to convert everything to K's and realize that $K_{net} = K_1 \times K_2$:

For an equilibrium: $-nFE^{\circ} = -RTIn K = -2.303RTlog K$ So, for this equilibrium at standard temperature: $logK_1 = (-nFE^{\circ}_1)/(-2.303RT) = 26.92$ $K_{net} = K_1K_2 = (10^{26.92})(1.2x10^{-18}) = 9.98x10^8$

Then $E^{\circ}_{net} = (2.303 \text{RT/nF})\log K = (0.05916 \text{V}/2)\log(9.98 \times 10^8) = +0.266 \text{V}$

Yet another approach would be to determine the $[Hg_2^{2+}]$ from the K_{sp} under standard conditions and insert that into the Nernst equation for the redox reaction

	Hg ₂ Cl ₂ (s)	⇔	Hg ₂ ²⁺ (<i>aq</i>)	+	2Cl ⁻ (aq) ⁻
I.			0		1.00 M
С			+x		+ 2x
Е			x		1.00 + 2x

 $K_{sp} = [Hg_2^{2+}][Cl^-]^2 = x(1.00+2x)^2$ but since K_{sp} is so small, we may assume 2x<<1 so that: $K_{sp} = x(1.00)^2$ or $x = [Hg_2^{2+}] = 1.2x10^{-18}$ M

For the redox reaction, the Nernst equation is:

$$\mathbf{E} = +0.796 \, \text{V} - \underbrace{0.05916 \, \text{V}}_{2} \log \underbrace{1}_{[\text{Hg}_2^{2^+}]} = +0.266 \, \text{V}$$

6. You need to do a pH measurement and have a pH electrode, pH 4.00, 7.00, and 10.00 buffers, but <u>no pH meter</u>! You do, however, have access to a voltmeter capable of measuring potential differences at the millivolt level. Using these materials, describe how you could determine the pH of an unknown aqueous solution. Include a description of how you would collect the data and how you would use the data to find the pH of your unknown. (*hint: a pH electrode is an ISE for H⁺*)

In your description, you should address the following items.

- 1. Connect the leads of the pH electrode to the voltmeter.
- 2. Measure E_{cell} for each buffer. (You should briefly describe how this is done)
- 3. Plot E_{cell} vs pH, you should expect a straight line with a slope of ~59mV/pH unit. (Why should this relationship be linear?)
- 4. Measure E_{cell} for the unknown and extract the unknown pH from your calibration curve.
- 7. Consider a spectrophotometry experiment like we did for the iron lab. Address the following items.
 - a. How is an appropriate wavelength chosen for an absorbance measurement? Why is this choice made? (4 points) (*limit your response to three sentences or less*)
 You should talk about collecting a spectrum to determine the wavelength of maximum absorbance. At this wavelength, the measurement will be most sensitive as a small change in concentration will correspond to a larger change in absorbance. You might also mention that it is best if no other species in solution absorb at the chosen wavelength.
 - b. Why is a blank used in the measurement process? (4 points) (*limit your response to three sentences or less*)
 A blank is used to let the instrument know the response when no light is being absorbed. Since absorbance is a ratio, this measurement is critical.
 - c. How is the concentration of an unknown solution determined? What data is collected and how is it treated? (8 points)
 You should talk about making a series of standards, measuring their absorbance and plotting absorbance as a function of concentration to see the Beer's law relationship, and determine the slope and intercept. From the relationship and the absorbance of an unknown, the concentration of the unknown can be determined.