

Bonus (5 points):

Monday, Dr. Lamp wrote a potential on the board at 8:30 AM as he started class and said that the potential would be an answer to one of the exam 4 questions. What potential did he put on the board?

Complete five (5) of the following problems. Each problem is worth 16 points. CLEARLY mark the problem you do not want graded. You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures.

1. Outline an experiment for the determination of Ca^{2+} using a calcium ion-selective electrode. If the suspected $[\text{Ca}^{2+}]$ is ~ 0.0030 M, describe (qualitatively) how you would prepare a calibration curve given a standard solution of Ca^{2+} (~ 1.0 M)? Assume you have a well-stocked laboratory and a collection of salts, acids, and bases to work with. Sketch (qualitatively) how the calibration curve should appear. Include an estimate of the slope you would expect.

2. A 50.0 mL sample containing Cd^{2+} and Mn^{2+} was treated with 70.0 mL of 0.0500 M EDTA. Titration of the excess unreacted EDTA required 18.5 mL of 0.0200 M Ca^{2+} . The Cd^{2+} was displaced from EDTA by the addition of an excess of CN^- . Titration of the newly freed EDTA required 13.1 mL of 0.0200 M Ca^{2+} .
- (a) What were the molarities of Cd^{2+} and Mn^{2+} in the original solution? (12 points)

- (b) For this analysis to be successful, what must be true about the relative sizes of the formation constants for the Cd-EDTA and Mn-EDTA complexes compared to the formation constant for Ca-EDTA? (4 points)

3. Given your unnatural passion for analytical chemistry, you have been given the task of explaining to a new quant student, Irma Dorque, the fundamentals of pH measurement with a pH electrode.
- (a) Briefly describe the key components of a pH electrode and how it functions. (10 points)

- (b) Identify at least three potential problems that may occur when making a pH measurement and how to avoid them. (6 points)

4. Consider a solution containing 1.0 M $\text{Pb}(\text{NO}_3)_4$, 1.0 M $\text{Pb}(\text{NO}_3)_2$, 1.0 M KMnO_4 , 1.0 M $\text{Mn}(\text{NO}_3)_2$ and 1.0 M HNO_3 . For this solution, the following unbalanced reduction half-reactions occur.



- (a) Write the balanced reaction that occurs spontaneously in this solution. (6 points)

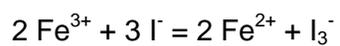
- (b) What is the E° for the reaction. (4 points)

- (c) What is the cell potential for the reaction if the solution is instead 0.15 M $\text{Pb}(\text{NO}_3)_2$, 1.5×10^{-6} M $\text{Pb}(\text{NO}_3)_4$, 1.5×10^{-6} M $\text{Mn}(\text{NO}_3)_2$, 0.15 M KMnO_4 , and 0.83 M HNO_3 ? Is this more spontaneous or less spontaneous than under standard conditions? (6 points)

5. (a) Calculate pCa^{2+} at **TWO** of the following points in the titration of 50.00 mL of 0.0400 M Ca^{2+} with 0.0800 M EDTA at a pH 10.00: (for Ca-EDTA, $\log K_f = 10.65$) (12 points)
- At the equivalence point
 - 10.00 mL prior to the equivalence point
 - 10.00 mL after the equivalence point

(b) How would the volume at the equivalence point compare if you had titrated 0.0400 M Al^{3+} instead of Ca^{2+} ? (6 points)

6. Calculate the equilibrium constant for the reaction shown below using standard reduction potentials from the table.



Reaction	Standard Reduction Potential
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.771 V
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe(s)}$	-0.440 V
$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.535 V
$\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$	+0.535 V

Possibly Useful Information

$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$E = E^0 - \frac{2.303RT}{nF} \log Q = E^0 - \frac{0.05916V}{n} \log Q$	$\Delta G^0 = -nFE^0 = -RT \ln K$
$F = 96485 \text{ C mol}^{-1}$	$R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$
$E = \text{const} + \beta \left(\frac{0.05916V}{n} \right) \log A_{\text{ion}}$	$y = mx + b, \quad m = \frac{\Delta y}{\Delta x}$

Values of α_{y4-} for EDTA at 20°C and $\mu = 0.10 \text{ M}$

pH	α_{y4-}	pH	α_{y4-}	pH	α_{y4-}
0	1.3×10^{-23}	5	3.7×10^{-7}	10	0.36
1	1.9×10^{-18}	6	2.3×10^{-5}	11	0.85
2	3.3×10^{-14}	7	5.0×10^{-4}	12	0.98
3	2.6×10^{-11}	8	5.6×10^{-3}	13	1.00
4	3.8×10^{-9}	9	5.4×10^{-2}	14	1.00

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	INERT GASES			
1 H 1.00797														1 H 1.00797	2 He 4.0026				
3 Li 6.939	4 Be 9.0122													5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312													13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80		
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30		
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra (226)	*89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)								

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
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† Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)
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