

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 as well as a voltmeter and reference electrode. Sketch (qualitatively) how the calibration curve should appear. Include an estimate of the slope you would expect.

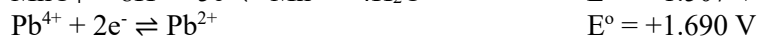
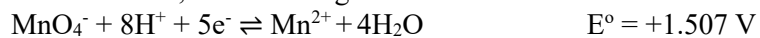
2. A 50.0 mL sample containing Cd^{2+} and Mn^{2+} was treated with 70.0 mL of 0.0500 M EDTA. Titration of the excess unreacted EDTA required 18.5 mL of 0.0200 M Ca^{2+} . The Cd^{2+} was displaced from EDTA by the addition of an excess of CN^- . Titration of the newly freed EDTA required 13.1 mL of 0.0200 M Ca^{2+} . You may assume that each of the titration reactions goes to completion.
- (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 reduction half-reactions occur.



- (a) Write the balanced reaction that occurs spontaneously in this solution. (4 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? (8 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+} ? (4 points)

Possibly Useful Information

$K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$	$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$E = E^{\circ} - \frac{2.303RT}{nF} \log Q = E^{\circ} - \frac{0.05916V}{n} \log Q$	$\Delta G^{\circ} = -nFE^{\circ} = -RT \ln K$
$F = 96485 \text{ C mol}^{-1}$	$R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$
$E = \text{const} + \beta \left(\frac{0.05916V}{n} \right) \log A_{\text{ion}}$	$y = mx + b, \quad m = \frac{\Delta y}{\Delta x}$
$N = L/H$	$H = \frac{\sigma^2}{L} = L \left(\frac{W}{4t_R} \right)^2$
$N = \left(\frac{4t_R}{W} \right)^2 = \left(\frac{2.35t_R}{W_{1/2}} \right)^2$	$H \approx A + \frac{B}{u} + Cu$

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 Table of the Elements

1A 1 H Hydrogen 1.008	2 IIA 2A Li Lithium 6.941	3 IIIB 3B Be Beryllium 9.012	4 IVB 4B Na Sodium 22.990	5 VB 5B Mg Magnesium 24.305	6 VIB 6B Sc Scandium 44.956	7 VIIB 7B Ti Titanium 47.867	8 VIII 8 V Vanadium 50.942	9 VIII 9 Cr Chromium 51.996	10 VIII 10 Mn Manganese 54.938	11 IB 11 Fe Iron 55.845	12 IIB 12 Co Cobalt 58.933	13 IIIB 13 Ni Nickel 58.693	14 IVB 14 Cu Copper 63.546	15 VB 15 Zn Zinc 65.38	16 VIB 16 Al Aluminum 26.982	17 VIIB 17 Si Silicon 28.086	18 VIIIB 18 P Phosphorus 30.974	19 VIIIB 19 S Sulfur 32.066	20 VIIIB 20 Cl Chlorine 35.453	21 VIIIB 21 Ar Argon 39.948	22 VIIIB 22 K Potassium 39.098	23 VIIIB 23 Ca Calcium 40.078	24 VIIIB 24 Sc Scandium 44.956	25 VIIIB 25 Ti Titanium 47.867	26 VIIIB 26 V Vanadium 50.942	27 VIIIB 27 Cr Chromium 51.996	28 VIIIB 28 Mn Manganese 54.938	29 VIIIB 29 Fe Iron 55.845	30 VIIIB 30 Co Cobalt 58.933	31 VIIIB 31 Ni Nickel 58.693	32 VIIIB 32 Cu Copper 63.546	33 VIIIB 33 Zn Zinc 65.38	34 VIIIB 34 Ga Gallium 69.723	35 VIIIB 35 Ge Germanium 72.631	36 VIIIB 36 As Arsenic 74.922	37 VIIIB 37 Se Selenium 78.971	38 VIIIB 38 Br Bromine 79.904	39 VIIIB 39 Kr Krypton 83.798	40 VIIIB 40 Rb Rubidium 85.468	41 VIIIB 41 Sr Strontium 87.62	42 VIIIB 42 Y Yttrium 88.906	43 VIIIB 43 Zr Zirconium 91.224	44 VIIIB 44 Nb Niobium 92.906	45 VIIIB 45 Mo Molybdenum 95.95	46 VIIIB 46 Tc Technetium 98.907	47 VIIIB 47 Ru Ruthenium 101.07	48 VIIIB 48 Rh Rhodium 102.906	49 VIIIB 49 Pd Palladium 106.42	50 VIIIB 50 Ag Silver 107.868	51 VIIIB 51 Cd Cadmium 112.414	52 VIIIB 52 In Indium 114.818	53 VIIIB 53 Sn Tin 118.711	54 VIIIB 54 Sb Antimony 121.760	55 VIIIB 55 Te Tellurium 127.6	56 VIIIB 56 I Iodine 126.904	57 VIIIB 57 Xe Xenon 131.294	58 VIIIB 58 Cs Cesium 132.905	59 VIIIB 59 Ba Barium 137.328	60 VIIIB 60 La Lanthanum 138.905	61 VIIIB 61 Ce Cerium 140.116	62 VIIIB 62 Pr Praseodymium 140.908	63 VIIIB 63 Nd Neodymium 144.243	64 VIIIB 64 Pm Promethium 144.913	65 VIIIB 65 Sm Samarium 150.36	66 VIIIB 66 Eu Europium 151.964	67 VIIIB 67 Gd Gadolinium 157.25	68 VIIIB 68 Tb Terbium 158.925	69 VIIIB 69 Dy Dysprosium 162.500	70 VIIIB 70 Ho Holmium 164.930	71 VIIIB 71 Er Erbium 167.259	72 VIIIB 72 Tm Thulium 168.934	73 VIIIB 73 Yb Ytterbium 173.055	74 VIIIB 74 Lu Lutetium 174.967	75 VIIIB 75 Ac Actinium 227.028	76 VIIIB 76 Th Thorium 232.038	77 VIIIB 77 Pa Protactinium 231.036	78 VIIIB 78 U Uranium 238.029	79 VIIIB 79 Np Neptunium 237.048	80 VIIIB 80 Pu Plutonium 244.064	81 VIIIB 81 Am Americium 243.061	82 VIIIB 82 Cm Curium 247.070	83 VIIIB 83 Bk Berkelium 247.070	84 VIIIB 84 Cf Californium 251.080	85 VIIIB 85 Es Einsteinium [254]	86 VIIIB 86 Fm Fermium 257.095	87 VIIIB 87 Md Mendelevium 258.1	88 VIIIB 88 No Nobelium 259.101	89 VIIIB 89 Lr Lawrencium [262]
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