

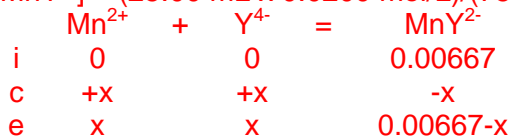
Complete five (5) of the following problems. Each problem is worth 16 points. CLEARLY mark the problems you do not want graded. You must show your work to receive credit for problems requiring math. Report your answers with the appropriate number of significant figures.

1. Consider the titration of 25.0 mL of 0.0200 M MnSO_4 with 0.0100 M EDTA in a solution buffered at pH 8.00. ($\log K_f = 13.89$ for MnY^{2-})
- a. Calculate pMn^{2+} at two of the volumes below. (12 points)
- At the equivalence point
 - 10 mL before the equivalence point
 - 10 mL after the equivalence point.

First locate the equivalence point:

$$25.00 \text{ mL} \times \frac{0.0200 \text{ mol Mn}^{2+}}{\text{L}} \times \frac{1 \text{ mol Y}^{4-}}{1 \text{ mol Mn}^{2+}} = \frac{1 \text{ L}}{0.0100 \text{ mol Y}^{4-}} = 50.00 \text{ mL}$$

At the equivalence point: $[\text{MnY}^{2-}] = (25.00 \text{ mL} \times 0.0200 \text{ mol/L}) / (75.00 \text{ mL}) = 0.00667 \text{ M}$



$$K_f' = \alpha_{\text{Y}^{4-}} K_f = \frac{[\text{MnY}^{2-}]}{[\text{Mn}^{2+}][\text{Y}^{4-}]} = (0.0056)(7.76 \times 10^{13}) = \frac{0.00667-x}{(x)(x)}$$

Solving for x yields $[\text{Mn}^{2+}] = 1.24 \times 10^{-7} \text{ M}$ or **pMn = 6.90**

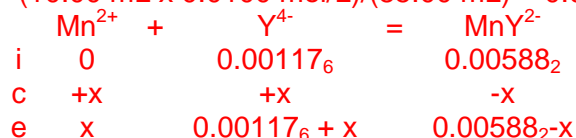
10 mL before the equivalence point: we will have consumed 4/5 of the Mn^{2+} , so 1/5 remains. Since K is large, we can assume that the dissociation of MnY^{2-} is negligible.

$$25.00 \text{ mL} \times \frac{0.0200 \text{ mol Mn}^{2+}}{\text{L}} \times \frac{1}{5} = 0.001538 \text{ M Mn}^{2+} \text{ or, pMn} = 2.81$$

10 mL after the equivalence point: we will have 10 mL extra EDTA.

$$[\text{MnY}^{2-}] = (25.00 \text{ mL} \times 0.0200 \text{ mol/L}) / (85.00 \text{ mL}) = 0.00588_2 \text{ M}$$

$$[\text{EDTA}] = (10.00 \text{ mL} \times 0.0100 \text{ mol/L}) / (85.00 \text{ mL}) = 0.00117_6 \text{ M}$$



$$K_f' = \alpha_{\text{Y}^{4-}} K_f = \frac{[\text{MnY}^{2-}]}{[\text{Mn}^{2+}][\text{Y}^{4-}]} = (0.0056)(7.76 \times 10^{13}) = \frac{0.00588_2-x}{(x)(0.00117_6 + x)}$$

Solving for x yields $[\text{Mn}^{2+}] = 1.16 \times 10^{-11} \text{ M}$ or **pMn = 10.94**

- b. Given that the fraction of the EDTA present as Y^{4-} does not reach its maximum until pH is over 12 or so, why would we choose to run the titration at pH 8.00 instead? (4 points)
- Increasing the pH favors the formation of insoluble metal hydroxides, therefore, the titration must be run at a higher pH or we must use an auxiliary complexing agent to prevent hydroxide formation at higher pH.

2. A 50.00 mL solution containing Ni^{2+} and Zn^{2+} was treated with 25.0 mL of 0.0452 M EDTA to bind all the metal. The excess unreacted EDTA required 12.4 mL of 0.0123 M Mg^{2+} for complete reaction. An excess of the reagent 2, 3-dimercapto-1-propanol was then added to displace the EDTA from zinc. Another 29.2 mL of Mg^{2+} were required for reaction with the liberated EDTA. Calculate the molarity of Ni^{2+} and the molarity of Zn^{2+} in the original solution.

This is problem 11-36 from the book.

$$25.0 \text{ mL} \times \frac{0.0452 \text{ mol EDTA}}{\text{L}} = 1.13 \text{ mmol EDTA delivered}$$

$$12.4 \text{ mL} \times \frac{0.0123 \text{ mol Mg}}{\text{L}} \times \frac{1 \text{ mol EDTA}}{1 \text{ mol Mg}} = 0.1525 \text{ mmol EDTA in excess}$$

So, $(1.13 - 0.1525) \text{ mmol} = 0.9775 \text{ mmol EDTA}$ was used to bind all of the metal. Therefore, $\text{mol Zn}^{2+} + \text{mol Ni}^{2+} = 0.9775 \text{ mmol}$

$$29.2 \text{ mL} \times \frac{0.0123 \text{ mol Mg}}{\text{L}} \times \frac{1 \text{ mol EDTA}}{1 \text{ mol Mg}} \times \frac{1 \text{ mol Zn}^{2+}}{1 \text{ mol EDTA}} = 0.3592 \text{ mmol Zn}^{2+}$$

$$[\text{Zn}^{2+}] = 0.3592 \text{ mmol}/50.00 \text{ mL} = \mathbf{0.00718 \text{ M Zn}^{2+}}$$

$$(0.9775 - 0.3592) \text{ mmol} = 0.6183 \text{ mmol Ni}^{2+}$$

$$[\text{Ni}^{2+}] = 0.6183 \text{ mmol}/50 \text{ mL} = \mathbf{0.0124 \text{ M Ni}^{2+}}$$

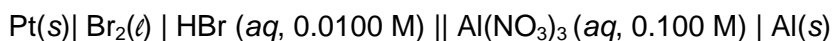
3. In our magnesium determination in the laboratory, we added a solution made from ammonia and ammonium chloride to each sample prior to titrating with EDTA. Explain what two primary purposes the addition of this solution served?

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 form as is reasonable. Keeping the pH high results in a larger fraction of all EDTA present as Y^{4-} . 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 Mg^{2+} 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.

4. You need to do a pH measurement and have a pH electrode, pH 4.00, 7.00, and 10.00 buffers, but no pH meter! 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.
 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 $\sim 59\text{mV/pH}$ unit. (Why should this relationship be linear?)
 4. Measure E_{cell} for the unknown and extract the unknown pH from your calibration curve.

5. Consider the electrochemical cell below:



Reaction (all species are aqueous unless noted)	E° (volts)
$\text{Br}_2(\text{aq}) + 2\text{e}^- = 2\text{Br}^-$	+1.098
$\text{Br}_2(\ell) + 2\text{e}^- = 2\text{Br}^-$	+1.078
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- = \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	+0.955
$\text{AgCl} + \text{e}^- = \text{Ag}(\text{s}) + \text{Cl}^-$	+0.199 (sat'd KCl)
$2\text{H}^+ + 2\text{e}^- = \text{H}_2(\text{g})$	0.000
$\text{Al}^{3+} + 3\text{e}^- = \text{Al}(\text{s})$	-1.677

a. Calculate E_{cell} for the conditions given. (8 points)



Nernst equation for each half cell:

$$E_{\text{anode}} = +1.078 \text{ V} - \frac{0.05916 \text{ V}}{2} \log[\text{Br}^-]^2 = +1.078 \text{ V} - \frac{0.05916 \text{ V}}{2} \log[0.0100]^2 = +1.196 \text{ V}$$

$$E_{\text{cathode}} = -1.677 \text{ V} - \frac{0.05916 \text{ V}}{3} \log \frac{1}{[\text{Al}^{3+}]} = -1.677 \text{ V} - \frac{0.05916 \text{ V}}{3} \log \frac{1}{[0.100]} = -1.697 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = (-1.697 - 1.196) \text{ V} = -2.893 \text{ V}$$

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

$$E_{\text{cell}} = -2.755 \text{ V} - \frac{0.05916 \text{ V}}{6} \log \frac{1}{[\text{Al}^{3+}]^2 [\text{Br}^-]^6} = -2.755 \text{ V} - \frac{0.05916 \text{ V}}{6} \log \frac{1}{[0.100]^2 [0.0100]^6} = -2.893 \text{ V}$$

Either approach is acceptable.

b. Is the reaction spontaneous in the direction written in part a? How do you know? (2 points)

Since the cell potential is negative, the reaction is not spontaneous.

c. Calculate the standard free energy change (ΔG°) and the free energy change (ΔG) for the conditions given. (3 points)

$$\Delta G^\circ = -nFE^\circ = -(6 \text{ mol e}^-)(96485 \text{ C/mole})(-2.755 \text{ V}) = +1,595,000 \text{ J} = +1,595 \text{ kJ}$$

$$\Delta G = -nFE = -(6 \text{ mol e}^-)(96485 \text{ C/mole})(-2.893 \text{ V}) = +1,675,000 \text{ J} = +1,675 \text{ kJ}$$

d. 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 ΔG less positive, the reaction is more favorable under standard conditions.

6. Calculate the E° for the half reaction $\text{Pd}(\text{OH})_2(\text{s}) + 2\text{e}^- = \text{Pd}(\text{s}) + 2\text{OH}^-$ given that the K_{sp} for $\text{Pd}(\text{OH})_2$ is 3.0×10^{-28} and the $E^\circ = +0.915 \text{ V}$ for $\text{Pd}^{2+} + 2\text{e}^- = \text{Pd}(\text{s})$.

This is problem 13-28 from the text. There are several approaches to solving this problem. Here's one:

	Reaction	E°	K	ΔG°
1	$\text{Pd}^{2+} + 2\text{e}^- = \text{Pd}(\text{s})$	+0.915 V		$\Delta G^\circ_1 = -nFE^\circ =$
2	$\text{Pd}(\text{OH})_2(\text{s}) = \text{Pd}^{2+} + 2\text{OH}^-$		3.0×10^{-28}	$\Delta G^\circ_2 = -RT \ln K =$
Net = 1 +2	$\text{Pd}(\text{OH})_2(\text{s}) + 2\text{e}^- = \text{Pd}(\text{s}) + 2\text{OH}^-$			$\Delta G^\circ_{\text{net}} = \Delta G^\circ_1 + \Delta G^\circ_2$

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.

$$\Delta G^\circ_1 = -nFE^\circ = -(2 \text{ mol e}^-)(96485 \text{ coul/mol e}^-)(+0.915\text{V}) = -176,568 \text{ J}$$

$$\Delta G^\circ_2 = -RT \ln K = -(8.31441 \text{ J/mol K})(298\text{K}) \ln(3.0 \times 10^{-28}) = 157,021 \text{ J}$$

$$\Delta G^\circ_{\text{net}} = \Delta G^\circ_1 + \Delta G^\circ_2 = 157021 \text{ J} + (-176568 \text{ J}) = -19,547 \text{ J}$$

$$E^\circ_{\text{net}} = \Delta G^\circ_{\text{net}} / (-nF) = -19547 \text{ J} / [-(2 \text{ mol e}^-)(96485 \text{ coul/mol e}^-)] = \mathbf{+0.101_3 \text{ V}}$$

Another approach would be to convert everything to potentials and realize that $E^\circ_{\text{net}} = E^\circ_1 + E^\circ_2$:

For an equilibrium: $-nFE^\circ = -RT \ln K = -2.300RT \log K$

So, for this equilibrium at standard temperature:

$$E^\circ_2 = (0.05916/n) \log K_{\text{sp}}$$

$$E^\circ_2 = (0.05916/2) \log (3.0 \times 10^{-28}) = -0.814 \text{ V}$$

$$\text{Then } E^\circ_{\text{net}} = E^\circ_1 + E^\circ_2 = +0.915\text{V} + (-0.814\text{V}) = \mathbf{+0.101\text{V}}$$

Bonus (5 points):

One day last week, 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? **+1.14 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	VIIIB	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 (261)	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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