

CHEM 121
Spring 2006
Pre-Exam Assignment 3

Name: _____

Instructions

Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't grade it.

Show all work for full credit! For the word problems write your final answer in a complete sentence. Indicate what you are doing at important steps (you do not need to tell me about every mathematical manipulation you do). If you change your mind on a question, cross out the incorrect answer and clearly indicate your final answer.

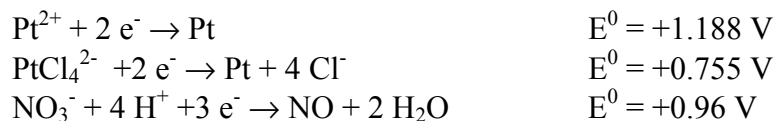
There are **8** pages, none blank.

You may use your book to look up any needed physical constants, equations, etc. However, you may not work with anyone else, and you may not ask any other faculty members to help you with the specific questions given here. You may ask any chemistry faculty member for help on the concepts involved, and you may ask me anything you want.

You may use the back of any page as additional workspace. Please indicate that you have done so.

Problem	Possible Points	Points Received
1	5	
2	20	
3	7	
4	10	
5	17	
6	20	
Free	21	21
Total	100	
	Bonus	
	Grand Total	

1. (5 Points) Explain why platinum will dissolve in *aqua regia* (a mixture of hydrochloric and nitric acids), but not in either concentrated nitric or concentrated hydrochloric acid individually.



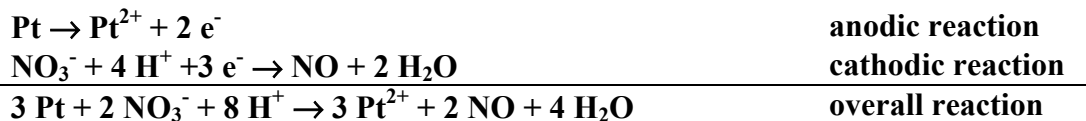
We want the Pt to dissolve, and to do this it must be the anode (Pt is oxidized to Pt²⁺). In hydrochloric acid, this means that the following reactions occur. Note that in the presence of Cl⁻ the “Pt/Pt²⁺” couple is shifted to lower potential because the PtCl₄²⁻ complex ion is formed.



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.000 \text{ V} - 1.188 \text{ V} = -1.188 \text{ V}$$

This reaction is not spontaneous.

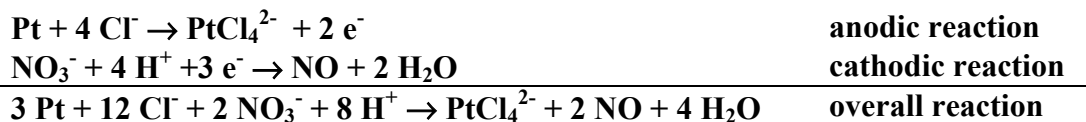
In nitric acid there is no Cl⁻ to complex with the Pt²⁺, so we will use the first reaction to describe how the Pt reacts (still at the anode). Nitrate ion must then be reduced at the cathode, and the reactions that occur at each electrode are as follows.



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.96 \text{ V} - 1.188 \text{ V} = -0.23 \text{ V}$$

This reaction is also not spontaneous

In a mixture of hydrochloric and nitric acids, the Cl⁻ complexes the Pt²⁺ and thus shifts the reduction potential. It is then possible for NO₃⁻ to serve as the oxidant; driving the oxidation of Pt (and thereby dissolving Pt). The relevant reactions are



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.96 \text{ V} - 0.755 \text{ V} = +0.21 \text{ V}$$

Since the potential for Pt reacting in an acidic solution containing both Cl⁻ and NO₃⁻ to give PtCl₄²⁻ is positive, Pt will dissolve in *aqua regia*.

2. One can buy a Ag/AgCl reference electrode like that shown in Figure 1, below. The electrode contains a Ag wire coated with solid AgCl and a saturated KCl solution inside the body of the electrode. A glass frit serves as the salt bridge to the test solution.

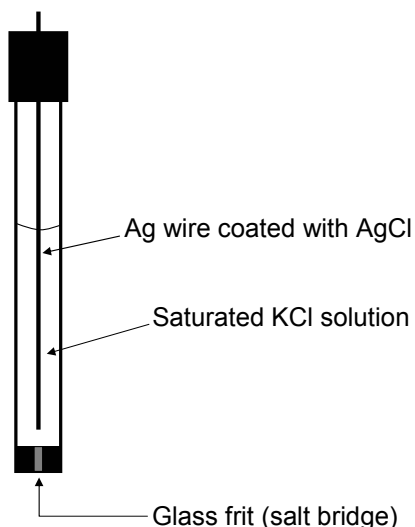


Figure 1. The Ag/AgCl reference electrode

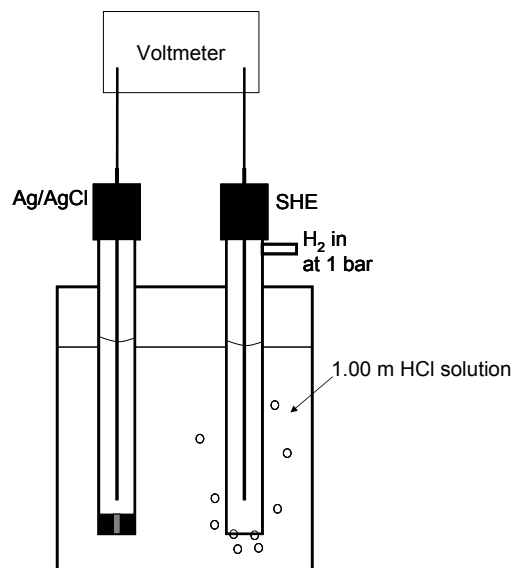
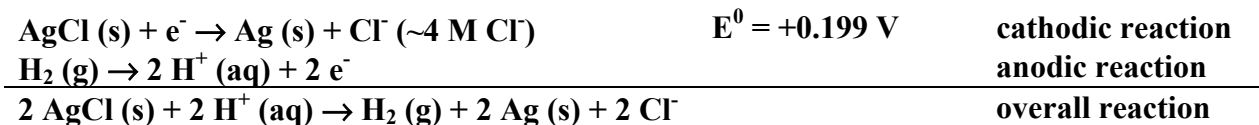
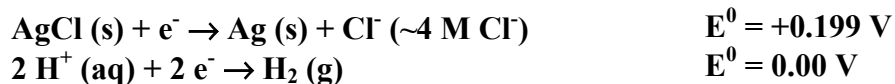


Figure 2. The Ag/AgCl reference electrode in a galvanic cell with the SHE.

a. (5 Points) Write the half reactions and balanced chemical reaction that describe the cell shown in Fig. 2 where the Ag/AgCl electrode is one half-cell and the SHE electrode is the other half-cell. Identify the anode and the cathode and determine the potential that the voltmeter will read.

We will assume that the convention of having the anode on the left is followed in this problem. *Note that we don't always have to have the anode on the left!*

The relevant standard reduction potentials are

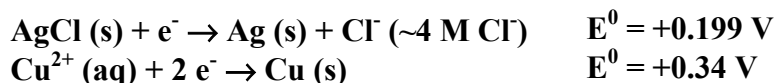


$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.199 \text{ V} - 0.00 \text{ V} = +0.199 \text{ V}$$

The Ag/AgCl electrode will function as the cathode and the SHE will be the anode. Since we have the anode and cathode reversed from the standard configuration, the electrons will flow from the SHE to the Ag/AgCl electrode; the exact opposite of how we set the meter up. Therefore, the voltmeter will read -0.199 V. This makes sense because the potential for the SHE is more negative than that of the Ag/AgCl electrode.

b. (5 Points) If the solution in Fig. 2 is replaced by a 1.00 M CuCl_2 solution (with HCl as the supporting electrolyte) and the SHE is replaced by a Cu electrode, what will the meter read?

The relevant standard reduction potentials are



Since E^0 for the Cu/Cu^{2+} redox couple is more positive than that of the Ag/AgCl electrode, the Cu electrode will be the cathode and the Ag/AgCl will be the anode. Because we have switched the identity of the Ag/AgCl electrode the electrons will flow in the opposite direction than in part a and the voltmeter will read the opposite sign.

The potential for the cell will be

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.34 \text{ V} - 0.199 \text{ V} = +0.14 \text{ V}$$

The meter will read +0.14 V. *Again this should make sense because the Cu/Cu^{2+} redox couple's potential is more positive than that of the Ag/AgCl reference electrode.*

c. (10 Points) What will the meter read when the solution in part b is replaced by a 1.00 M CuCl_2 solution buffered at pH 8.00?

The K_{sp} of $\text{Cu}(\text{OH})_2$ is 1.6×10^{-19} . So, it is likely that any Cu^{2+} solution that we would try to make at pH 8.00 will result in most of the Cu^{2+} sitting on the bottom as $\text{Cu}(\text{OH})_2$ and very little Cu^{2+} in solution.

Calculate Q to see if precipitation will occur.

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 8.00 = 6.00$$

$$[\text{OH}^-] = 1.0 \times 10^{-6} \text{ M}$$

$$Q = [\text{Cu}^{2+}][\text{OH}^-]^2 = (1.00 \text{ M})(1.0 \times 10^{-6})^2 = 1.0 \times 10^{-12}$$

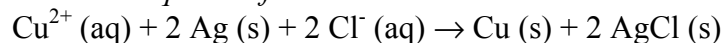
Since $Q > K$, precipitation will occur.

Determine the amount of Cu^{2+} remaining in solution when the $[\text{OH}^-] = 1.0 \times 10^{-6} \text{ M}$.

$$K_{\text{sp}} = (x)(1.0 \times 10^{-6})^2 = 1.6 \times 10^{-19}$$

$$x = 1.6 \times 10^{-7} \text{ M}$$

Set up the Nernst equation for the cell. The cell's overall reaction is:



$$E = E^{\circ} - \frac{RT}{nF} \ln Q = -0.14 \text{ V} - \frac{(8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15 \text{ K})}{(2)(96485 \text{ C} \cdot \text{mole}^{-1})} \ln \left(\frac{1}{[\text{Cu}^{2+}][\text{Cl}^{-}]^2} \right)$$

Note that we can eliminate the $[\text{Cl}^{-}]$ from the Nernst equation because it was already accounted for the standard potential of the Ag/AgCl electrode (remember it is a secondary reference electrode). We can also use the properties of logarithms to move the $[\text{Cu}^{2+}]$ from the denominator to the numerator.

$$E = E^{\circ} - \frac{RT}{nF} \ln Q = -0.14 \text{ V} + \frac{(8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15 \text{ K})}{(2)(96485 \text{ C} \cdot \text{mole}^{-1})} \ln(1.6 \times 10^{-7})$$

$$E = -0.14 \text{ V} + (0.01284_{\text{6}} \text{ V})(15.64_{\text{8}})$$

$$E = +0.14 \text{ V} - 0.2010 \text{ V} = -0.06 \text{ V}$$

The meter will read -0.06 V.

3. (7 Points) What is the molarity of a saturated solution of O_2 in water at an O_2 pressure of 1.00 atm and a temperature of 298.15 K? Assume that O_2 when dissolved in water obeys Henry's law and that the density of water is 1.00 g/cm^3 .

Henry's Law is $P = k_H \chi$. Rearrange this to solve for χ , which gives the following.

$$\chi_{\text{O}_2} = \frac{P}{k_H} = \frac{1.00 \text{ atm}}{4.34 \times 10^4 \text{ atm}} = 2.30_4 \times 10^{-5}$$

The mole fraction of O_2 is moles of O_2 divided by the total number of moles ($\text{O}_2 + \text{H}_2\text{O}$) present in the solution. With the small mole fraction for O_2 , we can assume that the total number of moles is approximately equal to the moles of H_2O . The mole fraction can then be written as shown below and converted to molarity.

$$\left(\frac{2.30_4 \times 10^{-5} \text{ mole O}_2}{1.00 \text{ mole H}_2\text{O}} \right) \left(\frac{1.00 \text{ mole H}_2\text{O}}{18.014_8 \text{ mole H}_2\text{O}} \right) \left(\frac{1.00 \text{ g}}{1 \text{ mL}} \right) \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) = 1.28 \times 10^{-3} \text{ M}$$

The concentration of O_2 in water under these conditions is $1.28 \times 10^{-3} \text{ M}$.

4. (10 Points) Benzene and toluene form ideal solutions. A solution of benzene and toluene was prepared at 25.0 °C and it was found that the mole fractions of the two compounds in the vapor phase were equal. Calculate the composition of the solution given that at 25.0 °C the vapor pressures of benzene and toluene are 95. and 28. torr, respectively.

Raoult's Law for two a solution of two volatile components is $P_{\text{total}} = \chi_B P_B^0 + \chi_T P_T^0$, where χ is the mole fraction in the solution and P^0 is the vapor pressure of the pure substance and the subscript "B" refers to benzene and the "T" subscript refers to toluene.

Since the mole fraction of each substance in the vapor phase are equal the partial pressures must be equal (remember $P_i = x_i P_{\text{total}}$, where x_i is the mole fraction of a substance in the vapor phase). Therefore, we can write

$$\chi_B P_B^0 = \chi_T P_T^0, \text{ which we can rearrange to give } \frac{\chi_B}{\chi_T} = \frac{P_T^0}{P_B^0} = \frac{28. \text{ torr}}{95. \text{ torr}} = 0.29_{47}.$$

Let x equal the moles of benzene in the solution and y equal the moles of toluene in the solution. We can then rewrite the previous equation as follows.

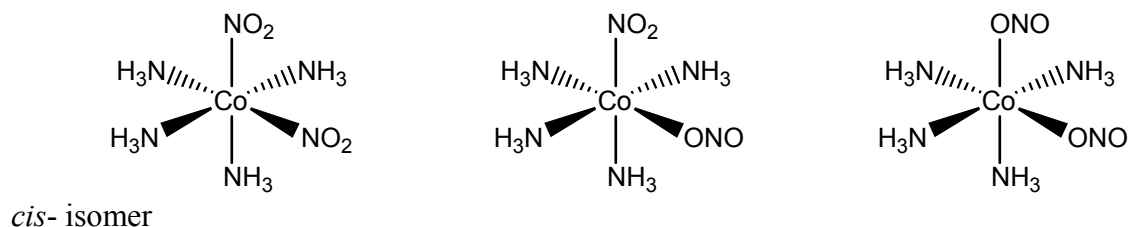
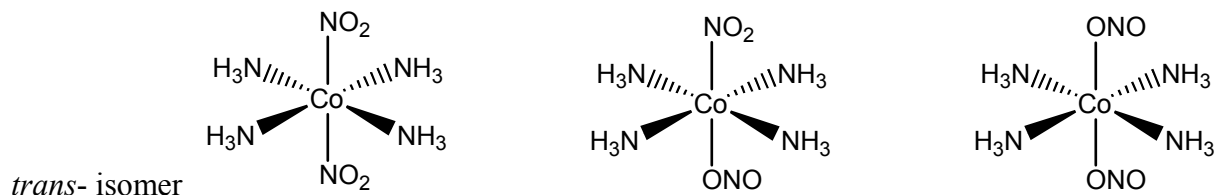
$$\frac{\chi_B}{\chi_T} = \frac{\left(\frac{x}{x+y}\right)}{\left(\frac{y}{x+y}\right)} = \frac{x}{y} = 0.29_{47}$$

So, $x = 0.29_{47} y$.

$$\text{The mole fraction of toluene is then } \chi_T = \frac{y}{x+y} = \frac{y}{0.29_{47} y + y} = \frac{y}{1.29_{47} y} = 0.77$$

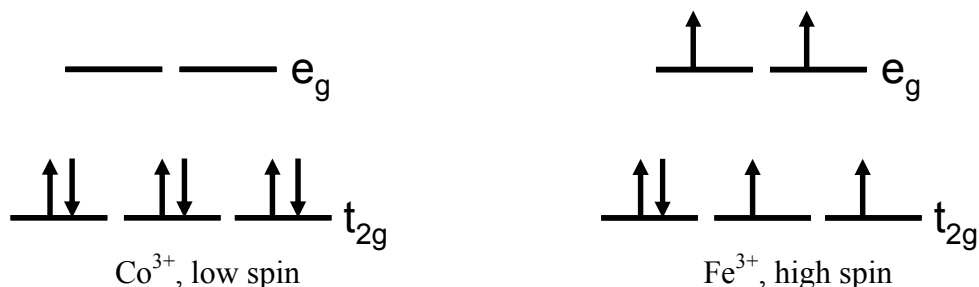
The solution has toluene present at a mole fraction of 0.77 (benzene in present in a mole fraction of 0.23).

5a. (7 Points) Draw all geometrical and linkage isomers for $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2$.

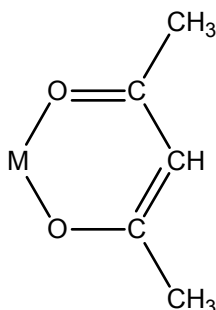


b. (4 Points) The $\text{Co}(\text{NH}_3)_6^{3+}$ ion is diamagnetic, but the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ is paramagnetic. Explain.

Both metals (Co^{3+} and Fe^{2+}) are d^6 . However, NH_3 has strong enough ligand field with Co^{3+} that it can force a low spin configuration, while H_2O is not strong enough to make Fe^{3+} go low spin.

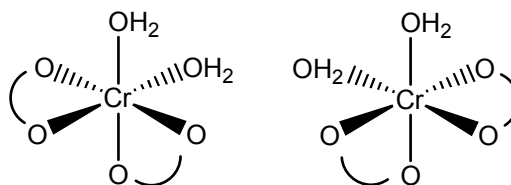


c. (6 Points) Acetylacetonate (acac^-) is a bidentate ligand. It loses a proton and coordinates to metal ions as acac^- , as shown below, where M is a transition metal ion.

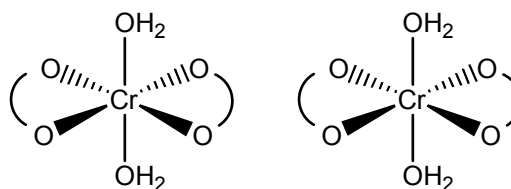


Which of the following complexes can be optically active (can have enantiomers): $\text{cis-Cr}(\text{acac})_2(\text{H}_2\text{O})_2$, $\text{trans-Cr}(\text{acac})_2(\text{H}_2\text{O})_2$ and $\text{Cr}(\text{acac})_3$? Hint: draw them.

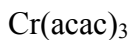
Let  be the acac^- ligand.



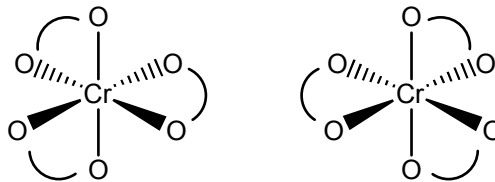
$\text{cis-Cr}(\text{acac})_2(\text{H}_2\text{O})_2$
can be optically active (has enantiomers)



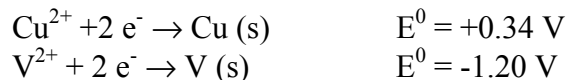
$\text{trans-Cr}(\text{acac})_2(\text{H}_2\text{O})_2$
is not optically active (no enantiomers)



Can be optically active (has enantiomers)



6. (20 Points) A galvanic cell is based on the following half reactions:



In this cell, the copper compartment contains a copper electrode and the [Cu²⁺] equals 1.00 M, and the vanadium compartment contains a vanadium electrode and V²⁺ at an unknown concentration. The compartment containing the vanadium (1.00 L of solution) was titrated with 0.0800 M H₂EDTA²⁻, resulting in the reaction



The potential of the cell was monitored to determine the equivalence point for the process, which occurred when a volume of 500.0 mL of the H₂EDTA²⁻ solution had been added. At the equivalence point, E_{cell} was observed to be 1.98 V. The solution was buffered at a pH of 10.00.

Calculate the following quantities. Write your answers in the space provided, show your work in the blank space below and attach additional sheets, as needed. Be sure to clearly label what work goes with which part of the problem.

- E_{cell} before the titration was carried out is **1.58 V**.
- The equilibrium constant for the titration reaction, K, is **2.x10⁸**.
- E_{cell} at the halfway point of the titration is **1.59 V**.

The standard reduction potentials for this cell are as follows.



The Cu electrode will be the cathode and the V electrode the anode.

The overall balanced chemical reaction is V (s) + Cu²⁺ → V²⁺ (aq) + Cu (s).

The standard cell potential is E⁰_{cell} = E⁰_{cathode} - E⁰_{anode} = +0.34 - 1.20 V = +1.54 V.

The Nernst equation for the cell will be as follows, assuming that $[Cu^{2+}] = 1.00\text{ M}$ and that it is constant. What we are saying is that we won't allow the cell to discharge so much that the concentrations change appreciably.

$$E = E^0 - \frac{RT}{nF} \ln Q = +1.54\text{ V} - \frac{RT}{nF} \ln[V^{2+}]$$

At the equivalence point the amount of $HEDTA^{2-}$ equals the amount of V^{2+} originally present.

$$500.0\text{ mL} \left(\frac{0.0800\text{ mmole } H_2EDTA^{2-}}{1\text{ L}} \right) \left(\frac{1\text{ mmole } V^{2+}}{1\text{ mmole } H_2EDTA^{2-}} \right) = 0.0400\text{ mmole } V^{2+}$$

The concentration of V^{2+} is thus

$$\frac{0.0400\text{ mmole } V^{2+}}{1.00 \times 10^3\text{ mL}} = 0.0400\text{ M}$$

The cell potential (assuming 298.15 K) is

$$E = +1.54\text{ V} - \frac{(8.31451\text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15\text{ K})}{(2)(96485\text{ C} \cdot \text{mole}^{-1})} \ln(0.0400) = +1.54\text{ V} - (-0.04135)\text{ V} = +1.58\text{ V}$$

To find the equilibrium constant, we need to know the concentrations of each species present in the solution at equilibrium.

The $[H_2EDTA^{2-}]$ and the initial $[V^{2+}]$ is found from the stoichiometry.

$$\frac{500.0\text{ mL} \left(\frac{0.0800\text{ mmole } H_2EDTA^{2-}}{1\text{ L}} \right)}{1.50 \times 10^3\text{ mL}} = 0.0266_6\text{ M}$$

The $[V^{2+}]$ is found from the cell potential at the equivalence point.

$$\ln[V^{2+}] = -\frac{(nF)(E - 1.54\text{ V})}{RT} = \frac{(2)(96485\text{ C} \cdot \text{mole}^{-1})(1.98\text{ V} - 1.54\text{ V})}{(8.31451\text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15\text{ K})} = -34.25$$

$$[V^{2+}] = 1.3 \times 10^{-15}$$

At the equivalence point the following pre-equilibrium conditions will exist. The low $[V^{2+}]$ at the equivalence point implies K is large and that this equilibrium lies to the right.

	$H_2EDTA^{2-}(\text{aq})$	$+ V^{2+}(\text{aq})$	\rightleftharpoons	$[VEDTA]^{2-}(\text{aq})$	$+ 2 H^+(\text{aq})$
Initial	0.0266₆	0.0266₆		0	1.0×10^{-10}
Initial'	0	0		0.0266₆	1.0×10^{-10}
Change	+x	+x		-x	-----
Equilibrium	x	x		0.0266₆ - x	1.0×10^{-10}

$$K = \frac{[\text{VEDTA}]^{2-} [\text{H}^+]^2}{[\text{V}^{2+} [\text{H}_2\text{EDTA}^{2-}]} = \frac{(0.02666)(1.0 \times 10^{-10})^2}{(1.3 \times 10^{-15})(1.3 \times 10^{-15})} = 1.6 \times 10^8$$

At halfway to the equivalence point the $[\text{V}^{2+}]$ is calculated as follows.

$$\frac{250.0 \text{ mL} \left(\frac{0.0800 \text{ mmole H}_2\text{EDTA}^{2-}}{1 \text{ L}} \right)}{1.25 \times 10^3 \text{ mL}} = 0.0160 \text{ M}$$

The potential is thus

$$E = +1.54 \text{ V} - \frac{(8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(298.15 \text{ K})}{(2)(96485 \text{ C} \cdot \text{mole}^{-1})} \ln(0.0160) = +1.54 \text{ V} - (-0.05312) \text{ V} = +1.59 \text{ V}$$