

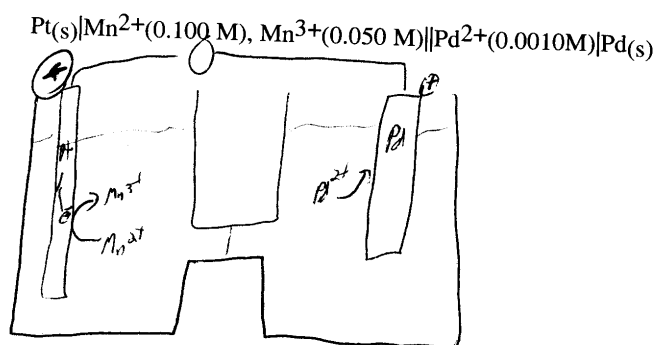
Chem 303 In-Class Exam 2

Name Key

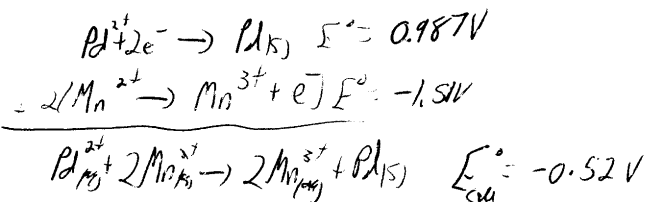
Useful information: $E = E^\circ - \frac{0.0592V}{n} \log Q$, $E^\circ = \frac{0.0592V}{n} \log K$, $\Delta G^\circ = -RT \ln K$,
 $R = 8.314 \text{ J/molK}$, $q = n \cdot F$, $F = 9.65 \times 10^4 \text{ C/mol}$, $E = E_{\text{red}} - E_{\text{ox}}$

(1)(30 points)

(a) Draw a picture of the following cell.



(b) Calculate the E° for the cell above.



(c) What is the measured E for the above cell?

$$Q = \frac{[\text{Mn}^{3+}]^2}{[\text{Pd}^{2+}][\text{Mn}^{2+}]^2} \quad E = E^\circ - \frac{0.0592}{2} \log Q$$

$$Q = \frac{(0.050 \text{ M})^2}{(0.0010 \text{ M})(0.100 \text{ M})^2} = 250 \quad E = -0.52 \text{ V} - \frac{0.0592 \text{ V}}{2} \log 250$$

$E = -0.594 \text{ V} \approx -0.59 \text{ V}$

(2)(30 points) (a) Why is EDTA a good molecule for complexometric titrations?

It ~~has~~ complexes strongly to all 1d + higher metals.
It only forms 1:1 complexes with metals.
Large formation constants due to the chelate effect

(b) What conditions have to be fulfilled for a practical EDTA titration? (one that will give you precise and accurate data in a reasonable amount of time)

- The metal ion must not precipitate
- The metal ion must complex with a high K value (high enough to complex 99.9% of the metal)
- The metal must react with EDTA at a reasonable rate

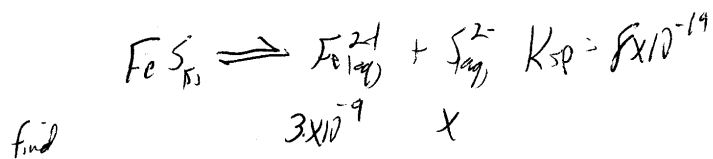
(c) What are three different EDTA titration methods? How do they work?

Direct titration - EDTA is added to the metal solution until the endpoint is noticed (indicator or electrochemically).

Back titration - a known (excess) amount of EDTA is added to a ~~known~~ metal ion solution. The excess EDTA is titrated with Mg^{2+} . The moles EDTA - moles Mg^{2+} = moles metal ions in the test soln.

Displacement titration - $(MgEDTA)^{2-}$ is added to a metal ion solution whose metal binds EDTA more strongly than Mg^{2+} . The Mg^{2+} is displaced by the analyte metal. The displaced Mg^{2+} is titrated with EDTA. moles EDTA = moles Mg^{2+} = moles analyte metal.

(3)(15 points) A gravimetric analysis was performed to analyze for Fe^{2+} . If the minimum $[\text{Fe}^{2+}]$ expected is $3 \times 10^{-6} \text{ M}$, what should the concentration of sulfide be to ensure that at least 99.9% of the Fe^{2+} has precipitated? $3 \times 10^{-6} \text{ M}$, 0.1% is 3×10^{-9}



$$(3 \times 10^{-9})(x) = 8 \times 10^{-19}$$

$$x = 2.7 \times 10^{-10} \text{ M}$$

$[\text{S}^{2-}]$ should be at least $2.7 \times 10^{-10} \text{ M}$

(4)(15 pts) To a (25.00 mL) solution of Al^{3+} was added 25.00 mL of 0.100 M Na_2EDTA at pH = 10. After stirring for 10 min, Eriochrome Black T was added and the solution titrated with 0.0120 M Mg^{2+} to an the endpoint. If it took 12.22 mL of the Mg^{2+} solution to reach the endpoint, what was the concentration of the original aluminum solution?

Back titration

$$\text{Total EDTA} = (0.100\text{M})(0.02500\text{L}) = 2.50 \times 10^{-3} \text{ moles}$$

$$\text{Mg}^{2+} \text{ used} = (0.0120\text{M})(0.01222\text{L}) = 1.46 \times 10^{-4} \text{ moles}$$

$$\text{moles Al}^{3+} = \text{moles EDTA} - \text{moles Mg}^{2+} = 2.50 \times 10^{-3} - 1.46 \times 10^{-4} \text{ moles} = 2.35 \times 10^{-3} \text{ moles Al}^{3+}$$

$$[\text{Al}^{3+}] = \frac{2.35 \times 10^{-3} \text{ moles}}{0.02500\text{L}} = \boxed{9.41 \times 10^{-2} \text{ M}}$$

Chem 303 Take-Home Exam 2. Due Friday, April 7 at 5 PM

Name Key

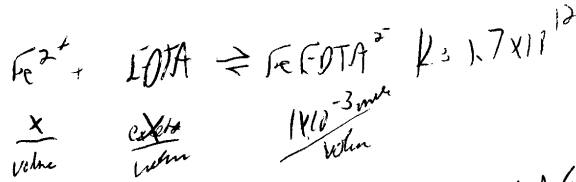
You may use your book and notes on this portion of the exam, but you may not collaborate with anyone else on it. Show all work for credit.

(1) A solution of 0.0200 M (50.00 mL) Fe²⁺ was titrated with 0.0500 M Na₂EDTA at pH = 8.00. Plot pFe²⁺ vs mL EDTA added from 0 to 30 mL using a spreadsheet. Plot the points every 0.50 mL. Include the spreadsheet and an explanation.

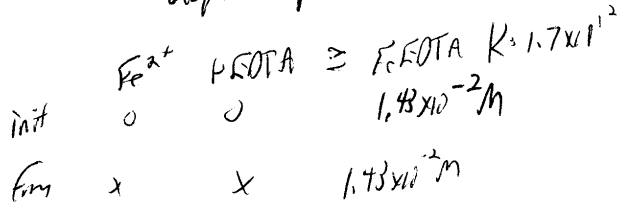
log K_f = 14.32 and α₄ = 5.6 × 10⁻³

$$K_f' = 1.17 \times 10^{12}$$

$$\text{initial moles Fe}^{2+} = 1.0 \times 10^{-3} \text{ moles}$$



equivalence point 20.0 mL EDTA added (1.00 × 10⁻³ moles EDTA)

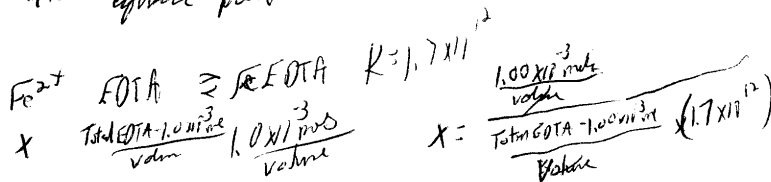


$$\frac{1.48 \times 10^{-2} \text{ M}}{x^2} = 1.7 \times 10^{12}$$

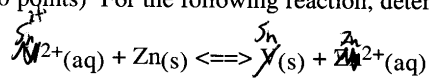
$$8.40 \times 10^{-15} = x^2$$

$$9.2 \times 10^{-8} \text{ M} = x$$

after equivalence point



(2)(20 points) For the following reaction, determine E° , ΔG° , and K . at 298K



$$\begin{aligned} \text{Sn}^{2+} + 2e^- &\rightarrow \text{Sn} & E^\circ &= -0.136\text{V} \\ \text{Zn}(\text{s}) &\rightarrow \text{Zn}^{2+} + 2e^- & E^\circ &= 0.763\text{V} \\ \hline E_{\text{cell}} &= 0.627\text{V} & & -1.21 \times 10^5 \text{ J} = \Delta G^\circ \\ \Delta G^\circ &= -nFE^\circ = -2(96,500 \frac{\text{C}}{\text{mol e}^-})(0.627\text{V}) & & \\ \Delta G^\circ &= -RT \ln K & & \\ -121,000 \text{ J} &= (-8.314 \frac{\text{J}}{\text{mol K}})(298\text{K})(\ln K) & & \\ &48.8 = \ln K & & K = 1.6 \times 10^{21} \end{aligned}$$

(3)(15 points) A solution of 0.0500 M Na₂EDTA (25.00 mL) was added to a 50.00 mL solution of Al³⁺. Eriochrome Black T was added and 5.10 mL of a 0.0455 M Mg²⁺ solution was needed to reach the endpoint. What was the original concentration of Al³⁺?

$$\begin{aligned} \text{EDTA} &= 1.25 \times 10^{-3} \text{ mol} \\ \text{Mg}^{2+} &= 2.32 \times 10^{-4} \text{ mol} \\ \text{mol Al}^{3+} &= 1.25 \times 10^{-3} \text{ mol} - 2.32 \times 10^{-4} \text{ mol} = 1.02 \times 10^{-3} \text{ mol} \\ [\text{Al}^{3+}] &= \left(\frac{1.02 \times 10^{-3} \text{ mol}}{0.0500\text{L}} \right) = \boxed{0.0204\text{M}} \end{aligned}$$

(4) (20 points) Using EDTA titrations, devise a method to determine the specific amount of each metal in a water sample containing Al^{3+} , Fe^{3+} , and Ca^{2+} .

First the total moles of metal can be determined by a direct titration (or a back titration)

Then, Al^{3+} & Fe^{3+} can be masked by F^- & a titration can be done

to determine Ca^{2+} only.

Then, another sample of the water can be masked by CN^- to mask Fe^{3+} only

and the Ca^{2+} and Al^{3+} can be determined

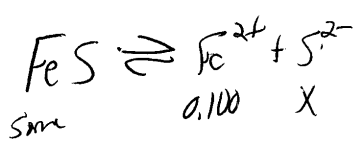
known titrat 1 - total moles $\text{Al}^{3+} + \text{Ca}^{2+} + \text{Fe}^{3+}$
 titrat 2 - moles Ca^{2+}
 titrat 3 moles $\text{Ca}^{2+} + \text{Al}^{3+}$

\therefore moles Ca^{2+} = titrat 2 moles Al^{3+} = titrat 3 - titrat 2 moles Fe^{3+} = titrat 1 - titrat 3

(5) (20 points) A solution of 0.200 M Pb^{2+} , 0.100 M Fe^{2+} , and 0.05 M Mn^{2+} is to be separated by precipitation with Na_2S . List the concentration of sulfide that should be used to precipitate the first metal without precipitating the second, then the second concentration (to precipitate the second) and so forth.

$\text{PbS } K_{sp} = 3 \times 10^{-28}$ $\text{FeS } K_{sp} = 8 \times 10^{-19}$ $\text{MnS } K_{sp} = 3 \times 10^{-11}$

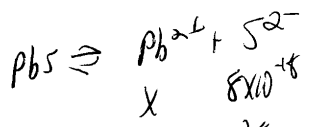
The FeS will precipitate when $[\text{S}^{2-}] = \frac{K_{sp}}{[\text{Fe}^{2+}]}$



FeS precipitates when $[\text{S}^{2-}] > 8 \times 10^{-18} \text{ M}$

$$x(0.100) = 8 \times 10^{-18}$$

$$x = [\text{S}^{2-}] = 8 \times 10^{-18} \text{ M}$$

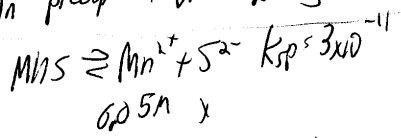


$$x(8 \times 10^{-18}) = 3 \times 10^{-28}$$

$$[\text{Pb}^{2+}] = 1.7 \times 10^{-9} \text{ M}$$

$\therefore [\text{S}^{2-}] = 1 \times 10^{-10} \text{ M}$ or
 S^{2-}
 to precipitate $[\text{Pb}^{2+}]$

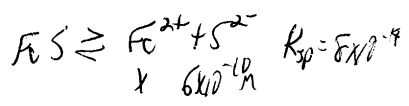
Mn^{2+} precipitates when $[\text{S}^{2-}] = 6 \times 10^{-10} \text{ M}$



$$x(0.05 \text{ M}) = 3 \times 10^{-11}$$

$$x = 6 \times 10^{-10} \text{ M } [\text{S}^{2-}]$$

max of $[\text{Fe}^{2+}]$ at that $[\text{S}^{2-}]$ level is

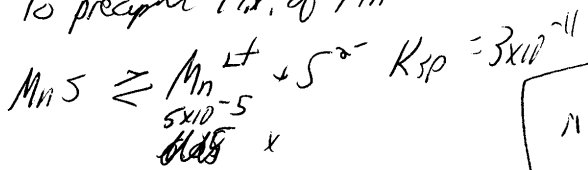


$$x(6 \times 10^{-10}) = 8 \times 10^{-9}$$

$$x = 1.3 \times 10^{-9} \text{ M}$$

\therefore use $[\text{S}^{2-}]$ of $1 \times 10^{-10} \text{ M}$ or to ppt Fe^{2+}

To precipitate 99% of Mn^{2+}



$$x(5 \times 10^{-5}) = 3 \times 10^{-11}$$

$$x = 6 \times 10^{-7} \text{ M } = [\text{S}^{2-}]$$

\therefore use $[\text{S}^{2-}]$ of $6 \times 10^{-7} \text{ M}$
 or greater to
 ppt Mn^{2+} .