

Pay attention to Significant Figures in all calculations.

1. Assume that your extensive experience in Quantitative Analysis has helped you land a summer job as a lab tech for a small water analysis company in west Texas.
- (a) (8 points) **SHOW ALL WORK.** On the first day at work, your boss hands you a bottle labeled "Na₂H₂EDTA·2H₂O (FM = 372.24)" and says, "mix us up a half-liter of 5.00 mM EDTA." What do you do? (Resigning is not an option!)

$$(0.500 \text{ L}) (0.0050 \text{ mole/L}) (372.24 \text{ g/mole}) = 0.9306 \text{ g}$$

Weigh ~ 0.93 g (to the nearest 0.1 mg) of Na₂H₂EDTA·2H₂O, transfer it quantitatively to a 500-mL volumetric flask, and dilute to the mark with DI water.

- (b) (10 points) **SHOW ALL WORK.** The boss returns later, hands you a bottle of water, and says, "this here stuff's from the well out at my daddy's place, see if ya can't figure out how hard it is." Using your best lab technique from TCU, you carefully pipet a 50.00 mL sample of the water into an Erlenmeyer flask, add 3 mL of ammonia buffer and a few drops of Eriochrome black T indicator. You then titrate the sample with your standard EDTA solution (5.015 mM) and find that it takes 41.05 mL for the color to change from red to blue. Determine the water hardness, expressed as mg of CaCO₃ (FM = 100.09) per liter.

$$(0.04105 \text{ mL}) (0.005015 \text{ mole EDTA / L}) (1 \text{ mole Ca}^{2+} / 1 \text{ mole EDTA})$$

$$= 2.0587 \times 10^{-4} \text{ mole Ca}^{2+}$$

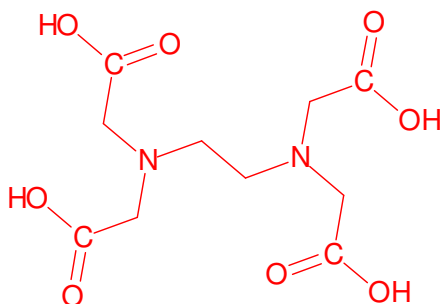
$$= 2.0587 \times 10^{-4} \text{ mole CaCO}_3$$

$$(2.0587 \times 10^{-4} \text{ mole CaCO}_3) (100.09 \text{ g/mole}) (1 \text{ mg} / 10^{-3} \text{ g}) = 20.61 \text{ mg}$$

$$(20.61 \text{ mg}) / (0.05000 \text{ L}) = 412.2 \text{ mg CaCO}_3 / \text{L}$$

2. These four questions are related to the Mg-EDTA experiment.

- (a) (5 points) Write a complete, **structural formula** for ethylenediaminetetraacetic acid, i.e., "EDTA" (which is sometimes written H₄EDTA or H₄Y).

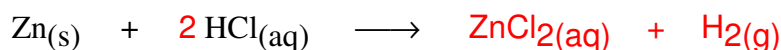


- (b) (6 points) Explain briefly (with a few words and a chemical equation) how the calmagite indicator functions in the Mg-EDTA titration. (**Note:** A chemical formula for calmagite is not required here!)

Calmagite is a "metal ion indicator" which binds weakly with Mg²⁺, forming a wine-red colored complex ion. As the titration proceeds, this is displaced by the much stronger complexing agent, EDTA. The end-point corresponds to the appearance of the blue color of the free indicator, In.



- (c) (6 points) A standard solution in this experiment was prepared by "dissolving" zinc metal in concentrated HCl. **Complete and balance** the following chemical reaction. What was this standard solution used for in this analysis?



This Zn²⁺ solution was then used to standardize the EDTA solution.

- (d) (10 points) **SHOW ALL WORK. Include any appropriate equilibrium reactions.** An "ammonia buffer" was prepared in this experiment by mixing 20 mL of concentrated NH₃ (14.8 M) with 2.7 g of NH₄Cl (FM = 53.49) and diluting to 500 mL in a volumetric flask. Calculate the pH of this buffer solution. (**Note:** for NH₃, pK_b = 4.74)



$$[\text{OH}^-] = K_b [\text{NH}_3] / [\text{NH}_4^+] = K_b (\text{moles NH}_3) / (\text{moles NH}_4^+)$$

$$(0.020 \text{ L}) (14.8 \text{ mole NH}_3 / \text{L}) = 0.296 \text{ mole NH}_3$$

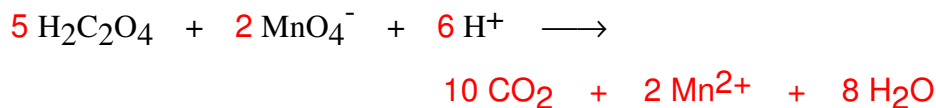
$$(2.7 \text{ g}) (1 \text{ mole NH}_4\text{Cl} / 53.49 \text{ g}) = 0.0505 \text{ mole NH}_4\text{Cl}$$

$$[\text{OH}^-] = (10^{-4.74}) (0.296 / 0.0505) = 1.07 \times 10^{-4}$$

$$\text{pOH} = -\log (1.07 \times 10^{-4}) = 3.97$$

$$\therefore \text{pH} = 10.03$$

3. (8 points) **Complete and balance** the following **net ionic equation** for the essential redox reaction that was used in the limestone (CaO) analysis. Circle the oxidizing agent.



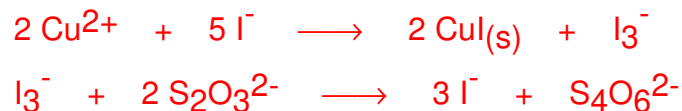
The oxidizing agent is MnO_4^- .

4. (10 points) **SHOW ALL WORK.** A 25.00 mL portion of a solution containing La^{3+} was treated with excess sodium oxalate to precipitate $\text{La}_2(\text{C}_2\text{O}_4)_3$ (FM = 541.9). The precipitate was collected by filtration, washed with DI water, re-dissolved in acid, and then titrated with 26.35 mL of 0.0736 M KMnO_4 . Calculate the molarity of La^{3+} in the original solution.

$$\begin{aligned} & (0.02635 \text{ L}) (0.0736 \text{ mole MnO}_4^- / \text{L}) (5 \text{ mole C}_2\text{O}_4^{2-} / 2 \text{ mole MnO}_4^-) \\ & = 4.848 \times 10^{-3} \text{ moles C}_2\text{O}_4^{2-} \\ & (4.848 \times 10^{-3} \text{ moles C}_2\text{O}_4^{2-}) [1 \text{ mole La}_2(\text{C}_2\text{O}_4)_3 / 3 \text{ mole C}_2\text{O}_4^{2-}] \\ & = 1.616 \times 10^{-3} \text{ mole La}_2(\text{C}_2\text{O}_4)_3 \\ & (1.616 \times 10^{-3} \text{ mole La}_2(\text{C}_2\text{O}_4)_3) (2 \text{ mole La}^{3+} / 1 \text{ mole La}_2(\text{C}_2\text{O}_4)_3) \\ & = 3.232 \times 10^{-3} \text{ mole La}^{3+} \\ & (3.232 \times 10^{-3} \text{ mole La}^{3+}) / (0.02500 \text{ L}) = 0.129 \text{ M La}^{3+} \end{aligned}$$

5. **Recall the iodometric copper experiment!** In a similar procedure, a 2.526-g sample of a copper ore was dissolved in strong acid and diluted to 250.0 mL using a volumetric flask. A 50.00-mL aliquot was analyzed by adding 1 g of KI and then titrating with 43.58 mL of 0.04670 M $\text{Na}_2\text{S}_2\text{O}_3$ to reach the starch-iodine end-point.

- (a) (8 points) Write balanced, **net-ionic equations** for **both of the redox reactions** in this analysis, i.e., (1) the reaction of Cu^{2+} with I^- and (2) the reaction of something with $\text{S}_2\text{O}_3^{2-}$ in the actual titration.



- (b) (4 points) Briefly explain how the "starch-iodine" indicator works, including the relevant color changes.

Starch is used as an indicator because it forms an intense blue color with I_2 (actually, I_3^-). The end-point, when all of the I_3^- has been consumed by the $\text{S}_2\text{O}_3^{2-}$ titrant, is signaled by the *disappearance* of the blue color.

- (c) (8 points) **SHOW ALL WORK.** Calculate the weight percentage of Cu (FM = 63.55) in the ore sample.

$$\begin{aligned} & (0.04358 \text{ L}) (0.04670 \text{ mole } \text{S}_2\text{O}_3^{2-} / \text{L}) (1 \text{ mole } \text{Cu}^{2+} / 1 \text{ mole } \text{S}_2\text{O}_3^{2-}) \\ & = 2.035 \times 10^{-3} \text{ mole } \text{Cu}^{2+} = 2.035 \times 10^{-3} \text{ mole Cu} \\ & (2.035 \times 10^{-3} \text{ mole Cu}) (63.55 \text{ g / mole}) = 0.1293 \text{ g Cu (in 50 mL aliquot)} \\ & \therefore \text{mass of Cu in unknown sample} = 5 (0.1293 \text{ g}) = 0.6467 \text{ g} \\ & (0.6467 \text{ g}) / (2.526 \text{ g}) \times 100 \% = 25.60 \% \text{ Cu} \end{aligned}$$

6. Chloroacetic acid, $\text{ClCH}_2\text{CO}_2\text{H}$ (call it HA for short) is a moderately weak acid with $\text{p}K_a = 2.865$. In a simple acid-base experiment, a 50.00 mL portion of 0.09500 M $\text{ClCH}_2\text{CO}_2\text{H}$ was titrated with 0.1250 M KOH.

- (a) (5 points) **SHOW ALL WORK.** Determine the volume (in mL) of KOH that is required to reach the equivalence point.

$$\text{moles HA} = \text{moles OH}^- = (50.00 \text{ mL}) (0.09500 \text{ moles} / 1000 \text{ mL})$$

$$= 0.004750 \text{ moles}$$

$$(0.004750 \text{ mole KOH}) (1000 \text{ mL} / 0.1250 \text{ mole}) = 38.00 \text{ mL KOH}$$

- (b) (12 points) **SHOW ALL WORK.** *Include the appropriate equilibrium reaction.* Calculate the pH of the solution at the equivalence point.

At the equivalence point, all HA has been neutralized leaving a solution of the "salt of a weak acid" A^- . So, the equilibrium Rx is:



$$K_b = K_w / K_a = 10^{-14} / 10^{-2.865} = 7.33 \times 10^{-12} = x^2 / [\text{A}^-]$$

$$\text{where } x = [\text{OH}^-] = [\text{HA}]$$

$$[\text{A}^-] = \text{moles A}^- / \text{total volume} = (0.004750 \text{ mole}) / (0.0880 \text{ L})$$

$$[\text{A}^-] = 0.0540 \text{ M}$$

$$7.33 \times 10^{-12} = x^2 / (0.0540)$$

$$x = [\text{OH}^-] = 6.29 \times 10^{-7}$$

$$\text{pOH} = 6.20 \quad \text{and} \quad \text{pH} = 7.80$$