Analysis of Zinc Tablets: An Extension to a Stoichiometry Experiment[1]

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Learning Objectives

Upon completion of this experiment, students will have experienced:
1. Preparation of standard solutions.
2. Use of volumetric flasks and burets.
3. Determination of the stoichiometry of a reaction in solution.
4. Determination of the concentration of a ferrocyanide solution.

Text Topics

Molarity, standard solutions, titrations, stoichiometry of reactions in solution

Discussion

Consider the chemical reactions that you have run in the last few weeks. Most were performed in solution. Why? Reactions between two solids are rare because of the immobility of bound ions. The high degree of ionic mobility available in solution makes solution the preferred medium for most preparative chemical reactions. As chemical reactions and analysis are usually performed in solution, it is imperative that we be able to prepare solutions of known concentrations accurately and be familiar with the techniques for determining unknown concentrations.

As you have probably learned, chemists prefer the use of molarity (moles/liter = M) to express the concentration of a solute in a solution. Make sure you remember that the denominator represents total volume or liters of solution and not just liters of solvent. This means solutions must be prepared by dilution **to** the desired volume, **not with** the desired volume.

Your goals will be to prepare solutions of known concentration of potassium ferrocyanide and zinc sulfate, determine the stoichiometry of the reaction between zinc ion and ferrocyanide and determine the ferrocyanide molarity in a solution of unknown concentration or the zinc ion content in a commercial tablet. Solutions of known concentration are usually prepared by one of three techniques: diluting a measured mass of substance to a certain volume, quantitative dilution of a solution of known concentration, or by preparation of an approximately known concentration followed by a quantitative chemical reaction technique (such as a titration).
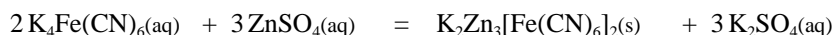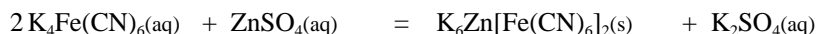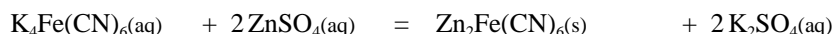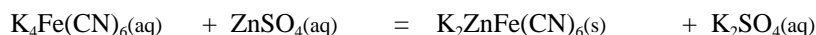
Solutions of accurately known concentrations can only be prepared directly by weighing out a solute that can be obtained in pure form (>99.9%) and is relatively nonhygroscopic. Compounds that meet these criteria are called primary standards. Concentrations of other compounds must be determined by a quantitative chemical technique and their solutions are called secondary standards. Titration is the name of a commonly used technique that utilizes a primary standard to standardize a solution whose concentration either is not known or not known accurately enough. Ideally in a titration, you will determine the volume of a solution of accurately known concentration that is required to exactly complete a stoichiometric reaction with a solution of unknown concentration.

For the known, molarity multiplied by volume (in Liters) gives the number of moles used. Now multiplication by the mole ratio from the balanced equation gives the moles of the other reactant or product. The number of moles can then be used depending on what else is known to calculate concentration, molecular mass or mass percent. To determine when a stoichiometric mixture has been achieved, either a chemical indicator or an instrumental technique is utilized. It should be recognized, however, that although indicators are selected because they change color just as the desired stoichiometric reaction is complete, the color change does not occur at the

exact equivalence point. Thus there are small but real errors inherent in an indicator monitored titration that can be minimized by careful indicator selection.

Procedure

A. Stoichiometry of the reaction. The titration of ferrocyanide with zinc ion will be studied. The usual goal is to use one solution of known concentration to determine the concentration of the second solution. Today, however, both reactants will be considered to be primary standards and you will use the titration to determine the stoichiometry of the reaction. The four most reasonable reactions are:

$$K_4Fe(CN)_6(aq) \quad + \; ZnSO_4(aq) \quad = \quad K_2ZnFe(CN)_6(s) \quad + \; K_2SO_4(aq)$$

$$K_4Fe(CN)_6(aq) \quad + \; 2\,ZnSO_4(aq) \quad = \quad Zn_2Fe(CN)_6(s) \quad + \; 2\,K_2SO_4(aq)$$

$$2\,K_4Fe(CN)_6(aq) \quad + \; ZnSO_4(aq) \quad = \quad K_6Zn[Fe(CN)_6]_2(s) \quad + \; K_2SO_4(aq)$$

$$2\,K_4Fe(CN)_6(aq) \quad + \; 3\,ZnSO_4(aq) \quad = \quad K_2Zn_3[Fe(CN)_6]_2(s) \quad + \; 3\,K_2SO_4(aq)$$

The products for 3 of the 4 reactions are called mixed salts because there are 2 different cations, potassium and zinc. The experiment will enable you to calculate the molar ratio of potassium ferrocyanide to zinc sulfate which should enable you to select among the four most reasonable reactions. Once this has been accomplished, you will perform additional titrations to determine the concentration of potassium ferrocyanide or the amount of zinc ion in a commercially available tablet.

0.025 M Potassium ferrocyanide solution. Calculate the amount of potassium ferrocyanide trihydrate $[K_4Fe(CN)_6 \cdot 3H_2O]$ needed to prepare 250 mL of 0.025 M solution. *The stockroom should provide $K_4Fe(CN)_6 \cdot 3H_2O$ that is as pure as possible.* Weigh out about the calculated amount in a beaker to at least the nearest 0.001 g. Transfer it using a funnel to a 100 mL volumetric flask. Rinse the beaker with deionized water and add this to the funnel. Repeat the washing process until all of the solids in the beaker and the funnel have been washed into the volumetric flask. Add water until the bulb is about ⅔ full and swirl until the solids are totally dissolved. Add water up to the mark using a dropper as you approach the mark. Stopper, invert and swirl and repeat several times. Calculate the concentration of $K_4Fe(CN)_6$ to the appropriate number of significant figures.

0.050 M Zinc sulfate solution. Calculate the amount of zinc sulfate heptahydrate $(ZnSO_4 \cdot 7H_2O)$ needed to prepare 250 mL of 0.050 M solution. *The $ZnSO_4 \cdot 7H_2O$ should be as pure as possible.* Weigh out about the calculated amount in a beaker to a least the nearest 0.001 g. Transfer it to a funnel in a 250 mL volumetric flask as above for $K_4Fe(CN)_6 \cdot 3H_2O$, dilute to the mark with deionized water and swirl. Calculate the concentration of $ZnSO_4$ to the appropriate number of significant figures.

Additional solutions. Also needed for the titrations are freshly prepared aqueous 1% potassium ferricyanide and a solution of 1% diphenylamine in sulfuric acid. The latter solution should be prepared by the instructor. To prepare 200 mL of diphenylamine indicator, dissolve 2.0 grams of diphenylamine in 100 mL of concentrated sulfuric acid. Weigh 100 grams of ice into a 400 mL beaker. Add the diphenylamine in sulfuric acid to the ice with stirring. Cool the mixture in an ice bath.

Using a buret. To rinse a 25 mL buret (if water beads in the buret, it needs further cleaning), add about 5 mL of the zinc sulfate solution. Run a little through the stopcock, then tip it horizontally and rotate it to wet all of the inside with the solution and pour it out the top. Repeat two more times and fill the buret with zinc sulfate solution. Mount the buret in a buret clamp and open the stopcock and allow the solution to flow out until the air bubbles in the tip are gone. The reading at the top should be at or below 0.00 mL. Remember we read one digit beyond the last set of graduations and this means **you estimate the reading to the nearest 0.01 mL**.

Pipet 25.00 mL of the $K_4Fe(CN)_6$ solution into a 250 mL Erlenmeyer flask. Add ~5 mL of 3.0 M sulfuric acid, 3 drops of freshly prepared 1% potassium ferricyanide (oxidizes the diphenylamine to its colored form in the absence of ferrocyanide) and 4 drops of diphenylamine indicator. Set the flask on a white piece of paper directly below the buret with the buret tip about 1 cm into the flask. Read the buret and add the zinc sulfate solution at a moderate rate with swirling until you approach the end point. At this time, you should add titrant in half drop quantities pausing and checking for the end point each time after swirling. Half drops are easily delivered by quickly turning the closed stopcock 180°. The end point will be observed with the appearance of a tinge of blue-violet color which will intensify slightly upon standing. Repeat the titration two more times and determine the stoichiometry of the reaction.

B. (Option 1) Concentration of ferrocyanide in an unknown. Your instructor will give you a potassium ferrocyanide solution of unknown concentration. Perform three titrations on the unknown using the same procedure as in the previous paragraph (except that the endpoint probably will require a different volume of titratnt) and determine the concentration of the ferrocyanide in the solution by using the mole ratio of potassium ferrocyanide to zinc sulfate determined in the first part of this experiment.

C. (Option 2) The amount of zinc ion in a commercially available tablet. Pipet 25.00 mL of the 0.025 M $K_4Fe(CN)_6$ solution into a 250 mL Erlenmeyer flask. Grind up a commercial zinc tablet containing 50 mg of zinc in a mortar and transfer the solid quantitatively to the ferrocyanide solution. Add ~5 mL of 3 M sulfuric acid, 3 drops of freshly prepared 1% potassium ferricyanide and 4 drops of diphenylamine indicator. If the solution is milky white, it is ready for titration. Be aware that the titration will only take a few mL so titrate slowly from the start (Note: If the solution is blue, pipet 10.00 additional mL of the ferrocyanide into the flask. The solution should turn white and can now be titrated with the zinc ion.) Repeat the titration at least once.

Hazards

Diphenylamine is toxic and the indicator solution is strongly acidic. The dispensing bottle should have toxic and corrosive warning labels. While ferrocyanide and ferricyanide ions have fairly low toxicities, they can decompose in the presence of heat and/or strong acids to produce hydrogen cyanide. Precautions should be taken so that waste containing ferrocyanide and ferricyanide does not come into contact with strongly acidic solutions.

CAS registry numbers

zinc sulfate heptahydrate   7446-20-0
potassium ferrocyanide trihydrate   14459-95-1
potassium ferricyanide   13746-66-2
diphenylamine   00122-39-4

Prelaboratory Problems

1. Molecules are mobile in a gas and some reactions can be run in the gas phase. Give several reasons solutions are preferable for synthetic reactions.

2. Sodium hydroxide comes in pellet form in bottles from laboratory supply companies but it cannot be used as a primary standard. Why not?

3. Why is there an error in molarity if you dilute <u>with</u> 100 mL of water rather than <u>to</u> the 100 mL mark with water?

4. 10.00 mL of a silver nitrate solution is titrated to the equivalence point with 8.50 mL of a 0.1100 M HCl solution. What is the concentration of the silver nitrate solution?

5.   For the titration in #4, what are the consequences if the indicator changes at the 8.75 mL point?

6.   15.50 mL of a 0.1075 M NaOH solution are required to neutralize 15.00 mL of a sulfuric acid solution. What is the concentration of the sulfuric acid solution?

7.   22.87 mL of a 0.1075 M NaOH solution are required to neutralize 0.300 grams of an unknown monoprotic acid. What is the molecular mass of the acid?

8.   What is the function of an indicator in a titration?

9.   Suggest at least two different ways an indicator could work in this experiment.

Results and Discussion

A. Stoichiometry of the reaction

1. Formula Mass of $K_4Fe(CN)_6 \cdot 3H_2O$ _____

2. Mass of $K_4Fe(CN)_6 \cdot 3H_2O$ needed for 100 mL of 0.025 M soln. _____

3. Mass of beaker + $K_4Fe(CN)_6 \cdot 3H_2O$ _____

4. Mass of beaker _____

5. Mass of $K_4Fe(CN)_6 \cdot 3H_2O$ _____

6. Moles of $K_4Fe(CN)_6 \cdot 3H_2O$ _____

7. Concentration of $K_4Fe(CN)_6$ solution _____

8. Formula mass of $ZnSO_4 \cdot 7H_2O$ _____

9. Amount of $ZnSO_4 \cdot 7H_2O$ needed for 250 mL of 0.050 M solution _____

10. Mass of beaker + $ZnSO_4 \cdot 7H_2O$ _____

11. Mass of beaker _____

12. Mass of $ZnSO_4 \cdot 7H_2O$ _____

13. Moles of $ZnSO_4 \cdot 7H_2O$ _____

14. Concentration of $ZnSO_4$ _____

15. Volume of $K_4Fe(CN)_6$ solution for each titration _____

16. Moles of $K_4Fe(CN)_6$ titrated _____

Titration with $ZnSO_4$	1st	2nd	3rd
17. Final buret reading	_____	_____	_____
18. Initial buret reading	_____	_____	_____
19. Volume of $ZnSO_4$	_____	_____	_____
20. Moles of $ZnSO_4$	_____	_____	_____

21. Average number of moles of $ZnSO_4$ _____

22. Mole ratio of $K_4Fe(CN)_6$ to $ZnSO_4$ (Also enter on line 9 on next page) _____

23. Which of the four possible equations (page 2) agrees most closely with the mole ratio in *# 22*? Write down the equation and explain your choice.

24. Balanced net ionic equation for the reaction:

B. Concentration of ferrocyanide in an unknown

1. Unknown identification number   _____

2. Concentration of $ZnSO_4$ _____

3. Volume of unknown $K_4Fe(CN)_6$ solution   _____

Titration with $ZnSO_4$	1st	2nd	3rd
4. Final buret reading	_____	_____	_____
5. Initial buret reading	_____	_____	_____
6. Volume of $ZnSO_4$	_____	_____	_____
7. Moles of $ZnSO_4$	_____	_____	_____

8. Average number of moles of $ZnSO_4$ _____

9. Mole ratio of $K_4Fe(CN)_6$ to $ZnSO_4$ _____

10. Moles of $K_4Fe(CN)_6$ _____

11. Concentration of $K_4Fe(CN)_6$ in unknown solution   _____

C. (Option 2) The amount of zinc ion in a commercially available tablet.

1. Amount of zinc ion in tablet according to label   _____

2. Concentration of $ZnSO_4$ _____

3. Volume of 0.025 M $K_4Fe(CN)_6$ solution   _____
    (If not 25.00 mL, then the calculations below need to be modified)

Titration with $ZnSO_4$	1st	2nd	3rd
4. Final buret reading	_____	_____	_____
5. Initial buret reading	_____	_____	_____
6. Volume of $ZnSO_4$	_____	_____	_____

8. Average volume of $ZnSO_4$ _____

9. Average volume of $ZnSO_4$ used in Part A   _____

10. Volume of $ZnSO_4$ equivalent to amount of zinc in tablet (#9 - #8)   _____

11. Moles of $ZnSO_4$ equivalent to amount of zinc in tablet   _____

12. Grams of zinc ion experimentally determined in tablet   _____

13. Percent difference between label and experiment   _____

14. Critically comment on the claim on the bottle that it contains 50 mg of zinc.