An Oxidation-Reduction Titration: The Reaction of Fe$^{2+}$ and Ce$^{4+}$

A titration, as you recall, is a convenient method of learning more about a solution by reacting it with a second solution of known molar concentration. There are a number of ways to measure the progress of a titration. The method used in this experiment is called a potentiometric titration, in which the electric potential of a reaction is monitored. All acid-base titrations that are measured by a pH probe are potentiometric; thus, this method is not as unusual as it may seem.

You will conduct an oxidation-reduction reaction in this experiment in order to determine the amount of iron (II) ions in a solid sample of ferrous ammonium sulfate hexahydrate, (NH$_4$)$_2$Fe(SO$_4$)$_2$•6H$_2$O. The oxidizing agent for the sample will be ammonium cerium (IV) nitrate, (NH$_4$)$_2$Ce(NO$_3$)$_6$. The net ionic equation for the reaction is shown below.

$$\text{Ce}^{4+} (\text{aq}) + \text{Fe}^{2+} (\text{aq}) \rightarrow \text{Ce}^{3+} (\text{aq}) + \text{Fe}^{3+} (\text{aq})$$

This experiment illustrates the electrical nature of chemical reactions, and offers practice with a process for observing and measuring an oxidation-reduction reaction.

OBJECTIVES

In this experiment, you will

- Conduct the potentiometric titration of the reaction between ferrous ammonium sulfate hexahydrate and ammonium cerium (IV) nitrate.
- Measure the potential change of the reaction.
- Determine the molar concentration of iron (II) ions in a sample of ferrous ammonium sulfate hexahydrate.
CHOOSING A METHOD

If you choose Method 1, you will conduct the titration in a conventional manner. You will deliver volumes of Ce<sup>4+</sup> titrant from a buret. You will enter the buret readings manually to store and graph each potential-volume data pair.

If you choose Method 2, you will use a Vernier Drop Counter to conduct the titration. Ce<sup>4+</sup> titrant is delivered drop by drop from the reagent reservoir through the Drop Counter slot. After the drop reacts with the reagent in the beaker, the volume of the drop is calculated and a potential-volume data pair is stored.

MATERIALS

**Materials for both Method 1 (buret) and Method 2 (Drop Counter)**
- Vernier computer interface
- computer
- Vernier ORP Sensor
- magnetic stirrer
- stirring bar or Microstirrer
- 0.100 M (NH₄)₂Ce(NO₃)₆ in 1 M H₂SO₄
- distilled water
- (NH₄)₂Fe(SO₄)₂•6H₂O solution
- ring stand
- 50 mL graduated cylinder
- utility clamp

**Materials required only for Method 1 (buret)**
- 50 mL buret
- 10 or 25 mL pipet and pump
- buret clamp
- 150 mL beaker

**Materials required only for Method 2 (Drop Counter)**
- Vernier Drop Counter
- 100 mL beaker
- 60 mL reagent reservoir
- 10 mL graduated cylinder
- 5 mL pipet
- two 250 mL beakers

**METHOD 1: Measuring Volume Using a Buret**

1. Obtain and wear goggles.

2. Measure out precisely 25.00 mL of a ferrous ammonium sulfate solution of unknown molar concentration and transfer it to a 150 mL beaker.

3. Place the beaker of ferrous ammonium sulfate solution on a magnetic stirrer and add a stirring bar. If no magnetic stirrer is available, stir the mixture with a stirring rod during the titration.

4. Connect an ORP Sensor to Channel 1 of a Vernier computer interface. Connect the interface to the computer with the proper cable.

5. Start the Logger Pro program on your computer. Open the file “08a Potentiometric” from the Advanced Chemistry with Vernier folder.

6. Set up a ring stand, buret clamp, and 50 mL buret to conduct the titration (see Figure 1). Rinse and fill the buret with 0.100 M Ce<sup>4+</sup> solution. **CAUTION:** Handle the solution with care; it contains 1.0 M sulfuric acid. It can cause painful burns if it comes in contact with the skin.
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7. Place a utility clamp on the ring stand to hold the ORP Sensor in place during the titration. Position the ORP Sensor so that its tip is immersed in the Fe$^{3+}$ solution but does not interfere with the movement of the magnetic stirring bar. Gently stir the beaker of solution.

8. You are now ready to begin the titration. The objective of your first trial is to determine the region of the titration curve near the equivalence point, and not to precisely determine the equivalence point.
   
   a. Before adding Ce$^{4+}$ titrant, click [Collect]. Once the displayed potential reading has stabilized, click [Keep]. In the edit box, type “0” (for 0 mL added). Press the ENTER key to store the first data pair.

   b. Add 1 mL of the Ce$^{4+}$ titrant. Stir the solution gently at all times. When the potential stabilizes, again click [Keep]. In the edit box, type the current buret reading. Press ENTER to store the second data pair.

   c. Add Ce$^{4+}$ solution in 1 mL increments and enter the buret reading after each increment. Continue adding Ce$^{4+}$ solution until the potential value remains constant.

   d. Click [Stop] when you have finished collecting data.

   e. Examine the titration curve and estimate the volume of Ce$^{4+}$ solution used to reach the equivalence point of the titration. Record this value in your data table for Trial 1.

9. When you have completed the titration, dispose of the reaction mixture as directed. Rinse the ORP Sensor with distilled water in preparation for the second trial.

10. Repeat the necessary steps to conduct a second titration with a new sample of (NH$_4$)$_2$Fe(SO$_4$)$_2$•6H$_2$O solution.

11. When you conduct the second trial, carefully add the Ce$^{4+}$ solution drop by drop in the region near the equivalence point so that you can precisely identify the equivalence point of the reaction.

12. Follow the steps below to find the equivalence point, which that is the largest increase in potential upon the addition of a very small amount of Ce$^{4+}$ solution. A good method of determining the precise equivalence point of the titration is to take the second derivative of the potential-volume data, a plot of $\Delta^2$potential/$\Delta^2$vol$^2$.

   a. View a plot of the second derivative on Page 3 by clicking on the Next Page button, [Next].

   b. Analyze the second derivative plot and record the volume of Ce$^{4+}$ at the equivalence point.

13. At the direction of your instructor, conduct a third trial. Use your titration data from the second (or third) trial to determine the equivalence point of the reaction.

14. Print a copy of the trial and the data set that you intend to use in your data analysis.

METHOD 2: Measuring Volume with a Drop Counter

1. Obtain and wear goggles.

2. Add 40 mL of distilled water to a 100 mL beaker. (You can add less, about 20 mL, if you will be using a stirring bar instead of the Microstirrer.) Use a pipet bulb (or pipet pump) to transfer 5.0 mL of the ferrous ammonium sulfate solution of unknown molar concentration into the 100 mL beaker with distilled water. **CAUTION:** Handle the hydrochloric acid with care. It can cause painful burns if it comes in contact with the skin.

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3. Connect the ORP Sensor to CH 1 of the computer interface. Lower the Drop Counter onto a ring stand and connect its cable to DIG/SONIC 1 (see Figure 2).

4. Start the Logger Pro program on your computer. Open the file “08b Potentiometric (Drop)” from the Advanced Chemistry with Vernier folder.

5. Obtain the plastic 60 mL reagent reservoir. Close both valves by turning the handles to a horizontal position. Follow the steps below to set up the reagent reservoir for the titration.
   a. Rinse the reagent reservoir with a few mL of the 0.100 M Ce$^{4+}$ solution and pour it into an empty 250 mL beaker.
   b. Use a utility clamp to attach the reservoir to the ring stand.
   c. Fill the reagent reservoir with slightly more than 60 mL of the 0.100 M Ce$^{4+}$ solution.
   d. Place the 250 mL beaker, which contains the rinse Ce$^{4+}$ solution, beneath the tip of the reservoir.
   e. Drain a small amount of the Ce$^{4+}$ solution into the 250 mL beaker to fill the reservoir’s tip. To do this, turn both valve handles to the vertical position for a moment, then turn them both back to horizontal.
   f. Discard the drained Ce$^{4+}$ solution in the 250 mL beaker as directed.

6. Calibrate the drops that will be delivered from the reagent reservoir. **Note:** If you are using the stored calibration (28 drops per mL), then skip this step.
   a. From the Experiment menu, choose Calibrate ▶ DIG 1: Drop Counter.
   b. Proceed by one of these two methods:
      • If you have previously calibrated the drop size of your reagent reservoir and want to continue with the same drop size, select the Manual button, enter the number of Drops/mL, and click OK. Then proceed directly to Step 7.
      • If you want to perform a new calibration, select the Automatic button, and continue with this step.
   c. Place a 10 mL graduated cylinder directly below the slot on the Drop Counter, lining it up with the tip of the reagent reservoir.
d. Open the bottom valve on the reagent reservoir (vertical). Keep the top valve closed (horizontal).

e. Click the Start button on the dialog box.

f. Slowly open the top valve of the reagent reservoir so that drops are released at a slow rate (~1 drop every two seconds). You should see the drops being counted on the computer screen.

g. When the volume of the Ce4+ solution in the graduated cylinder is between 9 and 10 mL, close the bottom valve of the reagent reservoir.

h. Enter the precise volume of Ce4+ solution (read to the nearest 0.1 mL) in the edit box. Record the number of Drops/mL displayed on the screen for possible future use.

i. Click [OK]. Discard the Ce4+ solution in the graduated cylinder as directed and set the graduated cylinder aside.

7. Assemble the apparatus.
   a. Place the magnetic stirrer on the base of the ring stand.
   b. Insert the ORP Sensor through the large hole in the Drop Counter.
   c. Attach the Microstirrer to the bottom of the ORP Sensor. Rotate the paddle wheel of the Microstirrer, and make sure that it does not touch the bulb of the ORP Sensor.
   d. Adjust the positions of the Drop Counter and reagent reservoir so they are both lined up with the center of the magnetic stirrer.
   e. Lift up the ORP Sensor, and place the 100 mL beaker containing the ferrous ammonium sulfate solution onto the magnetic stirrer. Lower the ORP Sensor into the beaker.
   f. Adjust the position of the Drop Counter so that the Microstirrer on the ORP Sensor is just touching the bottom of the beaker.
   g. Adjust the reagent reservoir so its tip is just above the Drop Counter slot.

8. Turn on the magnetic stirrer so that the Microstirrer is stirring at a fast rate.

9. You are now ready to begin collecting data. Click [Collect]. No data will be collected until the first drop goes through the Drop Counter slot. Fully open the bottom valve, but do not touch the top valve. After the first drop passes through the Drop Counter slot, check the data table to see that the first data pair was recorded.

10. Watch your graph to see when a large increase in potential takes place. This will be the equivalence point of the reaction. When this jump in potential occurs, let the titration proceed for several more milliliters of titrant, then click [Stop]. Turn the bottom valve of the reagent reservoir to a closed (horizontal) position. Dispose of the reaction mixture as directed.

11. Follow the steps below to find the **equivalence point**, which is the largest increase in potential upon the addition of a very small amount of Ce4+ solution. A good method of determining the precise equivalence point of the titration is to take the second derivative of the potential-volume data, a plot of Δ²potential/Δvol².
   a. View a plot of the second derivative on Page 3 by clicking on the Next Page button, [Next].
   b. Analyze the second derivative plot and record the volume of Ce4+ at the equivalence point.

12. Print a copy of the graph and the data set. If you wish to save the results of the first titration, choose Store Latest Run in the Experiment menu.

13. Repeat the titration with a second ferrous ammonium sulfate solution. Analyze the titration results in a manner similar to your first trial and record the equivalence point.
DATA TABLE

<table>
<thead>
<tr>
<th>Volume of Fe(^{2+}) solution (mL)</th>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of Ce(^{4+}) solution used to reach equivalence point (mL)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DATA ANALYSIS

1. Calculate the molar amount of Ce\(^{4+}\) used to reach the equivalence point of the reaction.

2. Calculate the molar amount of iron in the sample of ferrous ammonium sulfate solution.

3. Calculate the molar concentration of the ferrous ammonium sulfate solution.

4. The ferrous ammonium sulfate solution that you tested was prepared by dissolving 40.0 g of solid \((\text{NH}_4)_2\text{Fe(SO}_4)_2\cdot6\text{H}_2\text{O}\) in 1.00 liter of solution. This substance is often impure.
   a. Calculate the theoretical percent Fe in a pure sample of \((\text{NH}_4)_2\text{Fe(SO}_4)_2\cdot6\text{H}_2\text{O}\).
   b. Calculate the percent Fe in the sample that you tested.
   c. Compare your experimental percent Fe to the theoretical percent Fe. How pure was your sample? Use a calculation to support your assertion.
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