Experiment 4*  
Separation of the Beautiful Oxidation States of Vanadium:  
\[ \text{VO}_3^-, \text{VO}^{2+}, \text{V}^{3+}, \text{V}^{2+} \]

*This lab has been adapted from “Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience,” 1991, John Wiley and Sons, New York, NY, p 246

Purpose
The purpose of this lab is to apply reduction potentials to a synthetic procedure, to build skills in ion-exchange chromatography, and to appreciate the beautiful colors of first-row transition metals.

Introduction
The transition element vanadium has four common oxidation states: \( V^{5+}, V^{4+}, V^{3+}, \) and \( V^{2+} \). The stabilities and colors of these are investigated using ion exchange chromatography in this experiment. Starting with \( V^{5+} \) in the form of ammonium metavanadate, \( \text{NH}_4\text{VO}_3 \), a series of reductions is carried out with either HCl to yield vanadium(IV), in the form of the vanadyl ion, \( \text{VO}^{2+} \):

\[ \text{VO}_3^- + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}^{2+} + 2\text{H}_2\text{O} \quad (1) \]

A second reduction with zinc amalgam yields \( \text{[V(H}_2\text{O)}_6]^3+ \) and \( \text{[V(H}_2\text{O)}_6]^2+ \).

\[ \text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{V}^{3+} (\text{aq}) + \text{H}_2\text{O} \quad (2) \]

\[ \text{V}^{3+} (\text{aq}) + \text{e}^- \rightleftharpoons \text{V}^{2+} (\text{aq}) \quad (3) \]

Each oxidation state of vanadium exists as an aquo complex, where \( \text{H}_2\text{O} \) or \( \text{OH}^- \) fills the coordination shell to make a tetrahedral or octahedral complex. Under our experimental conditions, the species in solution are as follows:

<table>
<thead>
<tr>
<th>oxidation state</th>
<th>short-hand notation</th>
<th>complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V^{5+} )</td>
<td>( \text{VO}_3^- )</td>
<td>( [\text{V(OH)}\text{O}_3]^{2-} )</td>
</tr>
<tr>
<td>( V^{4+} )</td>
<td>( \text{VO}^{2+} )</td>
<td>( [\text{V(H}_2\text{O)}_5\text{O}]^{2+} )</td>
</tr>
<tr>
<td>( V^{3+} )</td>
<td>( \text{V}^{3+} )</td>
<td>( [\text{V(H}_2\text{O)}_6]^{3+} )</td>
</tr>
<tr>
<td>( V^{2+} )</td>
<td>( \text{V}^{2+} )</td>
<td>( [\text{V(H}_2\text{O)}_6]^{2+} )</td>
</tr>
</tbody>
</table>

These oxidation states are readily distinguishable by their different colors, the \( \text{VO}^{2+} \) ion giving blue aqueous solutions, while \( \text{V(H}_2\text{O)}_6^{3+} \) and \( \text{V(H}_2\text{O)}_6^{2+} \) give green and violet colored solutions, respectively.

Ion exchange: Ion exchange chromatography uses a charged resin that binds ions of the opposite charge (remember Coulomb’s law?). In the present lab, you will use a cation-exchange resin that is composed of an inert polymer, with sulfonate (-SO_3^-) functional groups. By equilibrating the resin with HCl, you ensure that H^+ is the only cation on the column initially. Other cations, such as \( \text{VO}^{2+} \) (which is really \( [\text{V(H}_2\text{O)}_5\text{O}]^{2+} \)) compete with H^+ for the negatively charged sulfonate, and therefore cations are retained by the column according to their charge. The concentration of
H⁺ also plays a role, as high [H⁺] will tend to push off all other cations. Please note that the charge of the molecular species (the coordination complex) is NOT the same as the oxidation state of vanadium.

**Experimental Procedure**

**Preparation of the Chromatographic Column and Solutions.** Use a glass rod to push a small wad of glass wool down to the stopcock of a 25-mL buret. With the stopcock of the buret closed, fill the buret with an aqueous slurry of AG50W-X2 cation exchange resin (100-200 mesh, H⁺ form). Allow the resin to settle. Open the stopcock and continue adding the slurry of resin until the amount of the settled resin is ~4-5 in. high. Make sure the resin settles to form a tightly packed column. Close the stopcock as necessary to keep the level of liquid above the top of the resin.

After preparing the slurry and allowing it to settle, equilibrate the resin with 3 M HCl (~15mL), elute the acid, and then rinse the column with two volumes of distilled water (~20mL). Wash the resin with distilled water until the eluate is clear. This regenerates your resin, so that H⁺ is the only cation bound to the column, and washing with water removes excess acid.

**NOTE:** During the course of this experiment, do not allow the level of the liquid to fall below the top of the settled resin, or it will start to channel.

While settling, equilibrating, etc. are being completed, get ready for the next portion of your experiment by doing the following: Obtain ~25-30 test tubes and a rack for collecting fractions before you apply the solution to the column. In separate flasks, make up 50 mL each of 3, 1 and 0.4 HCl, starting with dilute HCl (6M). Use the approximate (10% accuracy) gradations of your glassware for measuring your water and HCl, as you only need 1 significant figure in your final acid concentrations.

**Separation of VO₃⁻ and VO²⁺.** *In the hood,* add 2.0 mL of concentrated HCl to 200 mg (1.71 mmol) of NH₄VO₃ in a 150-mm test tube. Heat the mixture to boiling over a microburner for 2-3 min. *Keep test tube pointed away from persons near you!* To prevent bumping, do not heat the test tube at the bottom, but rather heat along the edges while gently moving the tube. Once the mixture boils, dilute it with 10 mL of distilled water, mixing well. The solution should change from its original color to a bright green color. VO₃⁻ is yellow, whereas VO²⁺ is electric-blue – this solution is green, as it is a mixture of these two vanadium oxidation states.

Pour the bright green solution onto the cation exchange column. After applying the solution to the column, begin collecting 3 mL fractions immediately, as a yellow fraction comes of the column quite quickly. Allow the level of liquid to fall to the top of the resin, and then add 0.4 HCl as necessary to keep the buret full during elution. The upper band is readily detected by its green color (it is actually blue, but the orange color of the resin makes it appear to be green).

Once all the yellow fractions have eluted, or when the eluate begins to turn green or blue, change the solution on the top of the column to 1.0 M HCl. Continue collecting fractions of 3 mL until all of the blue band has eluted. You will elute ~9 mL of yellow and ~25 mL of ‘electric-blue’ solution from this preparation, with a few mL of a blue-green mixture in between. Combine the blue fractions (you should have ~25-30 mL in all). Combine the darkest yellow fractions, but do not combine any fractions that are yellow-green or blue-green. Make sure that the column is still wet.
Separation of \( \text{V(H}_2\text{O)}_6^{3+} \) and \( \text{V(H}_2\text{O)}_6^{2+} \). Place two thirds of the blue solution (~15-20 mL) in a 25-mL Erlenmeyer flask and add 2 g of zinc-mercury amalgam. The amalgam is easy to measure: tare the flask, and use your scoopula to weigh out the material. Stopper the flask and shake vigorously. After ~3 min. of shaking the solution will turn dark green (\( \text{V}^{3+} \)), then it will turn violet (\( \text{V}^{2+} \)) after about 1 additional minute. Stop the shaking at the first appearance of violet color (do not allow it to become all violet), so that a mixture of \( \text{V}^{3+} \) and \( \text{V}^{2+} \) is present. This solution is then decanted onto the chromatographic column. Allow the level of the liquid to fall to the top of the resin, and then add 1.0 M HCl as necessary to keep the buret full. Distinct green and violet bands should form. Collect the violet band in the 3-mL fractions as it elutes. After the violet band has eluted from the column, use 3.0 M HCl to elute the green species. Collect this in the same way. Combine the individual fractions in the same manner as in the first separation. To regenerate the column, wash with 3.0 M HCl until the eluate is clear, then pass 20-30 mL of water over the column. Remove the resin from the buret and collect the resin through gravity filtration.

Characterization of the Different Oxidation States. Titrate each fraction with \( \text{KMnO}_4 \) to determine the oxidation state of vanadium. Place 1 mL of each of the four eluted solutions in a series of test tubes, and add 0.001 M \( \text{KMnO}_4 \)(aq.) dropwise (via a Pasteur pipet) to each tube. \( \text{KMnO}_4 \) is a strong oxidizing agent, which should react with the other oxidation states of vanadium to form \( \text{V}^{5+} \).

Note which fractions decolorize the permanganate solution, and the approximate amount of drops needed to give the first trace of the permanganate color (pale pink).

Questions
1. For each reaction that you carried out in this experiment, give a balanced equation indication the oxidation state of the vanadium species and its color. Include in this list the reactions with \( \text{KMnO}_4 \), which re-oxidizes vanadium to \( \text{V}^{5+} \). A list of half-reactions is given below to facilitate this answer.
2. Compare the amount of \( \text{KMnO}_4 \) needed to reoxidize the different fractions obtained from your chromatographic column. Do these correspond to 1, 2, or 3 electron oxidations?
3. Cation exchange chromatography uses resins that have negative charges, so that positively charged ions will bind to the resins. Draw Lewis structures for vanadium in each oxidation state (as 4 or 6-coordinate complexes with \( \text{H}_2\text{O} \)). Draw a Lewis structure for the negatively charged functional group on AG50W-X2.
4. What ion competes with the vanadium complexes for binding sites on the resin?
5. Draw the d-orbital splitting, and electron population, for vanadium in each of the aquo complexes described in this experiment.
**Table 1.** Reduction Potentials relevant to this lab.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$</td>
<td>1.52</td>
</tr>
<tr>
<td>2. $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$</td>
<td>1.36</td>
</tr>
<tr>
<td>3. $\text{VO}_3^- + 4\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + 2\text{H}_2\text{O}$</td>
<td>1.00</td>
</tr>
<tr>
<td>4. $\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}$</td>
<td>0.34</td>
</tr>
<tr>
<td>5. $2\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O}$</td>
<td>0.17</td>
</tr>
<tr>
<td>6. $\text{V}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{V}^{2+}(\text{aq})$</td>
<td>-0.26</td>
</tr>
<tr>
<td>7. $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn(Hg)}$</td>
<td>-0.76</td>
</tr>
</tbody>
</table>