13. Synthesis and Analysis of Ammonium Decavanadate[21]

Green Profile
See Section 0

The species of aqueous V^{5+} depend on both pH and concentration (Figure 1).

$$VO_4^{3-} \rightleftharpoons V_2O_7^{4-} \rightleftharpoons V_4O_{12}^{4-} \rightleftharpoons HV_{10}O_{28}^{5-} \rightleftharpoons VO_2^{+}$$

In strong base

In strong acid

NH_4^+, acetic acid, alcohol

$$(NH_4)_6V_{10}O_{28} \cdot 6H_2O$$

FM 1 173.7

The decavanadate ion ($V_{10}O_{28}^{6-}$), which we will isolate in this experiment as the ammonium salt, consists of 10 VO_6 octahedra sharing edges with one another (Figure 2).

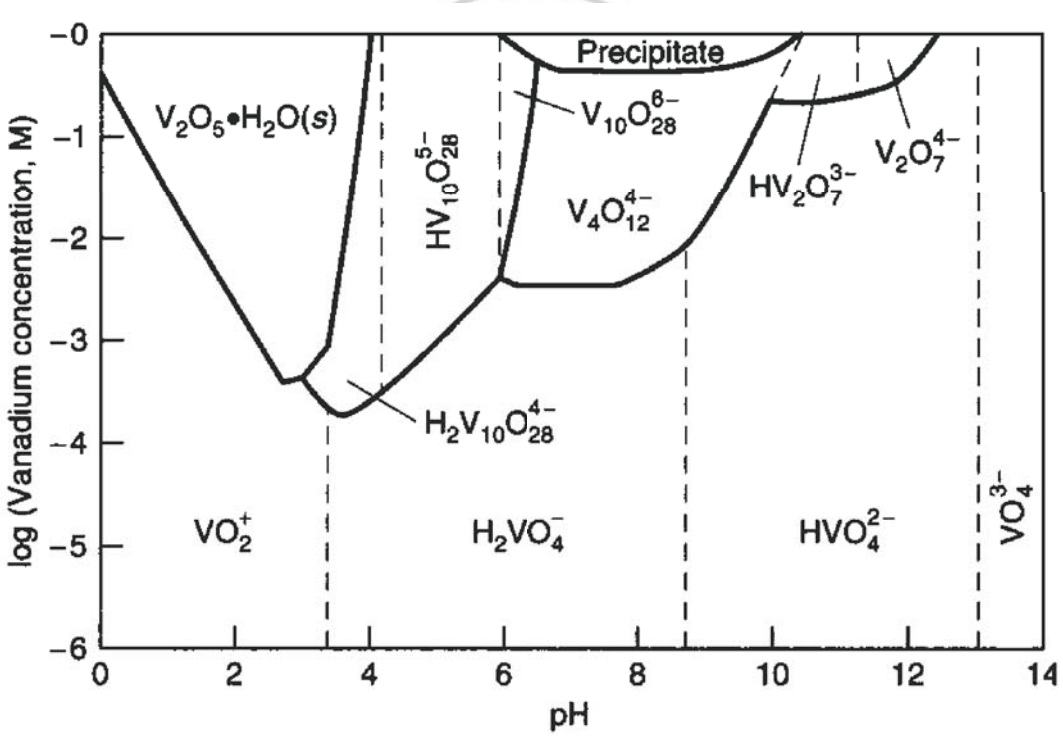

Figure 1. Phase diagram for aqueous vanadium(V) as a function of total vanadium concentration and pH. [From J. W. Larson, *J. Chem. Eng. Data* **1995**, *40*, 1276.] The region marked "precipitate" probably refers to a vanadium hydroxide.

21. G. G. Long, R. L. Stanfield, and F. C. Hentz, Jr., *J. Chem. Ed.* **1979**, *56*, 195.

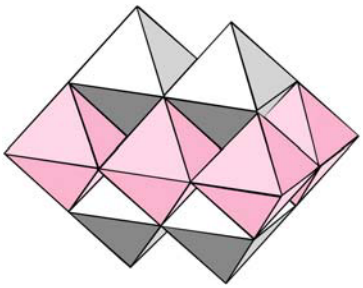

Figure 2. Structure of $V_{10}O_{28}^{6-}$ anion, consisting of VO_6 octahedra sharing edges with one another. There is a vanadium atom at the center of each octahedron.

After preparing this salt, we will determine the vanadium content by a redox titration and NH_4^+ by the Kjeldahl method. In the redox titration, V^{5+} will first be reduced to V^{4+} with sulfurous acid and then titrated with standard permanganate.

$$V_{10}O_{28}^{6-} + H_2SO_3 \rightarrow VO^{2+} + SO_2$$

$$\underset{\text{blue}}{VO^{2+}} + \underset{\text{purple}}{MnO_4^-} \rightarrow \underset{\text{yellow}}{VO_2^+} + \underset{\text{colorless}}{Mn^{2+}}$$

Reagents

Ammonium metavanadate (NH_4VO_3): 3 g/student.

50 vol% aqueous acetic acid: 4 mL/student.

95 % ethanol: 200 mL/student.

$KMnO_4$: 1.6 g/student or prepare 0.02 M $KMnO_4$ (~300 mL/student) for use by the class.

Sodium Oxalate ($Na_2C_2O_4$): 1 g/student.

0.9 M H_2SO_4: (1 L/student) Slowly add 50 mL of concentrated (96–98 wt%) H_2SO_4 to 900 mL of H_2O and dilute to ~1 L.

1.5 M H_2SO_4: (100 mL/student) Slowly add 83 mL of concentrated (96–98 wt%) H_2SO_4 to 900 mL of H_2O and dilute to ~1 L.

Sodium hydrogen sulfite ($NaHSO_3$, also called sodium bisulfite): 2 g/student.

Standard 0.1 M HCl: (75 mL/student) From Experiment 6.

Standard 0.1 M NaOH: (75 mL/student) From Experiment 6.

Phenolphthalein indicator and bromocresol green indicators: Recipes in Experiment 7.

50 wt% NaOH: 60 mL/student. Mix 100 g NaOH with 100 mL H_2O and dissolve.

Synthesis

1. Heat 3.0 g of ammonium metavanadate (NH_4VO_3) in 100 mL of water with constant stirring (but not boiling) until most or all of the solid has dissolved. Filter the solution and add 4 mL of 50 vol% aqueous acetic acid with stirring.
2. Add 150 mL of 95% ethanol with stirring and then cool the solution in a refrigerator or ice bath.
3. After maintaining a temperature of 0˚–l0˚C for 15 min, filter the orange product with suction and wash with two 15-mL portions of ice-cold 95% ethanol.
4. Dry the product in the air (protected from dust) for 2 days. Typical yield is 2.0–2.5 g.

Analysis of Vanadium with $KMnO_4$

Preparation and Standardization of $KMnO_4$[22] (See Section 15-4 in the textbook)

1. Prepare a 0.02 M permanganate solution by dissolving 1.6 g of $KMnO_4$ in 500 mL of distilled water. Boil gently for 1 h, cover, and allow the solution to cool overnight. Filter through a clean, fine sintered-glass funnel, discarding the first 20 mL of filtrate. Store the solution in a clean glass amber bottle. Do not let the solution touch the cap.
2. Dry sodium oxalate ($Na_2C_2O_4$) at 105˚C for 1 h, cool in a desiccator, ~~and weigh three ~0.25-g samples into 500-mL flasks or 400-mL beakers~~. To each, add 250 mL of 0.9 M H_2SO_4 that has been recently boiled and cooled to room temperature. ~~Stir with a thermometer to dissolve the sample, and add 90–95% of the theoretical amount of $KMnO_4$ solution needed for the titration. (This can be calculated from the mass of $KMnO_4$ used to prepare the permanganate solution. The chemical reaction is given by Equation 1-7 in the textbook.)~~
3. Leave the solution at room temperature until it is colorless. Then heat it to 55˚–60˚C and complete the titration by adding $KMnO_4$ until the first pale pink color persists. Proceed slowly near the end, allowing 30 s for each drop to lose its color.
4. As a blank, titrate 250 mL of 0.9 M H_2SO_4 to the same pale pink color. Subtract the blank volume from each titration volume. Compute the average molarity of $KMnO_4$.

22. R. M. Fowler and H. A. Bright, *J. Res. National Bureau of Standards* **1935**, *15*, 493.

Vanadium Analysis

1. Accurately weigh two 0.3-g samples of ammonium decavanadate into 250-mL flasks and dissolve each in 40 mL of 1.5 M H_2SO_4 (with warming, if necessary).
2. In a fume hood, add 50 mL of water and 1 g of $NaHSO_3$ to each and dissolve with swirling. After 5 min, boil the solution gently for 15 min to remove SO_2.
3. Titrate the warm solution with standard 0.02 M $KMnO_4$ from a 50-mL buret. The end point is taken when the yellow color of VO_2^+ takes on a dark shade (from excess MnO_4^-) that persists for 15 s.
4. Calculate the average wt% of vanadium in the ammonium decavanadate and compare your result to the theoretical value.

Analysis of Ammonium Ion by Kjeldahl Distillation

1. Set up the apparatus in Figure 1 of Experiment 11 and press the stoppers to make airtight connections. Pipet 50.00 mL of standard 0.1 M HCl into the receiving beaker and clamp the funnel in place below the liquid level.
2. Transfer 0.6 g of accurately weighed ammonium decavanadate to the three-neck flask and add 200 mL of water. Add 5–10 drops of phenolphthalein indicator and secure the stoppers. Pour 60 mL of 50 wt% NaOH into the adding funnel and drip this into the distillation flask over a period of 1 min until the indicator turns pink. *(Caution:* 50 wt% NaOH eats people. Flood any spills on your skin with water.) Do not let the last 1 mL through the stopcock, so that gas cannot escape from the flask. Close the stopcock and heat the flask gently until two-thirds of the liquid has distilled.
3. Remove the funnel from the receiving beaker *before* removing the burner from the flask (to avoid sucking distillate back into the condenser). Rinse the funnel well with distilled water and catch the rinses in the beaker. Add 6 drops of bromocresol green indicator solution to the beaker and carefully titrate to the blue end point with standard 0. 1 M NaOH. You are looking for the first appearance of light blue color. (Several practice titrations with HCl and NaOH will familiarize you with the end point.)
4. Calculate the weight percent of nitrogen in the ammonium decavanadate.