

1. Estimating an Electrode Potential

Introduction

The reaction in the zinc-copper voltaic cell (Ebbing/Gammon, Section 20.2) occurs spontaneously because $\Delta G < 0$. Metallic zinc is oxidized at one electrode with the formation of Zn^{2+} ions. Simultaneously, Cu^{2+} ions are reduced at the other electrode, and metallic copper is deposited. Spontaneous oxidation-reduction reactions such as this one are not confined to voltaic cells. When a piece of zinc is placed in a beaker containing a solution of Cu^{2+} ions, an identical reaction occurs. Both reactions occur because they have favorable and, of course, identical changes in free energy.

We can see from this example that an oxidation-reduction reaction that is spontaneous in a single container, such as a beaker or flask, will also be spontaneous in a voltaic cell. Moreover, we can infer that a reaction that is not spontaneous in a single container will not be spontaneous in a voltaic cell. Behavior in a voltaic cell must be identical to behavior in a single container.

Often you can learn some of the characteristics of a particular electrode by observing its reactions with other substances in a single container. It is even possible to estimate the magnitude of the electrode potential of this electrode without using a voltmeter.

Purpose

You will estimate the standard electrode potential for the $\text{VO}_2^+(aq)$, $\text{VO}^{2+}(aq)$, $\text{H}^+(aq)|\text{Pt}$ electrode in this experiment. The results from the interaction of potential reducing agents with VO_2^+ ions and potential oxidizing agents with VO^{2+} ions will enable you to accomplish this goal.

Estimating E°

The standard electrode potential (Ebbing/Gammon, Section 20.5) for the reduction of a substance can sometimes be estimated without recourse to a voltaic cell or a voltmeter. The estimate is based on observation of the spontaneity of the substance's reactions with a series of other substances whose standard electrode potentials are known.

Suppose, for example, that we want to use this technique to estimate the standard electrode potential for the electrode

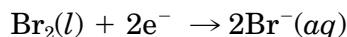
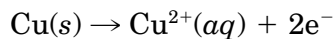


How should we proceed?

First, we might choose to explore the reaction



The appropriate half-cell reactions for this overall reaction are



If this reaction were conducted in an electrochemical cell, the electrodes and standard electrode potentials that correspond to these half-cell reactions would be



The anode can be established readily because it would be the site of oxidation. The overall reaction shows that metallic copper is oxidized. The cathode must then be the bromide electrode. The standard emf is

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= (1.07 - x) \text{ V} \end{aligned}$$

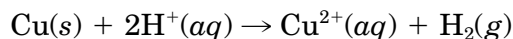
When we try to do this reaction, we find that it occurs readily. Consequently, it is spontaneous, and E_{cell}° must be positive (or $E_{\text{cell}}^{\circ} > 0$). We can then write

$$E_{\text{cell}}^{\circ} = (1.07 - x) \text{ V} > 0$$

If $1.07 - x$ is greater than zero, x must be less than 1.07. As a result, we can write

$$x < 1.07 \text{ V}$$

Next we might choose to explore the reaction



If this reaction were conducted in a voltaic cell, the electrodes and standard electrode potentials would be



The location of the anode can again be obtained from the overall reaction. Metallic copper is oxidized, so the copper electrode is once again the anode. Now we can write

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= (0 - x) \text{ V} = -x \text{ V} \end{aligned}$$

Experiments, however, would show us that metallic copper will not dissolve in strong acids, such as HCl or H_2SO_4 . Clearly, the overall reaction is not spontaneous, and E_{cell}° must be negative ($E_{\text{cell}}^{\circ} < 0$). We can then write

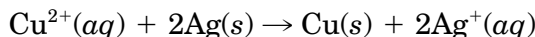
$$E_{\text{cell}}^{\circ} = -x \text{ V} < 0$$

Because $-x$ is less than zero, x must be greater than zero, or

$$x > 0 \text{ V}$$

Thus two experiments have been sufficient to show that x must lie between 0 and 1.07 V, or $0 < x < 1.07 \text{ V}$. However, this range is very broad. Additional observations with other reagents will enable us to narrow the permissible range.

Suppose that we next elect to examine the reaction



The electrodes and their standard potentials are

$$\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s}) \qquad E^{\circ} = x$$

$$\text{Ag}^{+}(\text{aq})|\text{Ag}(\text{s}) \qquad E^{\circ} = 0.80 \text{ V}$$

If this reaction occurs, metallic silver will be oxidized and Cu^{2+} ions will be reduced. We then know that the silver electrode is the anode and the copper electrode is the cathode. The standard emf of the voltaic cell is

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= (x - 0.80) \text{ V} \end{aligned}$$

An experiment would show that this reaction will not occur. We then know that

$$E_{\text{cell}}^{\circ} = (x - 0.80) \text{ V} < 0$$

If $x - 0.80$ is less than zero, x must be less than 0.80, or

$$x < 0.80 \text{ V}$$

This observation allows us to decrease the permissible range for x from $0 < x < 1.07 \text{ V}$ to $0 < x < 0.80 \text{ V}$. Additional studies with other reagents would lead to a range that spanned only one or two tenths of a volt. The correct value for x is 0.34 V.

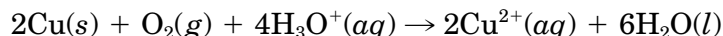
A special note

A standard electrode potential is the potential of an electrode with the molarities of ions and the pressure of gases (in atmospheres) equal to 1 at 25°C (Ebbing/Gammon, Section 20.5). These conditions do not have to be duplicated faithfully, however, if the standard electrode potential is to be estimated rather than measured directly. The reason is straightforward. As we have seen, the estimated potential will span at least one or two tenths of a volt. Even this limited range will introduce an uncertainty that will exceed the usual deviation from the standard electrode potential caused by nonstandard conditions. As a result, exact conformity to standard conditions or corrections using the Nernst equation (Ebbing/Gammon, Section 20.7) are usually pointless.

Reaction rate vs. spontaneity

Spontaneous reactions may or may not occur rapidly. Some spontaneous reactions may be so slow that for all practical purposes, they do not occur under ordinary conditions. Unfortunately, there is no easy way to decide whether a spontaneous reaction will be fast or slow.

Unless you are cautious, a very slow reaction can lead to an incorrect result when you are estimating an electrode potential. For example, when metallic copper is placed in an acidic solution that is saturated with O_2 , there is no immediate reaction. If the reaction occurs eventually, we write



In a voltaic cell, the electrodes and their standard potentials would be



Once again, the copper electrode is the anode, because oxidation occurs at that site. As a result, we write

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= (1.23 - x) \text{ V} \end{aligned}$$

We did not observe a reaction, so we might conclude that $1.23 - x$ is negative, or

$$1.23 - x < 0$$

and

$$x > 1.23 \text{ V}$$

This result is erroneous. As we have seen, our other observations have led us to the conclusion that $x < 0.80 \text{ V}$.

This example suggests an important piece of advice: Be suspicious when you observe no reaction. Be especially suspicious if you are using a strong oxidizing agent or a strong reducing agent. If you suspect that a slow reaction rate is responsible, how should you proceed? One approach is to be patient and give the reaction more time to occur. Another approach is to increase the temperature. As a general rule, the rate of a reaction approximately doubles for each 10° increase in the temperature.

Concept of the experiment

Table 1.1 contains the half-cell reactions that pertain to this experiment, along with the corresponding electrode potentials. The unknown electrode potential for the $\text{VO}_2^+(aq)$, $\text{VO}^{2+}(aq)$, $\text{H}_3\text{O}^+(aq)|\text{Pt}$ electrode is represented by x .

The oxidation numbers for vanadium in VO_2^+ and VO^{2+} are +5 and +4, respectively. Do you see how these numbers were obtained? If not, remember

Table 1.1 Standard Electrode Potentials at 25°C

Cathode Reaction	E° (V)
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O}$	x
$\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- \rightleftharpoons 4\text{H}_2\text{O}$	1.78
$\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	1.07
$\text{NO}_3^- + 3\text{H}_3\text{O}^+ + 2\text{e}^- \rightleftharpoons \text{HNO}_2 + 4\text{H}_2\text{O}$	0.94
$\text{SO}_4^{2-} + 4\text{H}_3\text{O}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{SO}_3 + 5\text{H}_2\text{O}$	0.17
$2\text{CO}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$	-0.49

that the oxidation number of oxygen in each of these ions is -2 (Ebbing/Gammon, Section 4.5). If you keep the oxidation numbers of vanadium in mind, you should be able to see that the half-reaction in the table that involves vanadium is a reduction.

All the substances to the left of the arrows in this table are potential oxidizing agents. All the substances to the right of the arrows are potential reducing agents. You will look for reactions between VO_2^+ —a potential oxidizing agent—and potential reducing agents. These are H_2O , Br^- , HNO_2 (nitrous acid), H_2SO_3 (sulfurous acid), and $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid), as shown in Table 1.1. You will also look for reactions between VO^{2+} —a potential reducing agent—and potential oxidizing agents. Because of the limited solubility of CO_2 in an acidic solution, the only potential oxidizing agents in Table 1.1 that you can use are H_2O_2 , Br_2 , NO_3^- , and SO_4^{2-} . The successful reactions and the failures (after you are satisfied that they really are failures) can be used to estimate the desired electrode potential.

How will you know whether a reaction has occurred? The signal will be a color change. The color of VO_2^+ is yellow, whereas the color of VO^{2+} is blue. As a result, the successful reduction of VO_2^+ with a colorless reducing agent causes the color to change from yellow to blue. Similarly, the successful oxidation of VO^{2+} with a colorless oxidizing agent causes the color to change from blue to yellow.

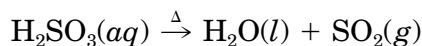
A reaction mixture may turn green, however. If it does so, there are two possible reasons. The green color may be due either to the presence of roughly equal quantities of yellow VO_2^+ and blue VO^{2+} or to a combination of blue VO^{2+} and a yellow color from a reagent you have added. You will have an opportunity to explore the implications further in the Prelaboratory Assignment. Nevertheless, if you obtain a green color, be prepared to expend some effort to discover which of these possibilities caused it. Some mental reflection and perhaps a little more experimental work will be necessary. Did you add the correct quantity of an oxidizing or reducing agent? If the reaction appears to be slow, did you have sufficient patience to observe the final outcome?

Additional note

The reaction mixtures in this experiment will be acidic because you will be using a 0.05 M solution of VO_2^+ ions in 1 M H_2SO_4 . The acidity plays a role that may not be obvious to you. During this experiment, you will add Na_2SO_3

(sodium sulfite) and NaNO_2 (sodium nitrite) to the solution of VO_2^+ ions. The acid in this solution will convert the sulfite and nitrite ions to the corresponding weak acids, H_2SO_3 and HNO_2 . As a result, H_2SO_3 rather than SO_3^{2-} and HNO_2 rather than NO_2^- are given in Table 1.1.

You will also need to generate VO^{2+} ions in this experiment. You will prepare a solution of these ions by reducing VO_2^+ ions with a tenfold excess of sodium sulfite. After the reduction has occurred, you will remove the remainder of the reducing agent by heating the solution. Heating allows SO_2 (sulfur dioxide) to escape from the solution according to the reaction



Unfortunately, sulfur dioxide has a foul, suffocating odor. This substance must be handled carefully so that its odor does not permeate your laboratory.

Procedure

Getting started

1. Obtain 5 small test tubes. Mark each one with a number for identification.
2. Set up a boiling water bath using a beaker of water, a ring stand, an iron ring, a wire gauze, and a laboratory burner. The bath should be placed in a hood if one is available. If not, use an inverted conical filter funnel connected by rubber tubing to a water aspirator. Clamp the funnel so that it is positioned directly over the beaker in which VO^{2+} will be prepared.

CAUTION: Avoid burning your fingers. Do not touch the iron ring or wire gauze during heating.

3. During this experiment, you will use solutions of oxalic acid. Observe the following safety precaution:

CAUTION: Wash your hands thoroughly after using solutions containing oxalic acid because they are poisonous.

Attempting reduction of VO_2^+

1. Add 2 mL of 0.05 M VO_2^+ in 1 M H_2SO_4 to each of the 5 test tubes.
2. To the first test tube, add a small portion (about a quarter the size of a pea) of solid Na_2SO_3 . Allow the test tube to stand for several minutes before placing it in the boiling water bath. Record your observations.

CAUTION: Sulfur dioxide has a foul, suffocating odor. Work under a hood if possible. If not, use the inverted conical filter funnel and water aspirator described earlier to suck away escaping SO_2 .

3. Test the effect of 20 drops of water in the second test tube, 20 drops of 0.2 M NaBr in the third test tube, 20 drops of 0.2 M NaNO₂ in the fourth test tube, and 20 drops of 0.2 M H₂C₂O₄ in the fifth test tube. Allow the test tubes to stand for about 3 min. If no reaction has occurred, place them in the boiling water bath for at least 10 min. Record your observations.
4. Wash the test tubes and rinse them with distilled water.

Preparing VO²⁺

1. Measure 15 mL of the 0.05 M VO₂⁺ solution, using a clean graduated cylinder. Pour the solution into a clean 150-mL beaker.
2. Use a platform balance, triple beam balance, or an electronic top-loading balance to measure the desired mass of Na₂SO₃ for the reduction of the VO₂⁺ ions. You calculated this quantity, which is 10 times the stoichiometric amount, in the Prelaboratory Assignment. Record your measurements.
3. Add this substance to the solution of the VO₂⁺ ions. Stir or swirl until all of the solid has dissolved. Allow the solution to stand for several minutes.
4. Replace the beaker of water from the water bath with this beaker. Heat the solution gently until all of the SO₂ has been expelled.

Attempting oxidation of VO²⁺

1. Add 2 mL of the solution of VO₂⁺ to each of 4 test tubes.
2. Test the effect of 20 drops of 3% H₂O₂ in the first test tube, 40 drops of bromine water in the second test tube, 20 drops of 0.2 M NaNO₃ in the third test tube, and 20 drops of 0.2 M Na₂SO₄ in the fourth test tube. Allow the test tubes to stand for about 3 min. If no reaction has occurred, place them in the boiling water bath for at least 10 min. Record your observations.
3. Wash the test tubes and rinse them with distilled water.

CAUTION: Before you leave the laboratory, make sure that your gas outlet and those of your neighbors are closed.

Estimating an Electrode Potential

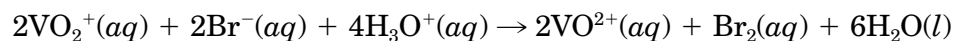
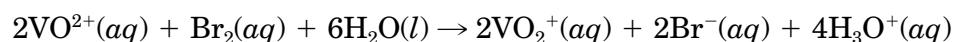
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Course: Team members:
Section:
Instructor:

Prelaboratory assignment

1. a. What electrode potential will you estimate in this experiment?

b. How will you make the estimate?

2. a. Calculate E°_{cell} for the following reactions in terms of x .



b. If the first reaction occurs but the second does not, what can be said about the value of x ?

3. What will you do if no immediate reaction occurs when you are attempting to reduce VO_2^+ ions or oxidize VO^{2+} ions?

4. a. What is the color of VO_2^+ ions? What is the oxidation number of vanadium?
- b. What is the color of VO^{2+} ions? What is the oxidation number of vanadium?
- c. Attempt to assign an oxidation number to vanadium for each color in the following sequence of color changes that might occur during the reduction of VO_2^+ ions. Assume that the reducing agent and its oxidation product are colorless.

yellow → green → blue

5. a. How will you prepare a solution of VO^{2+} ions in this experiment?
- b. Calculate the required mass of the reducing agent if a tenfold excess is to be used.
- c. Give reasons for using a tenfold excess of the reducing agent.

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- d. How will the remainder of the reducing agent be removed after the reduction has occurred? Show a chemical equation.
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6. What special safety precautions must be observed during this experiment?

Estimating an Electrode Potential

Date: Student name:
Course: Team members:
Section:
Instructor:

Results

1. *Attempting reduction of VO_2^+*

	Observations	Oxidation Number of V After Attempt
Na_2SO_3		
H_2O		
NaBr		
NaNO_2		
$\text{H}_2\text{C}_2\text{O}_4$		

2. *Preparing VO²⁺*

Mass of container and Na₂SO₃ (g):

Mass of empty container (g):

Mass of Na₂SO₃ (g):

3. *Attempting oxidation of VO²⁺*

	Observations	Oxidation Number of V After Attempt
H₂O₂		
Br₂		
NaNO₃		
Na₂SO₄		

Questions

1. a. Which reagents caused the reduction of VO₂⁺ ions?

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b. Give the complete reaction for each of these reagents with VO_2^+ .
Calculate E_{cell}° for each reaction in terms of x .

c. What are possible values of x in terms of these reactions?

2. a. Which reagents caused the oxidation of VO^{2+} ions?

b. Give the complete reaction for each of these reagents with VO^{2+} .
Calculate E_{cell}° for each reaction in terms of x .

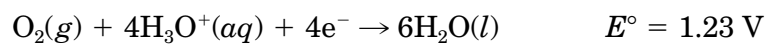
c. What are the possible values of x in terms of these reactions?

3. a. The narrowest range for x is given by

$$\dots\dots\dots < x < \dots\dots\dots \text{ V}$$

- b. As a crude estimate of x , obtain the mean value of these limits. This mean value should be used in the next question.

4. a. Using the crude estimate of x , calculate E°_{cell} for the reaction of VO^{2+} with O_2 if



- b. Explain why the solution of VO^{2+} ions did not react readily with O_2 in the air.