Experiment 4. Electrolytic Cells, Avogadro's Number



Objectives

- To identify the reactions occurring at the anode and cathode during the electrolysis of various aqueous salt solutions.
- To determine Avogadro's number and the Faraday constant.



Introduction

Electrolysis

Use of electrical energy to cause a chemical reaction to occur





Introduction

Electrolysis of Aqueous Solution

In an aqueous solution, however, the reduction of water at the cathodes and the oxidation of the anode are also possible reactions.

When two or more competing reduction reactions are possible at the cathode, the reaction that occurs most easily (the one with the higher reduction potential) is the one that usually occurs.



In the electrolysis of the aqueous copper(II) bromide solution, Cu^{2+} has a higher reduction potential than H₂O and is therefore preferentially reduced at the cathode.

Br has a greater tendency to oxidized than water, and so Br is oxidized at the anode.



Experimental procedure

Overview

The Product that result from the electrolysis of various salt solutions are observed and identified; these are qualitative measurements. An experimental setup is designed to measure quantitatively the flow of current and consequent changes in mass of the electrodes in an electrolytic cell; from these data, experimental constants are calculated.



A. Electrolysis of Aqueous Salt Solutions

- 1. SET UP THE ELECTROLYSIS APPARATUS.
- 1) Connect two wire leads (different colors) attached to alligator clips to a direct (dc) power supply.
- 2) Clean and mount the glass U-tube on a ring stand. Connect the alligator clips to the corresponding electrodes, listed in Table 33.1.



Table 33.1 Electrolytic Cells for Study

Solution No.	Solution	Electrodes (Cathode and Anode)	
1	2 g NaCl/100mL	Carbon (graphite)	
2	2 g NaBr/100mL	Carbon (graphite)	
3	2 g KI/100mL	Carbon (graphite)	
4	0.1 M CuSO ₄	Carbon (graphite)	
5	0.1 M CuSO ₄	Polished copper metal strips	

2. ELECTROLYZE THE SOLUTIONS.

1) Fill the U-tube three-fourths full with solution 1 from Table 33.1. Insert the corresponding electrodes into the solution and electrolyze for ~5 minutes.

2) During the electrolysis, watch for any evidence of a reaction in the anode and cathode chambers.

-Does the pH of the solution change at each electrode? Test each chamber with litmus or pH paper. Compare the color with a pH test on the original solution.

-Is a gas evolved at either or both electrodes?

-Look closely at each electrode. Is a metal depositing on the electrode or is the metal electrode slowly disappearing?





Solution	Electrodes	Litmus Test	Gas Evolved?	Balanced Equations for Reactions
NaCI	NaCl C (<i>gr</i>)		Anode	
				Cathode
				Cell
NaBr	[(<i>gr</i>)			
KI	[(<i>gr</i>)			
CuSO ₄	[(<i>gr</i>)			
CuSO ₄	Cu(s)			





3. ACCOUNT FOR YOUR OBSERVATIONS.

- 1) Write the equations for the reactions occurring at the anode and cathode and for the cell reaction.
- 2) Repeat for solutions 2-5.

B. Determination of Avogadro's Number and the Faraday Constant

1. SET UP THE APPARATUS. 1)

- Refer to Figure 33.4. The U-tube from Part A can again be used. We will use a dc power supply . Polish two copper metal strips (to be used as the electrodes) with steel wool or sandpaper. Briefly dip each electrode (use the fume hood) into 6 M HNO₃ (Caution: do not allow skin contact) for further cleaning, and then rinse with deionized water.
- 2) Add 90 mL of 1.0 M CuSO₄ (in 0.1 M H_2SO_4) to a 100mL beaker.



2. SET THE ELECTRODES.

- 1) Rinse the electrode with ethanol if available. When dry, label the two electrodes because the mass of each will be determined before and after the electrolysis.
- 2) Measure the mass $(\pm 0.001 \text{ g}, \text{ preferably } \pm 0.001 \text{ g})$ of each labeled electrode. The copper electrode with the lesser mass is to serve as the anode (+ terminal), and the other is to serve as the cathode (- terminal) for the electrolytic cell.
- 3) Connect the cathode (through the variable resistor and ammeter/multimeter) to the negative terminal of the dc power supply.
- 4) Before electrolysis begins, obtain your TA's approval of the complete apparatus.

3. ELECTROLYZE THE CUSO₄ SOLUTION.

- 1) Adjust the variable resistance to its maximum value. Be ready to start timing (a stopwatch is ideal). Attach the anode to the positive terminal of the dc power supply and START TIME.
- 2) During the electrolysis, do not move the electrodes; this changes current flow. Adjust the current with the variable resistor to about 0.5 A and, periodically during the course of the electrolysis, readjust the current to 0.5 A.
- 3) Discontinue the electrolysis after 20 ~ 30 minutes. Record the exact time (minutes and seconds) of the electrolysis process.





	Trial 1	Trial 2
1. Initial mass of copper anode (g)		
2. Initial mass of copper cathode (g)		
3. Instructor's approval of apparatus		
4. Time of electrolysis (s)		
5. Current (or average current) (A)		
6. Final mass of copper anode (g)		
7. Final mass of copper cathode (g)		

4. DRY AND MEASURE THE MASS.

- 1) Carefully remove the electrodes (be careful not to loosen the electroplated copper metal form the cathode); carefully dip each electrode into a 400-mL beaker of deionized water to rinse the electrodes (followed by ethanol if available).
- 2) Air-dry, measure the mass (±0.001 g, preferably ±0.0001 g) of each electrode, and record.
 (Acetone can be used to assist in the drying of the electrodes.)

5. REPEAT THE ELECTROLYSIS.

1) If time allows, repeat Part B using the same copper electrodes (with new mass measurements!) and 1.0 M CuSO₄ solution.







Have students clean and rinse (with tap water and distilled water) the U-tube (the electrolysis cell) and the carbon and copper electrodes. The dc power supply and the electrical connectors should be free of all solutions before returning them to the storage bench.



Rinse the beakers or U-tube with tap water and twice with deionized water. Discard each rinse as directed by your TA.

