Electrochemistry

CHEM 5390

CHEM 5390

- **Lecture:** TTh 8:00 – 9:20 a.m.
  Room 352 Chem

- **Instructor:** Dr. Teresa D. Golden,
  Chemistry 279, 565-2888, tgolden@unt.edu
  - **Office hours:** TTh 9:30 – 10:30 a.m. Room 279 or 207B, Chemistry.

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- **Textbook:** *Electrochemical Methods Fundamentals and Applications*, A.J. Bard and L.R. Faulkner, Wiley, 2nd edition, 2001, ISBN 0-471-04372-9
  - Can order Textbook online
  - Textbook is on reserved in Willis Library

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- **Exams:** There will be 2-3 exams, various assignments, and a final exam.
- Dates for each exam will be announced in class.
  - The final will be Tuesday, December 9th, 8:00 a.m. - 10:00 a.m.
- **Grading:**
  - A – 90% B – 80% C – 70% D – 55% F < 55%

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- **Topics:**

  Basic electronics,
  signals and noise,
  electrochemical theory,
  thermodynamics and kinetics,
  mechanisms,
  voltammetry,
  experiments and instrumentation,
  electrodeposition electroplating,
  batteries, sensors, fuel cells, solar cells,
  EIS and corrosion,
  potentiometry

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- **Research Paper:**
- A research paper will be required in class and count as 1 test grade. The topic must cover the latest advances in electrochemistry.
- A white paper (1-2 pages) indicating the student's topic of choice (with initial reference list) must be submitted to the instructor.

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- **Research Paper:**
- The grade will be based on the research idea, coverage of theory, and scope of literature review.
- *Any plagiarism in the report will result in a failing grade. No AI. Use your own words; if you are not sure about any section or part of your writing, come see me for help.

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- **Research Paper:**
  (1) Research the chemistry literature.
  (2) 6010 format – follow division guidelines.
  (3) Paper covering student's research project for publication in must follow journal guidelines.
  (4) Chapter for thesis or dissertation must follow UNT guidelines.
  (5) Not 2-4 – follow ACS research paper guidelines.

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- **Research Paper:**

♦ Good places to start:
  - Chemical Abstracts –Sci Scholar
  - Journal Electrochemical Society
  - ACS Journals - Analytical Chemistry Journal
  - Elsevier Journals under Science Direct

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- **Research Paper:**
  - Write a white paper (1-2 pages) indicating the student's topic of choice over the topic with a short reference list for approval – (10pts)
  - Write an extended detailed outline of your research paper with detailed reference list– (30 pts)
  - Complete Research Paper – (100 pts)

Class Assignment

- https://sites.chemistry.unt.edu/~tgolden

- Begin white paper and look for topic
- Due in class 9/30/25

Introduction

Electrochemistry

- Study of chemical changes caused by passage of an electric current and production of electrical energy by chemical reactions

Introduction

Includes:

- Electrophoresis
- Corrosion
- Sensors
- Batteries
- Fuel Cells
- Electroplating
- Solar Cells

Introduction

Electrochemistry

- Both kinetics and thermodynamics play a large role in electrochemical theory and electrochemical experiments.

- Electrochemistry can also be coupled with other techniques i.e.
  - spectroscopy
  - chromatography
  - silicon devices

Theoretical Concepts

Electrochemical Theory is defined by the interfaces present in the electrochemical cell.

Transport of charge occurs at these interfaces.

Introduction

Electrochemical cells consist of electrodes immersed in an electrolyte solution.

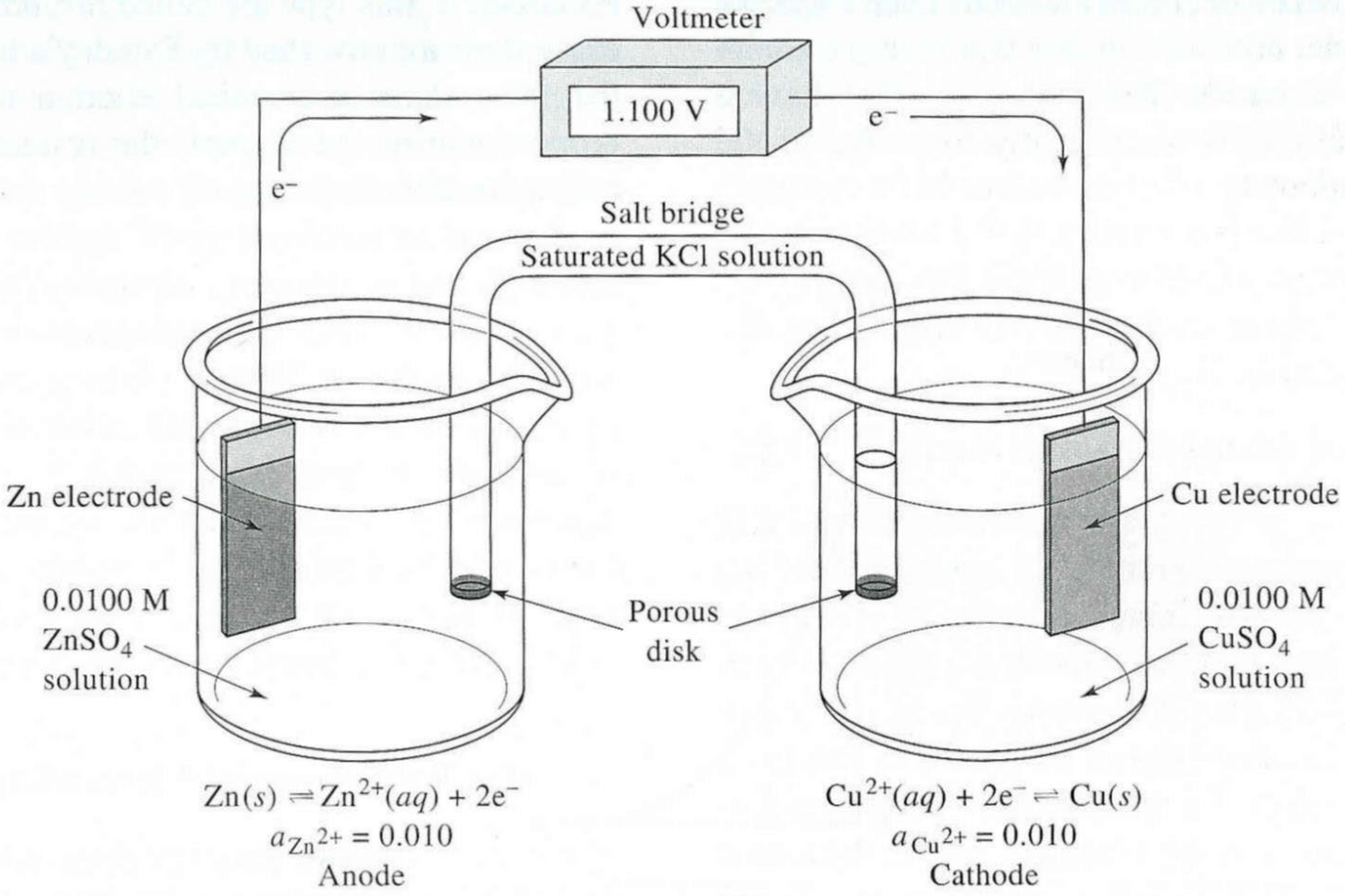

Figure 22-1 A galvanic electrochemical cell with a salt bridge.

Introduction

Type of cells

Galvanic – cells that produce electrical energy (voltaic) -- i.e. battery

- stores electrical energy. Reactions at the electrodes proceed spontaneously.

Electrolytic – cells that consume electrical energy

- consumes energy. Need an external source of electrolytic energy.

Type of electrodes

Cathode – electrode where reduction occurs

Anode – electrode where oxidation occurs

Introduction

Cell notation - Represent electrochemical cells by a shorthand method:

$$Cu \;|\; Cu^{+2}\ (0.0200M) \;\|\; Ag^{+}(0.0200M) \;|\; Ag$$

- Cu: Anode
- $|$: phase boundary (interface) potential occurs here
- $Cu^{+2}\ (0.0200M)$
- $\|$: 2 phase boundaries at either end of the salt bridge liquid junction potential.
- $Ag^{+}(0.0200M)$
- $|$: phase boundary
- Ag: cathode

Anode on left

Cathode on right

Single vertical line – represent phase boundary where potential may develop.

Double vertical line – represent junction between half cells.

Introduction

- Write the diagram for a cell that has a hydrogen electrode on the left, an iron(III)/iron(II) electrode on the right, and includes a salt bridge.

$Pt(s) \mid H_2(g) \mid H^+(aq) \parallel Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt(s)$

Introduction

Write the chemical equation for the cell reaction resulting from the following half-reactions:

$H_2(g)$ ---> $2H^+(aq) + 2e^-$

$Co^{3+}(aq) + 1e^-$ ---> $Co^{2+}(aq)$

Assume that platinum electrodes are used and write the cell diagram.

$H_2(g) + 2Co^{3+}(aq)$ ---> $2H^+(aq) + 2Co^{2+}(aq)$

Pt(s) l $H_2(g)$ l $H^+(aq)$ ll $Co^{3+}(aq)$, $Co^{2+}(aq)$ l Pt(s)

Introduction

Potential of a cell = $E_{cathode}$ - E_{anode} (half-reaction)

To generate the relative half -cell potentials use a standard.

i.e. Standard hydrogen reference electrode (SHE or NHE).

This is the standard reference half-cell to measure all other half-reactions against.

Introduction

Conduction in a cell

Charge is conducted by:

- The electrodes and leads – involves electrons
- The solution – involves migration of cations and anions
- The interface – involves oxidation and reduction

Introduction

Conduction in a cell

Charge is conducted by:

- **The electrodes and leads – involves electrons**
- The solution – involves migration of cations and anions
- The interface – involves oxidation and reduction

Electrochemical Cell

For two electrodes in solution (a cell) – there is a working electrode (WE) and a counter electrode (CE).

These two electrodes are connected to a circuit which applies a potential difference to the cell.

Electrochemical Cell

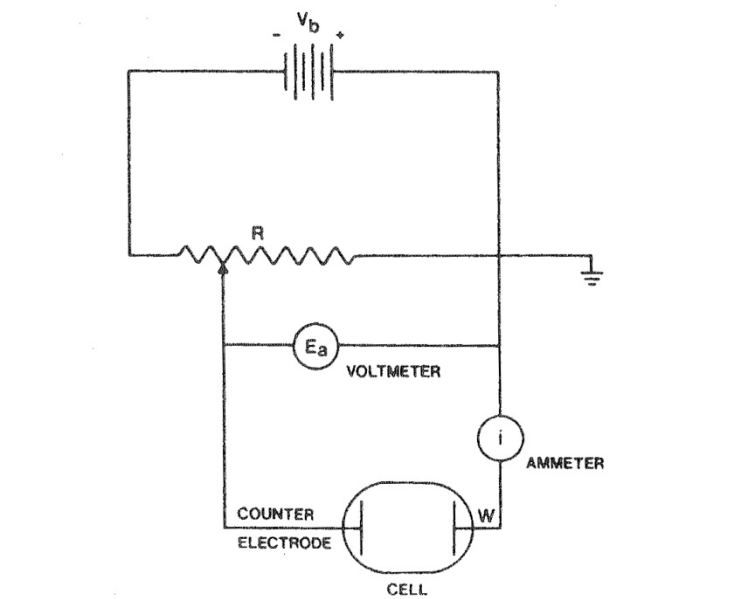

Figure 6.1 Classical two-electrode controlled-potential apparatus.

The applied potential, E_a is measured between the WE and CE and the resulting current is measured in the WE lead and WE is tied to ground potential.

Electrochemical Cell

The counter electrode in the two electrode system serves two functions:

- completes the circuit, allowing charge to flow through the cell
- maintains a constant interfacial potential difference regardless of the current

It is better if these 2 functions are separated to two electrodes.

Thus we can replace the CE with an auxiliary electrode (AUX) and a reference electrode (REF)

Electrochemical Cell

The auxiliary electrode (AUX)

- completes the circuit, allowing charge to flow through the cell

The reference electrode (REF)

- maintains a constant interfacial potential difference regardless of the current

Electrochemical Cell

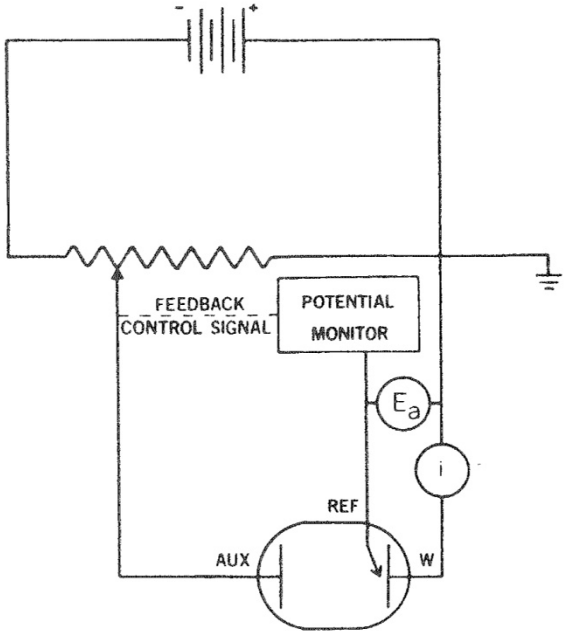

Figure 6.4 Schematic representation of a primitive three-electrode controlled-potential apparatus.

Electrochemical Cell

The reference electrode (REF) is used as a potentiometric (always zero current) probe to monitor $\Delta\phi_w$ relative to its own potential $\Delta\phi_r$.

This value is compared to E_a and if there is a difference (error), the potential applied by the potentiometer is adjusted.

This device is called a potentiostat.

Electrochemical Cell

This value is compared to E_a and if there is a difference (error), the potential applied by the potentiometer is adjusted.

When the potentiometer is adjusted to a value to initiate a reaction at the WE, the potential at which the reaction occurs is E_a vs Ref.

As the species is consumed at the WE, the current through the cell will decrease causing E_a to increase.

Electrochemical Cell

As the species is consumed at the WE, the current through the cell will decrease causing E_a to increase.

The voltage applied to the Aux is decreased by the potentiometer (through negative feedback) until E_a returns to the initial value.

Electrodes

Requirements for the electrodes:

- Working
- Counter (auxiliary)
- Reference

Class Assignment

- Research paper Topic
- Read Chapters 1

  “Electrochemical Methods” Bard