

## Chemistry 132 NT

**If you go flying back through time, and you see somebody else flying forward into the future, it's probably best to avoid eye contact.**

Jack Handey

---

---

---

---

---

---

---

---

Chem 132 NT

## Electrochemistry

### Module 3

Voltaic Cells

• Dependence of emf on Concentration

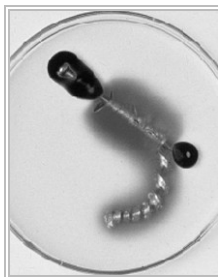
• Some Commercial Voltaic Cells

Electrolytic Cells

• Electrolysis of Molten Salts

• Aqueous Electrolysis

• Stoichiometry of Electrolysis



An experiment in corrosion of an iron nail and magnesium ribbon. Corrosion is an electrochemical process.

2

---

---

---

---

---

---

---

---

## Review

- ✎ Determining the relative strengths of oxidizing and reducing agents
- ✎ Determining the direction of spontaneity from electrode potentials
- ✎ Calculating the emf from standard potentials
- ✎ Calculating the free-energy change from electrode potentials
- ✎ Calculating the cell emf from free-energy change
- ✎ Calculating the equilibrium constant from cell emf

3

---

---

---

---

---

---

---

---

### Dependence of emf on Concentration

- ☛ Recall that the free energy change,  $\Delta G$ , is related to the standard free energy change,  $\Delta G^\circ$ , by the following equation.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- ☛ Here  $Q$  is the thermodynamic reaction quotient.

4

---

---

---

---

---

---

---

---

### Dependence of emf on Concentration

- ☛ Recall that the free energy change,  $\Delta G$ , is related to the standard free energy change,  $\Delta G^\circ$ , by the following equation.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- ☛ If we substitute  $\Delta G = -nFE_{\text{cell}}$  and  $\Delta G^\circ = -nFE_{\text{cell}}^\circ$  into this equation, we get

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q$$

5

---

---

---

---

---

---

---

---

### Dependence of emf on Concentration

- ☛ The result rearranges to give the **Nernst equation**, an equation relating the cell emf to its standard emf and the reaction quotient.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log Q$$

6

---

---

---

---

---

---

---

---

## Dependence of emf on Concentration

✎ The result rearranges to give the **Nernst equation**, an equation relating the cell emf to its standard emf and the reaction quotient.

◆ Substituting values for R and F at 25 °C, we get

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q$$

(values in volts at 25 °C)

7

---

---

---

---

---

---

---

---

## Dependence of emf on Concentration

✎ The result rearranges to give the **Nernst equation**, an equation relating the cell emf to its standard emf and the reaction quotient.

◆ The Nernst equation illustrates why cell emf decreases as the cell reaction proceeds.

◆ As reactant concentrations decrease and product concentrations increase, **Q increases**, thus increasing log Q which **in turn decreases the cell emf**.

8

---

---

---

---

---

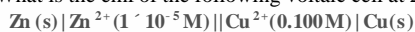
---

---

---

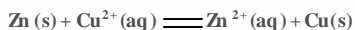
## A Problem To Consider

◆ What is the emf of the following voltaic cell at 25 °C?



The standard emf of the cell is 1.10 V.

◆ The cell reaction is



◆ The number of electrons transferred is 2; hence  $n = 2$ . The reaction quotient is

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1.00 \times 10^{-5}}{0.100} = 1.00 \times 10^{-4}$$

9

---

---

---

---

---

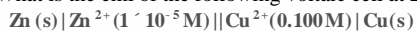
---

---

---

### A Problem To Consider

- What is the emf of the following voltaic cell at 25 °C?



The standard emf of the cell is 1.10 V.

- The standard emf is 1.10 V, so the Nernst equation becomes

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q$$

10

---

---

---

---

---

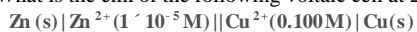
---

---

---

### A Problem To Consider

- What is the emf of the following voltaic cell at 25 °C?



The standard emf of the cell is 1.10 V.

- The standard emf is 1.10 V, so the Nernst equation becomes

$$E_{\text{cell}} = 1.10 \text{ V} - \frac{0.0592}{2} \log(1.00 \times 10^{-4})$$

11

---

---

---

---

---

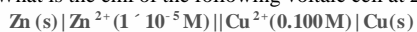
---

---

---

### A Problem To Consider

- What is the emf of the following voltaic cell at 25 °C?



The standard emf of the cell is 1.10 V.

- The standard emf is 1.10 V, so the Nernst equation becomes

$$E_{\text{cell}} = 1.10 \text{ V} - (-0.12) = 1.22 \text{ V}$$

- The cell emf is 1.22 V.

12

---

---

---

---

---

---

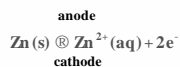
---

---

## Some Commercial Voltaic Cells

☛ The **Leclanché dry cell**, or zinc-carbon dry cell, is a voltaic cell with a **zinc can** as the anode and a **graphite rod** in the center surrounded by a paste of manganese dioxide, ammonium and zinc chlorides, and carbon black, as the cathode.

◆ The electrode reactions are



13

---

---

---

---

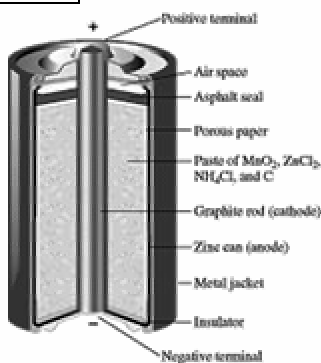
---

---

---

---

Leclanché dry cell.



14

---

---

---

---

---

---

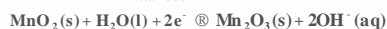
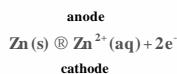
---

---

## Some Commercial Voltaic Cells

☛ The **alkaline dry cell**, is similar to the Leclanché cell, but it has potassium hydroxide in place of ammonium chloride.

◆ The electrode reactions are



15

---

---

---

---

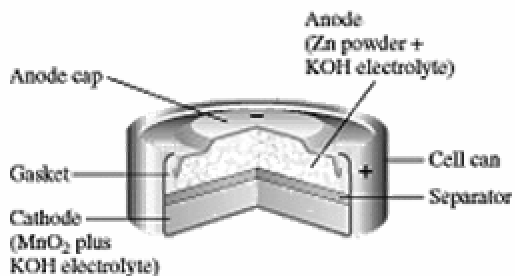
---

---

---

---

A small alkaline dry cell.



16

---

---

---

---

---

---

---

---

### Some Commercial Voltaic Cells

- ✱ The **lithium-iodine battery** is a solid state battery in which the anode is lithium metal and the cathode is an  $I_2$  complex.
  - ◆ The solid state electrodes are separated by a thin crystalline layer of lithium iodide.
  - ◆ Although it produces a low current, it is very reliable and is used to power pacemakers.

17

---

---

---

---

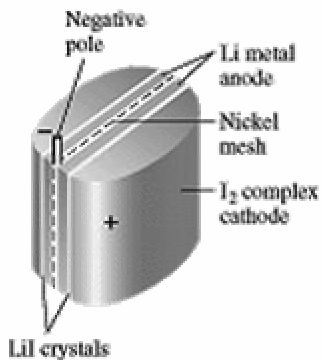
---

---

---

---

A solid-state lithium-iodine battery.



18

---

---

---

---

---

---

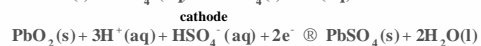
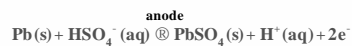
---

---

## Some Commercial Voltaic Cells

✎ The **lead storage cell** (a rechargeable cell) consists of electrodes of lead alloy grids; one electrode is packed with a spongy lead to form the anode, and the other electrode is packed with lead dioxide to form the cathode.

✦ The electrode reactions are



19

---

---

---

---

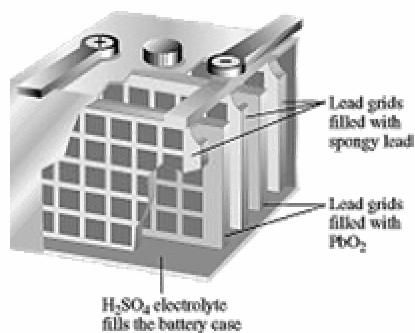
---

---

---

---

A lead storage battery.



20

---

---

---

---

---

---

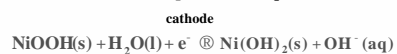
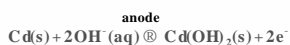
---

---

## Some Commercial Voltaic Cells

✎ The **nickel-cadmium cell (nicad cell)** consists of an anode of cadmium and a cathode of hydrated nickel oxide on nickel; the electrolyte is potassium hydroxide.

✦ The electrode reactions are



21

---

---

---

---

---

---

---

---

Nicad storage batteries



22

---

---

---

---

---

---

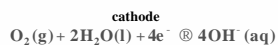
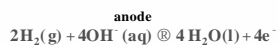
---

---

Some Commercial Voltaic Cells

✱ A fuel cell is essentially a battery, but differs by operating with a continuous supply of energetic reactants, or fuel.

◆ For a hydrogen-oxygen fuel cell, the electrode reactions are



23

---

---

---

---

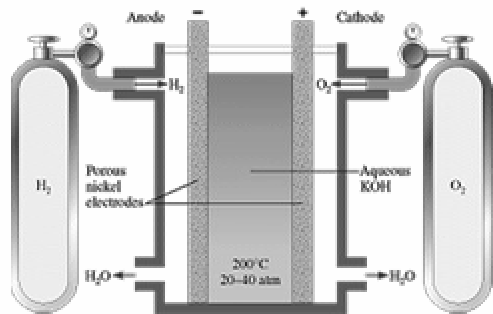
---

---

---

---

A hydrogen-oxygen fuel cell.



24

---

---

---

---

---

---

---

---

## Electrolytic Cells

⚡ An **electrolytic cell** is an electrochemical cell in which an electric current drives an otherwise nonspontaneous reaction.

- ◆ The process of producing a chemical change in an electrolytic cell is called **electrolysis**.
- ◆ Many important substances, such as aluminum metal and chlorine gas are produced commercially by electrolysis.

25

---

---

---

---

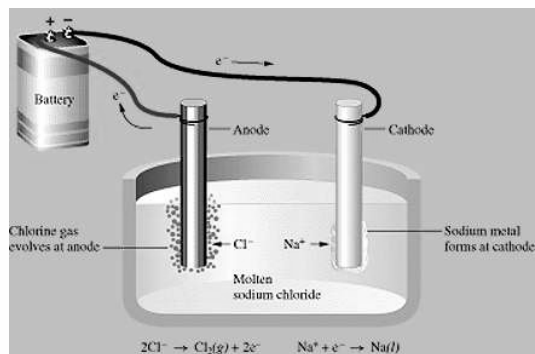
---

---

---

---

## Electrolysis of molten sodium chloride



26

---

---

---

---

---

---

---

---

## Electrolysis of Molten Salts

⚡ A **Downs cell** is a commercial electrochemical cell used to obtain sodium metal by electrolysis of molten NaCl.

- ◆ A number of other reactive metals are obtained by the electrolysis of a molten salt.
- ◆ Lithium, magnesium, and calcium metals are all obtained by the electrolysis of the chlorides.

27

---

---

---

---

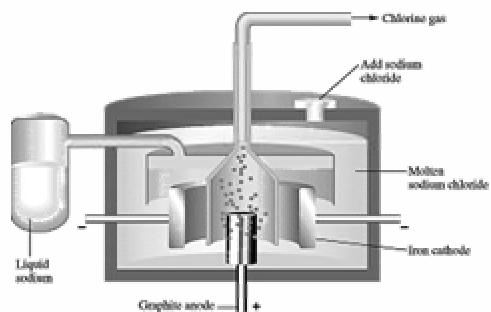
---

---

---

---

A Downs cell for the preparation of sodium metal.



28

---

---

---

---

---

---

---

---

## Aqueous Electrolysis

✎ In the electrolysis of a “molten” salt, the only possible half-reactions involve the ions of the salt.

◆ However, **in aqueous solution**, you must consider the possibility that water might be oxidized or reduced at one or both electrodes.

◆ The **oxidation of water** follows the mechanism below.



29

---

---

---

---

---

---

---

---

## Aqueous Electrolysis

✎ In the electrolysis of a “molten” salt, the only possible half-reactions involve the ions of the salt.

◆ However, **in aqueous solution**, you must consider the possibility that water might be oxidized or reduced at one or both electrodes.

◆ The **reduction of water** follows the mechanism below.



30

---

---

---

---

---

---

---

---

## Aqueous Electrolysis

⚡ In the electrolysis of a “molten” salt, the only possible half-reactions involve the ions of the salt.

- ◆ **Water may oxidize at the anode** if its oxidation potential (-1.23 V) is less negative than the oxidation potential of the **competing anion from the salt**.

31

---

---

---

---

---

---

---

---

## Aqueous Electrolysis

⚡ In the electrolysis of a “molten” salt, the only possible half-reactions involve the ions of the salt.

- ◆ **Water may be reduced at the cathode** if its reduction potential (-0.83 V) is less negative than the reduction potential of the **competing cation from the salt**.

32

---

---

---

---

---

---

---

---

## Stoichiometry of Electrolysis

⚡ What is new in this type of stoichiometric problem is the measurement of numbers of electrons.

- ◆ You do not weigh them as you do substances.
- ◆ Rather, you measure the **quantity of electric charge** that has passed through a circuit.
- ◆ You use the following fact:  
**OneFaraday( $9.65 \times 10^4 \text{ C}$ )  $\circ$  1 mol electrons**

33

---

---

---

---

---

---

---

---

## Stoichiometry of Electrolysis

What is new in this type of stoichiometric problem is the measurement of numbers of electrons.

- ◆ To determine this **we must know the current and the length of time** it has been flowing.
- ◆ Electric current is measured in amperes.
- ◆ An **ampere (A)** is the base SI unit of current equivalent to **1 coulomb/second**

34

---

---

---

---

---

---

---

---

## Stoichiometry of Electrolysis

What is new in this type of stoichiometric problem is the measurement of numbers of electrons.

- ◆ The quantity of electric charge passing through a circuit in a given amount of time is given by

Electric charge(coul) = electric current (coul/sec) × time lapse(sec)

$$\text{coulomb(C)} = \text{amps(coul/sec)} \times \text{time(sec)}$$

35

---

---

---

---

---

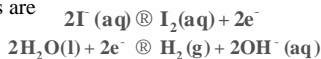
---

---

---

## A Problem To Consider

When an aqueous solution of potassium iodide is electrolyzed using platinum electrodes, the half-reactions are



How many grams of iodine are produced when a current of 8.52 mA flows through the cell for 10.0 min?

- ◆ When the current flows for  $6.00 \times 10^2$  s (10.0 min), the amount of charge is

$$(8.52 \times 10^{-3} \text{ A}) \times (6.00 \times 10^2 \text{ s}) = 5.11 \text{ C}$$

36

---

---

---

---

---

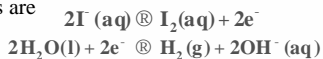
---

---

---

## A Problem To Consider

- When an aqueous solution of potassium iodide is electrolyzed using platinum electrodes, the half-reactions are



How many grams of iodine are produced when a current of 8.52 mA flows through the cell for 10.0 min?

- Note that two moles of electrons are equivalent to one mole of  $\text{I}_2$ . Hence,

$$5.11 \text{ C} \cdot \underbrace{\frac{1 \text{ mol e}^{-}}{9.65 \cdot 10^4 \text{ C}}}_{\text{Faraday constant}} \cdot \underbrace{\frac{1 \text{ mol I}_2}{2 \text{ mol e}^{-}}}_{\text{stoichiometry}} \cdot \underbrace{\frac{254 \text{ g I}_2}{1 \text{ mol I}_2}}_{\text{molar mass}} = 6.73 \cdot 10^{-3} \text{ g I}_2$$

37

---

---

---

---

---

---

---

---

## Operational Skills

- Calculating the cell emf for nonstandard conditions (Nernst Equation)
- Predicting the half-reactions in an aqueous electrolysis
- Relating the amounts of product and charge in an electrolysis

38

---

---

---

---

---

---

---

---

## Key Equations

$$w_{\text{max}} = -nFE_{\text{cell}}$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = \frac{0.0592}{n} \log K$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q$$

Time for a few review questions

39

---

---

---

---

---

---

---

---



---

---

---

---

---

---

---