Chemistry 132 NT

If you ever catch on fire, try to avoid seeing yourself in the mirror, because I bet that's what <u>really</u> throws you into a panic.

Jack Handey

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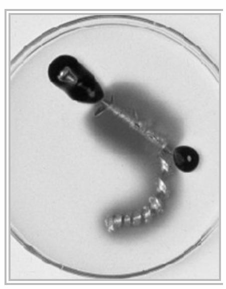
Chem 132 NT

Electrochemistry

Module 1

Half-Reactions and Voltaic Cells

- **Balancing Oxidation-Reduction Reactions**
- **Construction of Voltaic Cells**
- **Notation for Voltaic Cells**
- **Electromotive Force**



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

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Oxidation-Reduction Reactions

- In first-semester chemistry we we introduced the **half-reaction method** for balancing simple oxidation-reduction reactions.
  - Oxidation-reduction reactions always involve a **transfer of electrons** from one species to another.
  - Recall that the species losing electrons is **oxidized**, while the species gaining electrons is **reduced**.

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Oxidation-Reduction Reactions

- Describing Oxidation-Reduction Reactions
  - An **oxidizing agent** is a species that oxidizes another species; **it is itself reduced**.
  - A **reducing agent** is a species that reduces another species; **it is itself oxidized**.

Loss of 2 e^{-1} oxidation

reducing agent

$$Fe_{(s)} + Cu^{+2}_{(aq)} \rightarrow Fe^{+2}_{(aq)} + Cu_{(s)}$$

oxidizing agent

Gain of 2 e^{-1} reduction

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Oxidation-Reduction Reactions

- In this chapter we will show how a cell is constructed to **physically separate** an oxidation-reduction reaction into two **half-reactions**.
  - The force with which electrons travel from the oxidation half-reaction to the reduction half-reaction is measured as **voltage**.
  - Review the rules in your text concerning the balancing of oxidation reduction reactions.

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Electrochemistry

- An **electrochemical cell** is a system consisting of electrodes that dip into an electrolyte in which a chemical reaction either uses or generates an electric current.
  - A **voltaic**, or **galvanic**, cell is an electrochemical cell in which a **<u>spontaneous</u>** reaction generates an electric current.

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Electrochemistry

- An **electrochemical cell** is a system consisting of electrodes that dip into an electrolyte in which a chemical reaction either uses or generates an electric current.
  - An **electrolytic cell** is an electrochemical cell in which an electric current drives an otherwise **nonspontaneous** reaction.
  - In this chapter we will discuss the basic principles behind these cells and explore some of their commercial uses.

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Voltaic Cells

- A **voltaic cell** consists of two half-cells that are electrically connected.
  - Each **half-cell** is a portion of the electrochemical cell in which a half-reaction takes place.
  - A simple half-cell can be made from a metal strip dipped into a solution of its metal ion.
  - For example, the zinc-zinc ion half cell consists consists of a zinc strip dipped into a solution of a zinc salt.

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Voltaic Cells

- A **voltaic cell** consists of two half-cells that are electrically connected.
  - Another simple half-cell consists of a copper strip dipped into a solution of a copper salt.
  - In a voltaic cell, two half-cells are connected in such a way that **electrons flow from one metal electrode to the other through an external circuit**.
  - The figure on the next slide illustrates an atomic view of a zinc/copper voltaic cell.

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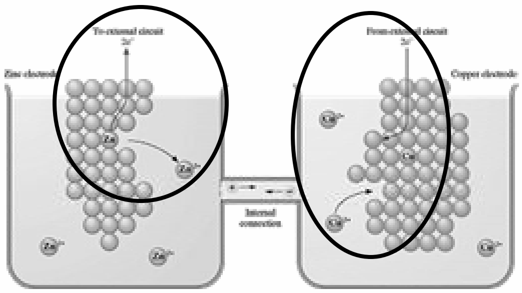
Atomic view of a voltaic cell.



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Voltaic Cells

- **As long as there is an external circuit, electrons can flow** through it from one electrode to the other.
  - Because **zinc has a greater tendency to lose electrons than copper**, zinc atoms in the zinc electrode lose electrons to form zinc ions.
  - The electrons flow through the external circuit to the copper electrode where copper ions gain the electrons to become copper metal.

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Voltaic Cells

- The two half-cells **must also be connected internally** to allow ions to flow between them.
  - Without this internal connection, too much positive charge builds up in the zinc half-cell (and too much negative charge in the copper half-cell) causing the reaction to stop.
  - The figures on the next slide show the two half-cells of a voltaic cell connected by **salt bridge**.

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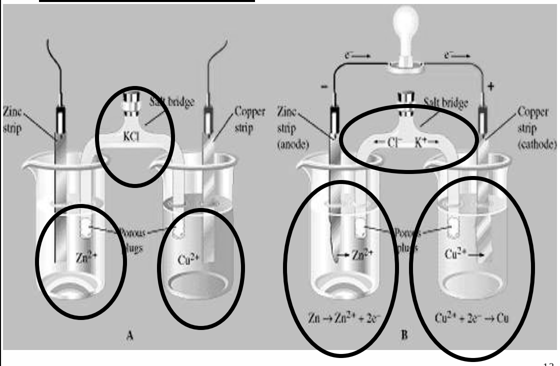
A zinc-copper voltaic cell.



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Voltaic Cells

- A **salt bridge** is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell.
  - The salt bridge allows the flow of ions but **prevents the mixing of the different solutions that would allow direct reaction** of the cell reactants.
  - The next slide shows an actual setup of the zinc-copper cell.

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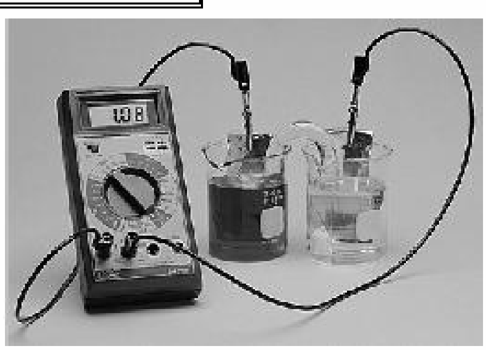
A zinc-copper voltaic cell



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Voltaic Cells

- The two half-cell reactions, as noted earlier, are:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad \text{(oxidation half-reaction)}$$
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad \text{(reduction half-reaction)}$$

  - The first reaction, in which electrons are lost, is the **oxidation half-reaction**.
  - The electrode at which oxidation occurs is the **anode**.

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Voltaic Cells

- The two half-cell reactions, as noted earlier, are:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad \text{(oxidation half-reaction)}$$
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad \text{(reduction half-reaction)}$$

  - The second reaction, in which electrons are gained, is the **reduction half-reaction**.
  - The electrode at which reduction occurs is the **cathode**.

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Voltaic Cells

- Note that the sum of the two half-reactions

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

is the <u>net reaction</u> that occurs in the voltaic cell; it is called the **cell reaction**

  - Note that electrons are <u>given up</u> at the anode and thus **flow from it** to the cathode where reduction occurs.

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Voltaic Cells

- Note that the sum of the two half-reactions

  $$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

  is the <u>net reaction</u> that occurs in the voltaic cell; it is called the **cell reaction**

  - The anode in a voltaic cell has a **negative** sign because electrons flow from it.
  - The cathode in a voltaic cell has a **positive** sign

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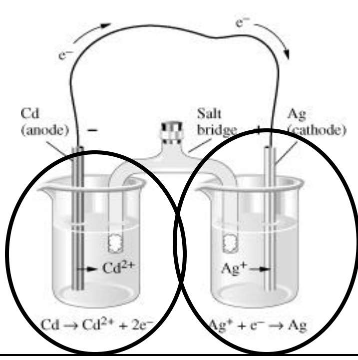
Cadmium-silver Cell



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Notation for Voltaic Cells

- It is convenient to have a **shorthand** way of designating particular voltaic cells.
  - The cell consisting of the zinc-zinc ion half-cell and the copper-copper ion half-cell, is written

  $$Zn(s) \,|\, Zn^{2+}(aq) \,||\, Cu^{2+}(aq) \,|\, Cu(s)$$

  anode **cathode**

  - The anode (oxidation half-cell) is written on the left. The cathode (reduction half-cell) is written on the right.

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Notation for Voltaic Cells

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$$Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$$

anode **salt bridge** **cathode**

  - The two electrodes are connected by a salt bridge, denoted by two vertical bars.

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Notation for Voltaic Cells

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  - The cell consisting of the zinc-zinc ion half-cell and the copper-copper ion half-cell, is written

$$Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$$

anode **salt bridge** **cathode**

  - The cell **terminals** are at the extreme ends in the cell notation.

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Notation for Voltaic Cells

- It is convenient to have a **shorthand** way of designating particular voltaic cells.
  - The cell consisting of the zinc-zinc ion half-cell and the copper-copper ion half-cell, is written

$$Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$$

anode **salt bridge** **cathode**

  - A single vertical bar indicates a phase boundary, such as between a solid terminal and the electrode solution.

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Notation for Voltaic Cells

- When the **half-reaction involves a gas**, an inert material such as platinum serves as a terminal and an electrode surface on which the reaction occurs.
  - The figure on the next slide shows a **hydrogen electrode**; hydrogen bubbles over a platinum plate immersed in an acidic solution.
  - The cathode half-reaction is

$$2H^{+}(aq) + 2e^{-} \text{ ® } H_2(g)$$

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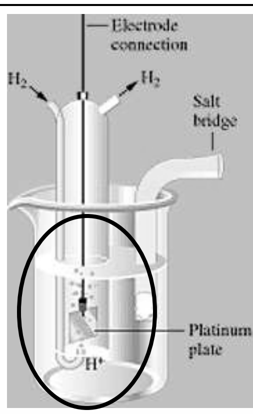
A hydrogen electrode.



Notation for Voltaic Cells

- When the **half-reaction involves a gas**, an inert material such as platinum serves as a terminal and an electrode surface on which the reaction occurs.
  - The notation for the hydrogen electrode, written as a cathode, is

$$H^{+}(aq) \,|\, H_2(g) \,|\, Pt$$

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Notation for Voltaic Cells

- When the **half-reaction involves a gas**, an inert material such as platinum serves as a terminal and an electrode surface on which the reaction occurs.
  - To write such an electrode as an anode, you simply reverse the notation.

$$Pt \mid H_2(g) \mid H^+(aq)$$

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Notation for Voltaic Cells

- To fully specify a voltaic cell, it is necessary to give the **concentrations of solutions** and the **pressure of gases**.
  - In the cell notation, these are written in parentheses. For example,

$$Zn(s) \mid Zn^{2+}(1.0\ M) \parallel H^+(aq) \mid H_2(1.0\ atm) \mid Pt$$

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A Problem To Consider

- Give the overall cell reaction for the voltaic cell

$$Cd(s) \mid Cd^{2+}(1.0\ M) \parallel H^+(aq) \mid H_2(1.0\ atm) \mid Pt$$

- The half-cell reactions are

$$Cd(s) \rightarrow Cd^{2+}(aq) + \cancel{2e^-}$$
$$2H^+(aq) + \cancel{2e^-} \rightarrow H_2(g)$$
$$Cd(s) + 2H^+(aq) \rightarrow Cd^{2+}(aq) + H_2(g)$$

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Electromotive Force

- The **movement of electrons** is analogous to the pumping of water from one point to another.
  - Water moves from a point of high pressure to a point of lower pressure. Thus, **a pressure difference is required**
  - The **work** expended in moving the water through a pipe depends on the volume of water and the pressure difference.

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Electromotive Force

- The **movement of electrons** is analogous to the pumping of water from one point to another.
  - An electric charge moves from a point of high electrical potential (**high electrical pressure**) to one of lower electrical potential.
  - The **work** expended in moving the electrical charge through a conductor depends on the amount of charge and the potential difference.

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Electromotive Force

- **Potential difference** is the difference in electric potential (electrical pressure) between two points.
  - You measure this quantity in volts.
  - The **volt, V,** is the SI unit of potential difference equivalent to 1 joule of energy per coulomb of charge.

$$1\ \text{volt} = 1\ \text{J}/\text{C}$$

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Electromotive Force

- The **Faraday constant, F**, is the magnitude of charge on one mole of electrons; **it equals 96,500 coulombs (9.65 x 10^4 C).**
  - In moving 1 mol of electrons through a circuit, the numerical value of the **work done by a voltaic cell** is the product of the Faraday constant (F) times the potential difference between the electrodes.

work(J)= - F(coulombs) ´ volts(J/coulomb)

work done by the system

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Electromotive Force

- The **Faraday constant, F**, is the magnitude of charge on one mole of electrons; **it equals 96,500 coulombs (9.65 x 10^4 C).**
  - In the normal operation of a voltaic cell, the potential difference (**voltage**) across the electrodes is **less than than the maximum** possible voltage of the cell.
  - The actual flow of electrons reduces the electrical pressure.

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Electromotive Force

- The **Faraday constant, F**, is the magnitude of charge on one mole of electrons; **it equals 96,500 coulombs (9.65 x 10^4 C).**
  - In the normal operation of a voltaic cell, the potential difference (**voltage**) across the electrodes is **less than than the maximum** possible voltage of the cell.
  - Thus, a cell voltage has its maximum value when **no current flows**.

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Electromotive Force

- The maximum potential difference between the electrodes of a voltaic cell is referred to as the **electromotive force (emf)** of the cell, or $\mathbf{E_{cell}}$.
  - It can be measured by an electronic digital voltmeter (next slide), which draws negligible current.

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A digital voltmeter

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Electromotive Force

- We can now write an expression for the **maximum work attainable** by a voltaic cell.
  - Let **n** be the number of (mol) electrons transferred in the overall cell reaction.
  - The **maximum work** for molar amounts of reactants is

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

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A Problem To Consider

- The emf of the electrochemical cell below is 0.650 V. Calculate the maximum electrical work of this cell when 0.500 g H_2 is consumed.

$$Hg_2^{2+}(aq) + H_2(g) \rightleftharpoons 2Hg(l) + 2H^+(aq)$$

  - The half-reactions are

$$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$$

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

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A Problem To Consider

- The emf of the electrochemical cell below is 0.650 V. Calculate the maximum electrical work of this cell when 0.500 g H_2 is consumed.

$$Hg_2^{2+}(aq) + H_2(g) \rightleftharpoons 2Hg(l) + 2H^+(aq)$$

  - n = 2, and the maximum work for the reaction is written as

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

$$w_{max} = -2 \times (9.65 \times 10^4 C) \times (0.650 V)$$

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A Problem To Consider

- The emf of the electrochemical cell below is 0.650 V. Calculate the maximum electrical work of this cell when 0.500 g H_2 is consumed.

$$Hg_2^{2+}(aq) + H_2(g) \rightleftharpoons 2Hg(l) + 2H^+(aq)$$

  - n = 2, and the maximum work for the reaction is written as

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

$$w_{max} = -1.25 \times 10^5 J$$

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A Problem To Consider

- The emf of the electrochemical cell below is 0.650 V. Calculate the maximum electrical work of this cell when 0.500 g H_2 is consumed.

$$Hg_2^{2+}(aq) + H_2(g) \rightleftharpoons 2Hg(l) + 2H^+(aq)$$

- For 0.500 g H_2, the maximum work is

$$0.500\,g\,H_2 \times \frac{1\,mol\,H_2}{2.02\,g\,H_2} \times \frac{-1.25 \times 10^5\,J}{1\,mol\,H_2} = -3.09 \times 10^4\,J$$

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Operational Skills

- Balancing oxidation-reduction reactions
- Sketching and labeling a voltaic cell
- Writing the cell reaction from the cell notation
- Calculating the quantity of work from a given amount of cell reactant

Time for a few review questions

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