

Electrochemistry

Oxidation-Reduction:

Review oxidation reactions and how to assign oxidation numbers (Ch 4 Chemical Reactions).

Half Reactions Method for Balancing Redox Equations:

Acidic solutions:

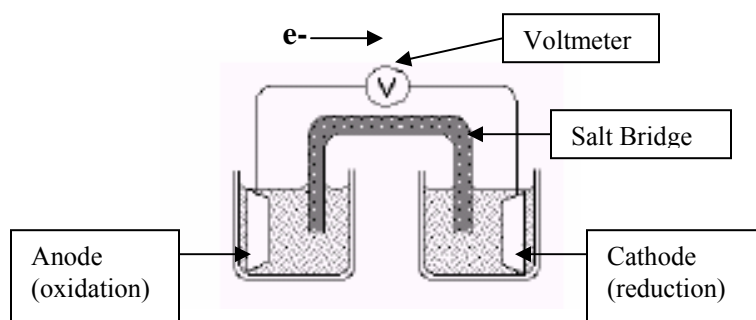
1. Divide the equation into two half-reactions (the reduction half-reaction and the oxidation half-reaction).
2. Balance atoms other than H and O.
3. Balance oxygens by adding H_2O to the side that needs O.
4. Balance hydrogens by adding H^+ to the side that needs H.
5. Balance the charge by adding electrons.
6. Make the number of electrons gained equal to the number of electrons lost.
7. Add the two half-reactions.
8. Cancel out anything that appears on both sides of the equation.

Basic solutions:

1. Follow the same steps above for acidic solutions.
2. For each H^+ , add the same number of OH^- ions to each side of the equation.
3. Combine H^+ and OH^- to form H_2O and cancel out any H_2O if possible.

Voltaic (Galvanic) Cells:

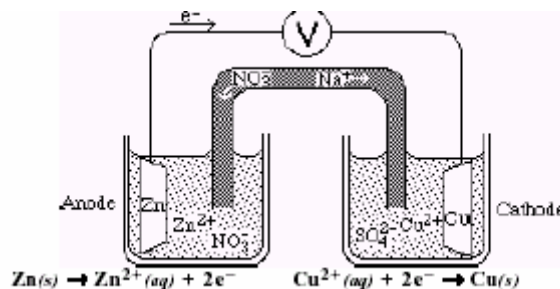
- Spontaneous redox reactions generate electrical current.



- **Half cells** – A metal electrode immersed in a solution of one of its ions.
- **Voltaic cells** – have two half-cells (one for the reduction reaction and one for the oxidation reaction).
- **Anode** – the negative electrode where oxidation occurs (**AN OX**)
- **Cathode** – the positive electrode where reduction occurs (**RED CAT**)
- **Salt bridge** – An inverted u-shaped tube which contains a non-reactive electrolyte and connects the two half-cells. It allows the migration of ions to balance the charge.
- **Electrons** move through the wire **from the anode to the cathode**.
- **Voltmeter** – measures the difference in electrical potential between 2 points in an electric circuit.
- **1 volt (V) = 1 J/C** (joule/coulomb)

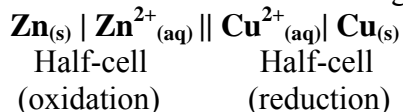
- **Cell potential (E_{cell}) / cell voltage** – the difference in potential energy between the anode and the cathode of the cell.
- **Cell reaction** – the overall redox reaction occurring in a voltaic cell.

Example:



Cell Diagrams:

- Conveniently represent an electrochemical cell.
- The anode goes on the left and the cathode on the right.
- A single vertical line represents the boundary between different phases (Ex: between an electrode and the solution).
- A double vertical line represents the salt bridge or porous barrier between the 2 half-cells.
- Example: For the above cell the cell diagram would be:



- Electrodes may also be inert (Ex: Platinum). These electrodes just give a surface to establish the electrical potential.

Standard Electrode Potentials (E°):

- Used to determine cell voltages and whether a redox reaction is spontaneous.
- Standard electrode potentials are given relative to the standard hydrogen electrode potential.
- The standard hydrogen electrode potential is 0 volts.
- E° is based on the tendency for reduction to occur at the electrode and all solution species are present in their standard state (about 1M (or 1 atm for gases)).
- The more positive E° the stronger the oxidizing agent and the weaker its conjugate reducing agent.
- E° for an oxidation half-reaction is the standard reduction potential with the opposite sign.

Standard Cell Potential (E°_{cell}):

- $E^{\circ}(\text{cell}) = E^{\circ}(\text{cathode}) + E^{\circ}(\text{anode})$
- Can also be used for redox reactions without regard to voltaic cells.
- Positive E°_{cell} means a spontaneous reaction.
- Negative E°_{cell} means a nonspontaneous reaction (the reverse reaction is spontaneous).
- 0 E°_{cell} means the reaction is at equilibrium.
- Electrode potentials and voltage are intensive properties. They depend on the species and concentration but not on the total amounts of substances present (not on the size of the cell or half-cell).

- For a single replacement reaction, a metal which is oxidized easily (has a more negative E°) will displace a metal with a more positive E° . ie: Those metals easily oxidized would be at the top of the activity series for metals.

Equilibrium and Spontaneity:

$$\Delta G = -nFE^\circ_{\text{cell}}$$

n = number of moles of electrons transferred

F = Faraday constant = 96,500 coulombs per mole of electrons

Nernst Equation

- Used to find cell voltage for nonstandard conditions.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q$$

Batteries:

(Note – the diagrams and half reactions are in the textbook and will be discussed in more detail in class).

A) Dry cell.

The LeClanche Cell (acid)

- Has a maximum cell voltage of 1.5 V
- Disadvantages: Cell voltage drops rapidly because of Zn^{2+} build up at anode and change of pH at cathode. Zinc slowly reacts with the electrolyte even when the cell is not connected.

Alkaline Battery.

- Uses NaOH or KOH instead of NH_4Cl .
- Has a longer shelf life.

B) Rechargeable Batteries:

Lead Storage Battery

- Used in cars.
- Rechargeable (cell reaction can be reversed). Products precipitate around the electrodes allowing the reverse reaction to take place when a current is applied.

Nickel Cadmium Battery

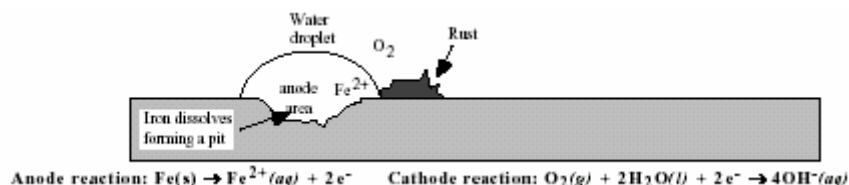
- Can also be recharged as products form around the electrodes.

C) Fuel Cells.

- Galvanic cells for which the reactants are continuously supplied.

Corrosion:

- The corrosion of iron is a spontaneous redox process and acts like a voltaic cell.
- The metal is oxidized while oxygen from the atmosphere is reduced.
- Oxidation and reduction occur at different points on the metal.
- Electrons move through the metal.
- The circuit may be completed by an electrolyte in aqueous solution (Ex: saltwater from the ocean, or from melting snow and road salt).



Protection:

- Metals can be protected from corrosion by coating them with a protective layer, such as paint.
- They may also be protected by **galvanizing** them – coating them with a more active metal such as zinc.
- **Cathodic protection** is also used. The object to be protected is connected to a piece of an active metal such as magnesium, aluminum, or zinc. The active metal is called a sacrificial anode as it undergoes oxidation instead of the metal to be protected.

Electrolytic Cells:

- An electrical current from an external source is passed through an electrochemical cell and causes a nonspontaneous reaction to occur – **electrolysis**.
- Oxidation occurs at the anode and reduction occurs at the cathode (as in voltaic cells).
- Because the external source is controlling the flow of electrons, the polarities of the electrodes are the **opposite** of those in voltaic cells – the anode of an electrolytic cell has a positive charge and the cathode has a negative charge.
- To determine which reactions will take place, the standard electrode potentials of possible half reactions must be considered – reactions that give the least negative value for E_{cell} are most likely to occur.
- **Overvoltage** – the excess voltage above the calculated E values that must be applied in order for the reactions to occur.
- Inert electrodes such as platinum, graphite, gold, stainless steel, or nichrome wire are often used. If not, the electrode may play an active part in the process and has to be considered when predicting electrolysis reactions.

Quantitative Electrolysis:

$$I = \frac{q}{t}$$

I=current (amperes) q=charge (coulombs) t=time(seconds)
1 ampere (A) = 1C/s

- The mass of product formed or reactant consumed in an electrolysis reaction can be calculated as follows.
 1. Determine the amount of charge using the above equation.

2. Convert charge to moles of electrons (1 mole e^- = 96,500C)
3. Using the balanced half reactions, convert moles of electrons to moles of reactant or product.
4. Convert moles to desired quantity (mass, volume etc.)

Applications:

- Electroplating – coating one metal with another.
- Electrolysis of water to give H_2 and O_2 .
- Electrolysis of solid sodium chloride to give sodium metal.
- Electrolysis of aqueous sodium chloride (brine) to give chlorine gas and sodium hydroxide solution.
- Production of aluminum.
- Electrorefining (purification) of metals.