

Electrochemistry: The study of chemical reactions that produce electricity, and chemical reactions that take place because electricity is supplied. Electrochemical reactions include: electroplating, electrolysis of water, the production of aluminum metal, the production and storage of electricity in batteries. All involve transfer of electrons and redox reactions.

(Make a foldable for these symbols and their equations)

I , E° , G° , q (charge, coulombs C), K , F , R

When would you use these equations?

$$I = q/t$$

$$\log K = nE^\circ/0.0592$$

$$\Delta G^\circ = -nFE^\circ$$

$$Q =$$

$$E_{\text{cell}} =$$

Electrochemical Cells

Galvanic and Electrolytic Cells

Oxidation-reduction or [redox reactions](#) take place in electrochemical cells. There are two types of electrochemical cells. Spontaneous reactions occur in galvanic (voltaic) cells; nonspontaneous reactions occur in electrolytic cells. Both types of cells contain [electrodes](#) where the oxidation and reduction reactions occur. Oxidation occurs at the electrode termed the **anode** and reduction occurs at the electrode called the **cathode**.

Electrodes & Charge The anode of an electrolytic cell is positive (cathode is negative), since the anode attracts anions from the solution. However, the anode of a galvanic cell is negatively charged, since the spontaneous oxidation at the anode is the **SOURCE** of the cell's electrons or negative charge. The cathode of a galvanic cell is its positive terminal. In both galvanic and electrolytic cells, oxidation takes place at the anode and electrons flow from the anode to the cathode.

Galvanic or Voltaic Cells The redox reaction in a galvanic cell is a spontaneous reaction. For this reason, galvanic cells are commonly used as batteries. Galvanic cell reactions supply energy which is used to perform work. The energy is harnessed by situating the oxidation and reduction reactions in separate containers, joined by an apparatus that allows electrons to flow. A common galvanic cell is the Daniell cell. The anode is always on the left and the cathode always on the right.

Composed of:

1/2 cells - oxidation or reduction occurs; consists of a metal rod in solution.

They are separated by a salt bridge (containing a conducting solution and allows the ions to pass through --however, the solutions don't mix)

electrode - carries electrons to and from a substance other than a metal.

Note about the picture: The two metal strips, our **electrodes**, are connected with some wire. We'll also place a voltmeter here so we can detect the electric current once we are up and running. This will be our **external circuit**.

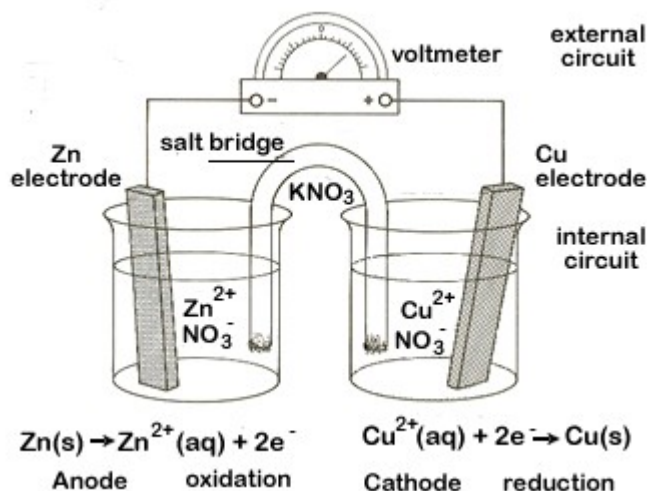
Add a **salt bridge**. A salt bridge is a U-shaped tube that contains an electrolytic solution (we'll use KNO_3). This electrolytic solution will allow ions to flow between the two beakers. This is our **internal circuit**.

External circuit - this is where the electrical work is done as electrons travel from one half-cell to the other. The electrons are produced at the zinc anode, where oxidation occurs. The electrons then travel through the wire of

the external circuit to the copper cathode. The electrons are then available for the copper ions (from the $\text{Cu}(\text{NO}_3)_2$ solution) and solid copper is produced.

Internal circuit -

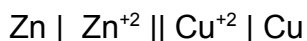
At the anode, Zn^{2+} ions are being produced and go into solution. This causes a build-up of positive ions in this solution. If this electrical imbalance is not corrected the reaction cannot continue. The excess positive charge attracts the negative NO_3^- ions (anions) from the salt bridge, thereby keeping the solution electrically neutral.



External Circuit	Internal Circuit
<p>Electrons flow from A to C</p> <p>Anode to Cathode</p>	<p>Anions to the Anode</p> <p>Cations to the Cathode</p>

Electricity is the flow of electrons from the anode (oxidation/ release of e^-) to the cathode(reduction/consumes e^-). Current is created.

SHORTHAND METHOD (cell notation)



When solutions are both 1.0 M, this cell (Daniell cell) generates a potential of 1.10 volts.

How can we find the electrochemical cell potential?

The driving force between half-reactions in a galvanic cell - CELL POTENTIAL (EMF). It has a unit of electrical potential measurement - Volt

Volt - 1 J of work per coulomb of charge transferred.

- To calculate the E° cell potential, standard potentials for each reduction half-reaction are used. These values were found by using reduction potential of H as 0 under standard conditions and ideal behavior is assumed. They are found in a table on p.
- A cell will always run spontaneously in the direction that produces a positive cell potential.

STANDARD REDUCTION POTENTIALS:

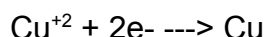
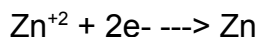
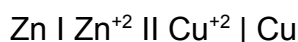
$$E^\circ_{\text{CELL}} = E^\circ_{\text{RED}} - E^\circ_{\text{OX}}$$

MEASURE OF CELL POTENTIAL AT 1 ATM AND 25° C.

HYDROGEN ELECTRODE= 0 VOLTS; IT IS THE STANDARD FOR DETERMINING OTHER POTENTIALS.

CALCULATING POTENTIALS:

THE 1/2-RXN. WITH THE MORE POSITIVE REDUCTION POTENTIAL OCCURS AT THE REDUCTION PART OF THE CELL.



*Electrons are balanced. If they are not, then you need to find a multiplier to equalize electron loss and gain. The half-cell potential remains the same, however. *Overall cell reaction must be balanced by electrons transferred and # of atoms.*

$$E^\circ \text{Zn}^{+2} = -0.76 \text{ V}$$

$$E^\circ \text{Cu}^{+2} = +0.34\text{V}$$

$$\begin{aligned} E^\circ \text{cell} &= E^\circ \text{red.} - E^\circ \text{oxid.} \\ &= 0.34 - (-0.76) \end{aligned}$$

$$E^\circ \text{cell} = 1.10 \text{ V}$$



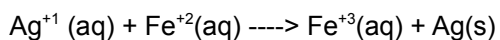
Remember - **An Ox and a Red Cat:**



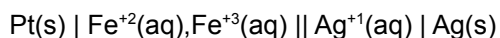
Lacking the conductive part: Sometimes the half reaction(s) don't have a conductive part to act as the electrode, so an inert electrode, a solid conducting electrode that doesn't take part in the redox reaction, is used.

ex. Graphite and platinum. The electrode must be a conductor on to which a wire may be attached. It can never be in solution.

If there is an inert electrode used, the electrode is shown with its phase boundary. If the electrode components are in the same phase, they are separated by commas, if not a vertical phase boundary line.



*The oxidation of the ferrous ion to ferric doesn't involve a suitable electrode material, so an inert electrode is needed, the cell notation is:



Where do the ions flow?

Always opposite of the e- flow. Current is the flow of positive charge.

A more compact way of generating electricity:

TWO EXAMPLES OF VOLTAIC CELLS

1. DRY CELLS - electrolyte is a paste; ex. Cd-Ni batteries

2. LEAD STORAGE BATTERIES

voltaic cells connected together

ex. 12 v battery in cars (6 voltaic cells that produce 2 V each and contains 2 Pb electrodes of grids)

grids: anode = spongy Pb cathode = PbO₂
located in sulfuric acid - 5M and separated by a plate

When the battery discharges the car starts (electric power!)
(spontaneous REDOX rxn)

When battery is recharged, the rxn, is non-spontaneous.
Recharging sometimes is not useful. Why?

- PbSO₄ is lost from the electrode and the cell is shorted out.
(Pb and PbO₂ are converted to PbSO₄ causing a decrease in concentration of sulfuric acid)

FUEL CELLS

These have renewable electrodes.

Fuel is oxidized and electrical energy is obtained continuously. They emit no air pollutants and are a cheap, convenient way to generate electricity.

H₂ - O₂ fuel cell - clean source of power. Waste products products is steam (pure water)

Electrolytic Cells

The redox reaction in an electrolytic cell is nonspontaneous. Electrical energy is required to induce the **electrolysis** reaction. Water can be decomposed into hydrogen and oxygen. Aluminum oxide can be electrolyzed to produced aluminum metal.

Introduction to Electrolysis

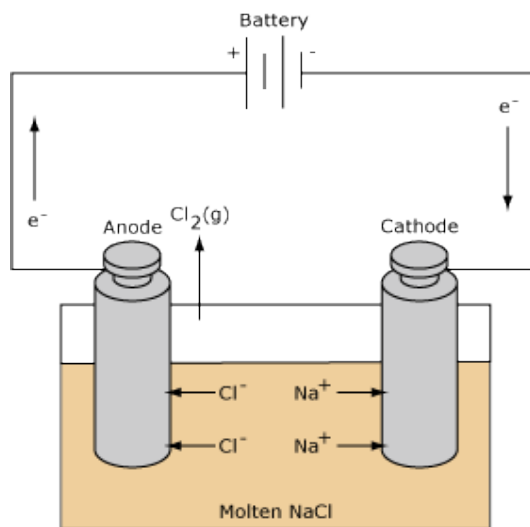
Think of electrolysis and electrolytic cells as the opposite of electrochemical cells:

	Electrochemical Cells	Electrolytic Cells
Energy conversion	Chemical \rightarrow Electrical	Electrical \rightarrow Chemical
Spontaneous chemical reaction?	Yes	No
Value of E°	Positive	Negative

In an electrochemical cell, a spontaneous redox reaction is used to create an electric current; in an electrolytic cell the reverse will occur - an electric current will be required in order to cause a non-spontaneous chemical reaction to occur.

We will look at three examples of the electrolytic process, keeping our discussion on a very basic level - the electrolysis of molten sodium chloride, the electrolysis of water, and electroplating.

An example of an electrolytic cell is shown below, in which molten NaCl is electrolyzed to form liquid sodium and chlorine gas. The sodium ions migrate toward the cathode, where they are reduced to sodium metal. Similarly, chloride ions migrate to the anode and are oxidized to form chlorine gas. This type of cell is used to produce sodium and chlorine. The chlorine gas can be collected surrounding the cell. The sodium metal is less dense than the molten salt and is removed as it floats to the top of the reaction container.



Electrolytic Cell

Electrolytic Cells

AP Question: When given an electric current, how much metal “plates out?”

1. Calculate the charge in coulombs. $I = q/t$
2. When you know the charge, you know how many e^- were involved:
moles of $e^- = \text{coulombs}/96,500 \text{ C/mol}$

3. When you know the number of moles of e⁻, and you know the ½ rxn for the metal, you can find out how many mole of metal plated out. ex. Au⁺³ + 3 e⁻ ---->Au (s)
(for every 3 mol of 3- consumed, you get 1 mol of Au then get the g)

Voltage and Spontaneity

A redox reaction will occur spontaneously if its potential has a positive value. We know from thermodynamics that a reaction that occurs spontaneously has a negative value for free-energy change. The relationship between reaction potential and free energy for a redox reaction is given by the equation below.

Questions may be: How long will it take? How much can be produced? What current must be used?

1 Faraday = 96,500 coulombs per mole of electrons (F=96,500C/mol e⁻ or 96,500 J/V)

1 ampere = 1 coulomb/sec (A=C/s)

ex. $\Delta G^0 = -nFE^0$

If E⁰ is +, ΔG^0 is – spontaneous

If E⁰ is -, ΔG^0 is + nonspontaneous

What is the value of ΔG^0 when the E⁰ = 1.10 V? This is based on the Daniell cell (2 electron transfer).

$$\Delta G^0 = -2 (96,500\text{C/mol}) (1.10\text{v})$$

$$= 212,300 \text{ C-V/mol}$$

$$= 212,300 \text{ J/mol}$$

$$= - 212 \text{ kJ/mol}$$

Voltage and Equilibrium

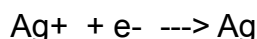
The standard reaction potential is related to the equilibrium constant for a reaction by the equation below.

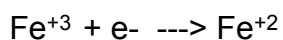
$$E^0 = \frac{RT}{nF} \ln K$$

If E⁰ = +, then K is > 1 and the forward reaction is favored

If E⁰ = -, then K is < 1 and the reversible reaction is favored

Ex. Problem: 2 half reactions follow. What is the cell potential?

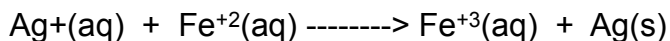




What is occurring at the cathode?

What is occurring at the anode?

Overall cell reaction:



$$E^{\circ} \text{ cell} = .03 \text{ V}$$

Electrons flow from Fe^{2+} to Ag^{+} (anode to cathode)

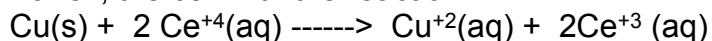
Write the shorthand method (line notation)

Concentration in Cells - Nernst Equation

Under standard conditions, all concentrations were 1.0M. What if the concentration was changed?

Using Le Chatelier's Principle (p. 640 - about equilibrium ch.13), we can predict the change.

For ex, the cell with the reaction:



The above rxn. Has a potential of 1.35 V. What would happen if the $[\text{Ce}^{4+}]$ were greater than the 1.0M? Because this is a reactant, according to Le Chatelier's principle, this would increase the driving force of e^{-} and increase the cell potential.

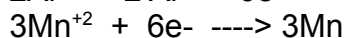
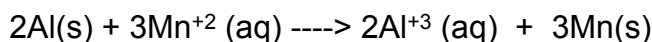
Le Chatelier's principle: If a component is added to a reaction system at equilibrium, the equilibrium position will shift in the direction that lowers the conc. of that component. If a component is removed, the opposite effect occurs. (component = reactant or product)

Nernst Equation: Shows the relationship between the cell potential and the concentrations of the cell components.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{.0591}{n} \log(Q)$$

Q – the reaction quotient; same as the equilibrium expression, but with initial concentrations instead of equilibrium concentrations

Using this equation will allow us to calculate the potential of a cell that may not have all components in their standard states.



$n = 6$ (n = electrons transferred)

In a galvanic cell where the concentrations are 1.0M, then the cell potential is 0.48V (E°_{cell})
What if this cell had $[\text{Mn}^{+2}] = 0.50\text{M}$ and $[\text{Al}^{+3}] = 1.50\text{M}$, then you would use the Nernst equation to find out the cell potential.

$$Q = \frac{[\text{Al}^{+3}]^2}{[\text{Mn}^{+2}]^3} = \frac{[1.50]^2}{[0.50]^3} = 18$$

Using the Nernst equation,

$$E_{\text{cell}} = 0.48 - \frac{0.0591}{6} \log(18) = .47\text{V}$$

Why Do Batteries Discharge More Quickly in Cold Weather?

Answer: The electric current generated by a battery is produced when a connection is made between its positive and negative terminals. When the terminals are connected, a chemical reaction is initiated that generates electrons to supply the current of the battery. Lowering the temperature causes chemical reactions to proceed more slowly, so if a battery is used at a low temperature then less current is produced than at a higher temperature. As the batteries run down they quickly reach the point where they cannot deliver enough current to keep up with the demand. If the battery is warmed up again it will operate normally.

***A dead battery is one in which the cell reaction has reached equilibrium and there is no longer any chemical driving force to push e^- (the two compartments have the same free energy - ΔG for the rxn. at the equilibrium concentration). The cell can't do any work